Identifying Street Conditions by Infrared Spectroscopy

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List of Abbreviations

laser  light amplification by stimulated emission of radiation
LED   light emitting diode
IR    infrared
FIR   far-infrared
MIR   mid-infrared
NIR   near-infrared
VIS   visible
FTIR  Fourier-transform infrared
DFT   discrete Fourier transformation
VASE  variable angle spectroscopic ellipsometer
EMT   effective medium theory
EMA   effective medium approximation
AFM   atomic force microscopy
POE   polarization opposition effect
DLP   degree of linear polarization
FWHM  full width at half maximum
BRDF  bidirectional reflectance distribution function
BSDF  bidirectional scattering distribution function
BTDF  bidirectional transmittance distribution function
BRF   bidirectional reflectance factor
RBRF  relative bidirectional reflectance factor
CCRF  biconical reflectance factor
RStO Richtlinien für die Standardisierung des Oberbaus von Verkehrsflächen
AC Asphalt Concrete
SMA Stone Mastic Asphalt
MA Mastic Asphalt
PA Porous Asphalt
OPA Open Porous Asphalt
LOA Noise Optimized Asphalt
WDA Wasserdurchlässiger Asphalt (water permeable asphalt)
PmB polymer modified bitumen
OVC outer vacuum chamber
DTGS Deuterated Triglycine Sulfate
MCT mercury cadmium telluride
WS white standard
WAsf Windows automatic spectrum fitters
SNR signal-to-noise ratio
AOI angle of incidence
FOV field of view
LO longitudinal optical
TO transverse optical
PTFE polytetrafluoroethylene
Abstract

The extensive demand for autonomous driving opens many new fields for existing and novel sensor types [1–4]. One of them is the task to measure the current condition of the road, since any intermediate layer between tires and road influences the dynamics of vehicle movement. In this regard, the different aggregate states of H₂O mainly determine the friction coefficient [5, 6], therefore, knowledge about the intermediate layer is necessary to adapt driving parameters such as velocity and acceleration. To that end, a sensor based on optics is one approach to enable a contactless measurement of the layered system.

As for developing any kind of sensor or measurement device, understanding the physical properties of the object under investigation is the essential basis, this thesis focuses on the investigation of a layered system of asphalt (as substrate) and aggregate states of H₂O as an intermediate layer to air.

The optical properties of pure H₂O are relatively well understood [7, 8], while there are still ongoing new physical discoveries for the molecule itself [9–13]. H₂O has three fundamental vibrational modes: the symmetric stretching ν₁, bending ν₂, and asymmetric stretching mode ν₃, which are all infrared active [8]. Considering its complex refractive index N, the MIR (mid-infrared) region delivers the strongest absorptions, since the fundamental modes are located in this region [7, 8], however, also components of the air exhibit strong absorptions in this range. Therefore, this thesis concentrates on the NIR (near-infrared) region, where overtones and combination bands of the fundamental modes dominantly influence the optical spectrum.

In order to allow conclusions about the intermediate layer, the optical properties of the substrate—in this case asphalt—has to be well understood. Asphalt is an inhomogeneous mixture of different kind of rocks and bitumen, thus a challenging target for spectroscopy. As a result, asphalt reflects light in a diffuse manner, which is mainly based on its surface structure.

For many diffuse reflecting materials, the Lambertian model is sufficient to describe its optical behavior, which is frequently done in astrophysics and for computer graphics [14–18]. However, in reality, no material exhibits a perfect Lambertian scattering characteristic, even though some materials (e. g. Spectralon or Zenith Polymer) are very close [19, 20]. For a more precise analysis, the BSDF (bidirectional scattering distribution function) or the BRDF (bidirectional reflectance distribution function) delivers the exact scattering or reflecting properties of a material [21–23].

Within the framework of this thesis, a broad variety of different asphalt types, mostly consisting of locally available stone materials (moraine from the Alps) [24], were in-
investigated. Moreover, we also analyzed asphalts which are made from igneous rocks from Norway and even of artificial stones (furnace slag). The coarse-grained samples require a big light spot in order to get an averaged signal with respect to their surface roughness and contained materials. Systematic studies on the dry samples reveal a correlation between their optical properties and the age of the asphalt layers, illustrated in Fig. 1. Freshly produced specimen exhibit a low reflectance factor, while already intermediate aged ones show values between further aged and new specimen. Determining the BSDF as well as the BRDF is extensive and time consuming. Such complex procedure is not necessary for angular ranges where the optical behavior is described in good approximation with Lambert’s law. Indeed, we show that for small incident angles (< 50°), the optical behavior of asphalt can be well described by Lambert’s law. In addition, we conclude that the scattering behavior is dominated by multiple surface scattering, although there is still evidence for a contribution of volume scattering to the total signal.

Figure 1: Averaged integral \( \int_{\text{840 nm}}^{\text{1650 nm}} RF \, d\lambda \) of the reflectance factor \( RF \) of all investigated dry asphalt samples for the covered NIR range. Black symbols highlight untreated (new specimen), red ones sandblasted (intermediate aged), and blue ones actual used asphalt samples (further aged).
For a deeper spectral analysis, we also performed broadband infrared spectroscopy on a characteristic subset of asphalt-pellets. From these measurements, the main ingredients of asphalt can be identified as different variations of SiO\(_2\) (quartz, α-cristobalite, coesite, etc.), CaCO\(_3\) (calcite, aragonite, etc.), and –OH groups bonded to other molecules (see Fig. 2). The low frequency regime is probably determined by inorganic, diatomic molecules, consisting of one metal and one halogen atom, and calcite, which displays some TO (transverse optical) and LO (longitudinal optical) modes in this region. In the NIR region of our main interest (which is covered by our grating spectrometer), the specimen shows only a very small feature which is assigned to an –OH vibrational overtone at \(\sim 7090\) cm\(^{-1}\) (\(\sim 1410\) nm). For the usage of asphalt as a substrate, such absence of sharp modes is an important prerequisite.

The investigations on the layered systems with different aggregate states of H\(_2\)O indicate four absorption features located within a wavelength range between 840 nm and 1650 nm. They can be attributed to overtone and combination bands of H\(_2\)O: \(\nu_{1m} \equiv \nu_1 + 2\nu_3\), \(\nu_{2m} \equiv \nu_1 + \nu_2 + \nu_3 \wedge 2\nu_1 + \nu_2\), \(\nu_{3m} \equiv \nu_2 + 2\nu_3\), and \(\nu_{4m} \equiv \nu_1 + \nu_3\) (from low to high wavelengths). The diffuse reflection of the substrate enables transmission measurements of liquid water and ice. For liquid water, we are able to determine the absorption coefficient \(\alpha\) in very good agreement with literature (see Fig. 3 a)). With our introduced setup and the analysis of diffuse reflection, the absorption coefficient can be determined from basically every liquid which does not possess a significant amount of diffuse reflection or scattering by itself.

Producing very clear ice on top of asphalt is rather challenging. During the freezing process, air bubbles get trapped within the ice, leading to specular reflections and thus in sum to a diffuse signal. As a result, the spectra gain an offset and are shifted towards larger reflectance factor values.

Snow layers exhibit significant larger reflectance values compared to the other investigated layers, caused by scattering effects. The absorption features are still the same as for ice. For typical snow layer thicknesses, the substrate does not contribute to the total signal anymore.

In Fig. 3 b), the typical curves for all investigated states are illustrated, with the ice spectrum being one example with very low air bubble content.

Additional to the measurements, simulations based on a Monte Carlo ray tracing approach in two dimensions were performed. Simulations of layered systems with liq-
Figure 3: Wavelength-dependent absorption coefficient $\alpha$ of water a) and typical wavelength-dependent reflectance factor for the different road conditions b). While the colored curves in a) are generated from our measurements, the black dashed line shows reference data from Kedenburg et al. [25].

uid water and ice are built up on a rough surface, where each facet exhibits a diffuse reflection described by Lambert’s law. The intermediate layer is given the complex refractive index $N$ from the respective aggregate state of H$_2$O. Simulation results fit well to results from actual measurements. For this, the three-dimensionality of the measurement and another factor—which will be called “second influence” from now on—has to be taken into account, because the relation between opening and solid angle is not linear.

In addition, a fitting function is presented, which is able to model the layer thickness-dependent reflectance factor from rough surfaces.

For snow, mostly hexagonal shaped particles are placed in a lattice-like pattern, where each particle has the complex refractive index of ice. Also for this, results are in good agreement with our own measurements and literature.

The presented simulations are the basis for investigating the optical properties of defined mixed states, for instance between water and snow. In the real world, such mixed states change continuously and are hard to realize in a well-defined manner. Thus, the here presented results provide the basic knowledge for future optical sensors, which can be utilized for a state detection of H$_2$O (water, ice, and snow), but also of many other materials on top of diffuse grounds.
Deutsche Zusammenfassung

Die großflächige Nachfrage nach dem automatisierten Fahren eröffnet viele neue Felder für bereits existierende und neuartige Sensortypen [1–4]. Eines dieser Felder ist die Aufgabe den aktuellen Straßenzustand zu messen, da jede Zwischenschicht zwischen Reifen und Fahrbahn die Fahrdynamik beeinflusst. In dieser Hinsicht bestimmt der Aggregatzustand von $H_2O$ den Reibwert [5, 6]. Daher ist die Kenntnis über die aktuelle Zwischenschicht erforderlich, um die Fahrparameter wie z. B. die Fahrgeschwindigkeit und Beschleunigung entsprechend anzupassen. Hierfür ist ein optisch basierter Sensor ein Ansatz, welcher eine kontaktlose Messung des Schichtensystems ermöglicht.

Da für die Entwicklung eines Sensors bzw. Messgeräts das Verständnis über die physikalischen Eigenschaften des zu messenden Objekts die unverzichtbare Grundlage ist, fokussiert sich diese Arbeit auf die Untersuchung von Schichtensystemen bestehend aus Asphalt als Substrat und den Aggregatzuständen von $H_2O$ als Zwischenschicht zur Luft.

Die optischen Eigenschaften von reinem $H_2O$ sind relativ gut bekannt und verstanden [7, 8], während für das Molekül selbst immer noch neue physikalische Eigenschaften entdeckt werden [9–13]. $H_2O$ besitzt drei grundlegende Vibrationsmoden: Die symmetrische Streck- $\nu_1$, Bieg- $\nu_2$ und asymmetrische Streckmode $\nu_3$, welche alle Infrarot aktiv sind [8]. Betrachtet man den komplexen Brechungsindex $N$ von $H_2O$, so birgt der MIR (mittlere Infrarot) Bereich die stärksten Absorptionen, da sich die grundlegenden Vibrationsmoden in diesem Bereich befinden [7, 8]. Allerdings besitzen auch einige Bestandteile der Luft starke Absorptionen in diesem Bereich. Daher konzentriert sich diese Arbeit auf den NIR (nahes Infrarot) Bereich, in welchem Obertöne und Kombinationsbänder der grundlegenden Vibrationsmoden das optische Spektrum hauptsächlich beeinflussen.

Um Schlussfolgerungen über die Zwischenschicht anstellen zu können, müssen die optischen Eigenschaften des Substrats – in diesem Fall Asphalt – gut verstanden sein. Asphalt ist ein inhomogenes Gemisch aus unterschiedlichsten Gesteinssorten und Bitumen, also ein herausforderndes Material für die Spektroskopie. Demzufolge wird Licht an Asphalt diffus reflektiert, was hauptsächlich durch seine Oberflächenstruktur verursacht wird.

Das Lambertscbe Gesetz reicht für viele diffus reflektierenden Materialien aus, um deren optisches Verhalten zu beschreiben, was auch häufig in der Astrophysik und für computergenerierte Grafiken zur Anwendung kommt [14–18]. Allerdings existiert in der Realität kein Material welches eine perfekte Lambertscbe Streueigenschaft aufweist, obwohl einige Materialien (z. B. Spectralon und Zenith Polymer)

Im Rahmen dieser Arbeit werden eine breite Auswahl von unterschiedlichen Asphalttypen untersucht, während die meisten davon aus lokal vorhandenem Gesteinsmaterial (Moräne von den Alpen) bestehen [24]. Darüber hinaus haben wir zusätzliche Asphalte untersucht, welche aus norwegischem Vulkangestein bestehen und sogar einen Asphalt der aus künstlichem Gestein (EloMinit – Elektroofenschlacke) zusammengesetzt ist. Die grobkörnigen Proben machen die Verwendung eines großen Lichtspots notwendig, damit über die Rauheit und unterschiedlichen Materialien gemittelt wird. Systematische Untersuchungen an trockenen Proben ergaben eine Korrelation zwischen den optischen Eigenschaften und dem Alter der Asphaltschicht, abgebildet in Abb. 4. Frisch hergestellte Proben weisen niedrige Werte für den Re-

![Figure 4: Gemitteltes Integral \( \int_{840\,\text{nm}}^{1650\,\text{nm}} RF \, d\lambda \) vom Reflektanzfaktor \((RF)\) von allen untersuchten trockenen Asphaltproben für den gemessenen NIR Bereich. Schwarze Symbole heben unbehandelte (neue Proben), rote sandbestrahlte (etwas gealtert) und blaue tatsächlich verwendete Asphaltproben (weiter gealtert) hervor.

flektanzfaktor auf, während bereits etwas gealterte Proben zwischen den noch weiter gealterten und den neuen Proben liegen.

Für eine genauere spektrale Analyse verwendeten wir die *Breitband-Infrarotspektroskopie* an einer Auswahl von Asphalt-Pellets. Von diesen Messungen können die Hauptbestandteile von Asphalt auf unterschiedlichen Variationen von SiO₂ (Quarz, α-Cristobalit, Coesit, etc.), CaCO₃ (Kalzit, Aragonit, etc.) und gebundenes −OH zurückgeführt werden (siehe Abb. 5). Das Spektrum bei niedrigen Frequenzen wird vermutlich von anorganischen zweiatomigen Molekülen, welche aus einem Metall- und einem Halogenatom bestehen, und Kalzit bestimmt. Letzteres weist TO (transversal optisch) und LO (längsgerichtet optisch) Moden in dieser Region auf. In dem für uns hauptsächlich interessanten NIR Bereich (welches von unserem Gitterspektrometer abgedeckt ist) weisen die Proben nur ein sehr schwaches Feature auf, welches einem Oberton von −OH bei ~ 7090 cm⁻¹ (~ 1410 nm) zugeordnet werden kann. Für die Verwendung von Asphalt als ein Substrat ist solch eine Abwesenheit von scharfen Moden eine wichtige Voraussetzung.

Die Untersuchungen an den Schichtensystemen mit unterschiedlichen Aggregatzuständen von H₂O deuten auf vier Absorptionsfeatures hin, welche sich zwischen 840 nm und 1650 nm befinden. Diese können *Obertönen und Kombinationsbändern* von H₂O zugeordnet werden: \( \nu_{1m} \equiv \nu_1 + 2\nu_3 \), \( \nu_{2m} \equiv \nu_1 + \nu_2 + \nu_3 + 2\nu_1 + \nu_2 \), \( \nu_{3m} \equiv \nu_2 + 2\nu_3 \) und \( \nu_{4m} \equiv \nu_1 + \nu_3 \) (von niedrigen zu hohen Wellenlängen). Die diffuse Reflexion des Substrats ermöglicht Transmissionsmessungen an flüssigem Wasser und Eis. Für flüssiges Wasser können wir den Absorptionskoeffizienten \( \alpha \) bestimmen, welcher mit der Literatur sehr gut übereinstimmt (siehe Abb. 5 a)). Mit unserem vorgestellten Messaufbau und der Auswertung diffuser Reflexion kann der Absorptionskoeffizient von prinzipiell jeder Flüssigkeit bestimmt werden, welche nicht selbst einen wesentlichen Anteil an diffuser Reflexion oder Streuung aufweist.

Die Herstellung von sehr klarem Eis auf Asphalt ist nicht einfach. Während des
Figure 6: Wellenlängenabhängiger Absorptionskoeffizient $\alpha$ von Wasser a) und typischer wellenlängenabhängiger Reflektanzfaktor für die unterschiedlichen Straßenzustände b). Die farbigen Kurven in a) resultieren aus unseren Messungen während die schwarz-gestrichelte Kurve Referenzdaten von Kedenburg et al. [25] zeigen.

Gefrierprozesse werden Luftblasen im Eis eingeschlossen welche zu gerichteten Reflexionen in alle Raumrichtungen und daher in Summe zu einem diffusen Signal führen. Als Folge dessen erlangen die Spektren einen Offset, bei dem das Signal zu höheren Reflektanzfaktoren geschoben wird.

Schneeschichten weisen deutlich stärkere Reflektanzfaktoren auf als die anderen untersuchten Schichten, was Streueffekten geschuldet ist. Die Absorptionsfeatures sind trotzdem dieselben wie für Eis. Für typische Schneeschichtdicken trägt das Substrat nicht mehr zum Gesamtsignal bei.

In Abb. 6 b) sind typische Spektren für die untersuchten Zustände abgebildet, indem das Beispiel für Eis einer Schicht mit nur wenig eingeschlossenen Luftblasen entspricht.


Zusätzlich wird eine Fitfunktion präsentiert, die von rauen Oberflächen den schichtdicken-abhängigen Reflektanzfaktor modelliert.

Für Schnee werden meist hexagonal geformte Partikel in einem gitterähnlichen Muster angeordnet wo jedes Partikel den komplexen Brechungsindex von Eis be-
sitzt. Auch hier passen die Ergebnisse gut zu unseren eigenen Messungen und zur Literatur.

Die vorgestellten Simulationen sind die Basis für Untersuchungen der optischen Eigenschaften von definierten Mischzuständen wie z. B. aus Wasser und Schnee. In der Realität verändern sich solche Mischzustände kontinuierlich und sind deshalb nur schwer auf einer definierten Weise zu realisieren.

Deshalb stellen die hier präsentierten Ergebnisse das Basiswissen für zukünftige optischen Sensoren zur Verfügung, welches z. B. zur Zustandsdetektion von H₂O (Wasser, Eis und Schnee), aber auch von einer Vielzahl anderer Materialien, auf einem diffus reflektierenden Boden verwendet werden kann.
Publications

Some results of this thesis are already published and can be found in:

- **A. Baumgartner**, S. Amann, M. Werz, A. Herkommer, M. Dressel, and S. Fella
  *Near-infrared optical investigations of snow, ice, and water layers on diffuse reflecting surfaces*

- **A. Baumgartner**, A. Amann, C. Müller, A. Herkommer, M. Dressel, and S. Fella
  *Infrared reflectance factor of various asphalts*

Other scientific publications which are not related to this thesis:

  *Reentrant phases in electron-doped EuFe$_2$As$_2$: Spin glass and superconductivity*

  *Effects of pressure and magnetic field on the reentrant superconductor Eu(Fe$_{0.93}$Rh$_{0.07}$)$_2$As$_2*

  *Tracing the $s_\pm$ symmetry in iron pnictides by controlled disorder*

Registered patents related to this work
Note: Up to now, the patents are only registered and not yet published.

- A. Baumgartner, S. Fella, S. Kuntz, and W. Welsch
  *Miniaturisierter optischer Sensor zur Straßenzustandsbestimmung*
• W. Welsch, S. Fella, A. Baumgartner, and S. Kuntz
  *Multiwellenlängen-bzw. Multipolarisations-LiDAR zur gleichzeitigen Bestim-
  mung des Umfelds und des Straßenzustands*
  **DE 10 2019 206 316.0**, registered: 2019 (03.05.2019)

• W. Welsch, S. Fella, A. Baumgartner, and S. Kuntz
  *Optischer Sensor zur Straßenzustandserkennung, inkl. Unterscheidung von
  Schnee und Eis*

• S. Fella, S. Kuntz, A. Baumgartner, and W. Welsch
  *Thermisches Konzept für einen optischen Sensor zur Straßenzustandsbestim-
  mung*
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1 Introduction

Light, it fascinates human mankind since ancient times and enables a broad variety of optical technologies. First recordings are about mirrors and date back to around 1200 BC [26]. Famous Greek philosophers like Pythagoras, Demokrit, Aristoteles, Plato, or Hero of Alexandria had their own theories about the nature of light [26, 27]. Already 300 BC, a law of reflection was established and it was known that light propagates rectilinearly [26, 27]. Claudius Ptolemy (130 AD) examined the refraction in form of a table with different incident and refracted angles of light on several materials; together with Hero’s principle that light always follows the shortest path between two points, giving the basis of geometrical optics [26, 27].

Till the late 16th century, basic empirical knowledge about reflexion and refraction was well established. One could produce mirrors and simple lenses, but the theoretical description for the latter one was still missing [26, 27]. In the early 17th century, Hans Lippershey submitted a patent for a simple telescope [26, 28, 29]. Shortly afterwards, different kinds of telescopes were built and improved for instance by Galileo Galilei and Johannes Kepler [26–29]. Telescopes helped to increase the scientific interest in optics and enabled new possibilities for astronomy.

In 1621, Willebrord Snell empirically found the law of refraction which is named after him (Snell’s law) even though it was René Descartes who formulated it in the form how we know it nowadays [26, 29]. Nearly parallel to Descartes, Pierre de Fermat derived the refraction law by his own principle based on the least time. While Descartes needs a medium for his theory of light, Fermat’s principle did not need any mechanical properties of light [26, 27]. Experimental findings like diffraction from Francesco Maria Grimaldi and further experiments with interference patterns from Robert Hooke led to the beginning of the wave theory of light [26, 27, 29]. Isaac Newton’s experiments with prisms showed that white light consists of colors. He concluded that light is made of several colored particles with different size [27]. He even considered that the particles might excite the aether to characteristic oscillations, however, since the wave theory based on longitudinal waves could not explain
the rectilinear propagation, Newton was an advocate of the corpuscular theory of light [26, 27, 29]. Besides, with his prism experiments, Newton built the basis for optical spectroscopy [30]. It was Christiaan Huygens who extended the wave theory by his finding that light propagates slower when entering a denser medium. From his experiments with calcite, he also found the polarization property of light. He concluded that the double refraction (birefringence) originates from two different kinds of light waves [26]. The twist between wave and particle theory advocates were profound. The only consensus was that light has to be very fast, up to infinity [26]. In 1676, it was Ole Christensen Rømer who proved that the speed of light is actually limited [26, 29]. In the 18th century, only a few supporters for the wave theory of light were left. One of them was Thomas Young (well known for his double-slit experiments) who could explain former observations by Newton—the so called Newton’s rings—by the principle of interference [27]. It was also the first time that wavelengths for the visible spectrum were determined [27, 30]. Still, the resistance against the wave theory was dominant. When Augustin-Jean Fresnel connected Huygens’ wave description with interference effects, he was able to explain the rectilinear propagation of light based on the wave theory. Additionally, he managed to calculate different diffraction patterns [26]. However, there was one problem, the longitudinal wave pattern could not explain the polarization property of light. At that point, Young had the idea that the oscillations of the aether are transversal. With this concept, the polarization could easily be included into the theory. By utilizing this idea, Fresnel derived the well known Fresnel equations for the amplitudes of reflected and transmitted light. At this point, only a few supporters for the particle description of light were left [26].

In 1845, Michael Faraday found a connection between electromagnetism and light where the polarization direction of a light ray can be changed by a strong magnetic field [26]. Later, James Clerk Maxwell formulated the famous Maxwell’s equations [27]. Now it was possible to derive a wave equation of electromagnetic fields [27] where also the speed of light could be identified via $c = 1/\sqrt{\varepsilon_0 \mu_0}$. With this approach, it was concluded that light has to be an electromagnetic wave which propagates through the aether. The experimental proof of this assumption was given by Heinrich Rudolf Hertz [26, 29]. Up to this point, the wave theory needed a carrier material; the aether. Several experiments like the Michelson-Morley experiment led Jules Henri Poincaré to a renunciation of the aether theory. Later, Albert Einstein also declined the aether theory, based on his own findings in his
special theory of relativity [26]. For the wave theory of light followed that electromagnetic waves have to propagate through empty space [26]. With the occurrence of the theory of quantum mechanics—mainly driven by Max Karl Ernst Ludwig Planck, Niels Henrik David Bohr, Arnold Johannes Wilhelm Sommerfeld, Werner Karl Heisenberg, Erwin Rudolf Josef Alexander Schrödinger, Max Born, and partly Albert Einstein—the particle description came back to life in form of photons; the wave–particle duality was born and accepted [26, 29].

In this brief summary of historical breakthroughs and events, only some of the major progresses made in optics are pointed out. Our modern world is based on a huge variety of optical applications, for instance light amplification by stimulated emission of radiation (laser) diodes in telecommunication, data storage, or gas detection. Another major breakthrough was the development of light emitting diodes (LEDs) which are used in displays, illumination, signal lights, and even in medical applications. Lasers as well as LEDs made it possible to build small and very fast optical spectrometers, since—compared to black-body sources—they can be modulated with high frequencies.

Basically every vehicle utilizes headlights. Back in the 19th century, the first cars actually used simple acetylene lamps to illuminate the front of the car [31], while right after, electrical based systems replaced that technology. Nowadays, halogen-based lamps are the most common type of headlight, which are going to be replaced by more complex LED and Laser based technologies [31, 32]. As vehicles have to endure harsh environmental conditions1, so all of its components has to do, which is especially challenging for optical systems.

Drivers can distinguish between dry, wet or snowy surfaces quite easily, however, distinguishing between wet and icy roads is already more difficult. Nevertheless, in 2016, 4.2% and in 2017, 4.6% of accidents with personal injury in Germany were caused by slippery road conditions [33, 34]. There exist several patents and concepts to determine the intermediate layer between tire and road, for instance a sensor placed inside the tire which concludes about the intermediate layer by acceleration features [35] or stationary sensors which measure the road temperature, ice percentage (via electrical conductivity) and water level (via radar) [36, 37]. There are also patents for acoustical concepts available [38, 39]. However, the most promis-

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1For instance components have operating temperature ranges between −40°C and typically 85°C (depending on its location in the car even up to 130°C).
CHAPTER 1. INTRODUCTION

ing type is an optical concept where already some automotive-unsuitable sensors are available [37]. Therefore, it can be concluded that an optical sensor based on near-infrared spectroscopy would contribute to reduce the number of accident due to slippery road conditions significantly.

Additionally, automated driving poses new challenges to sensors, especially optical sensors. Reputable manufacturers fear that if the trust is lost once in this new technology, it will be really hard to open this market to customers. In principle, for public acceptance of this technology, it has to cover two major tasks: the first one is to guarantee a save travel from point A to B; the second one is to do this fast. The latter requirement is hard to achieve if there is no information about the friction coefficient of the road. As long as there is no information available, an automated vehicle has to expect the most critical situation which would be an icy road or a thick water layer thickness (aquaplaning); thus the car has to drive slowly or cannot drive at all. For such a case, an optical sensor which detects the intermediate layer between road and tires could help to gather this necessary information.

To answer the question whether an optical sensor is able to satisfy the above mentioned requirements, a fundamental study on a broad variety of asphalt samples, with different intermediate layers is done in this thesis. Based on these findings, it is evaluated whether an optical sensor is capable to detect dry, wet, icy, and snowy road conditions. Since aquaplaning depends strongly on the water layer thickness, a determination of this layer thickness would also be favorable.

The following thesis will first give attention to the theoretical background followed by a brief introduction into asphalt itself. Afterwards, the used setups and measurement techniques are presented. Before the discussion part, the basic ideas as well as the concept of the simulations are introduced. Results from the measurements and simulations are discussed in the following chapters, separately for each aggregate state of H₂O. At the end, a summary and outlook provides the most important findings.
2 Theoretical background

In this chapter the physical background is provided which is essential for this thesis. It spans from the fundamental definitions up to current scientific findings regarding H₂O. Especially the first part of explanations follows Ref. 26 and Ref. 29.

2.1 Maxwell’s equations

All four of Maxwell’s equations are derived from observations and describe the classical electromagnetism. In differential notation one can write the microscopic form of Maxwell’s equations as [26]:

- The Gauss’s law:

  \[ \nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0 \epsilon_r} \quad (2.1) \]

  Electric charges generate a divergence of an electric field \( \vec{E} \), which means that a static electric field originates from positive (\( \nabla \cdot \vec{E} > 0 \)) or negative charges (\( \nabla \cdot \vec{E} < 0 \)), corresponding to the begin (positive) and end (negative) of the field lines. In integral notation it states that the electric flux through a closed surface is proportional to the amount of charge carriers inside a closed volume (charge density \( \rho \)) with the reciprocal absolute permittivity \( 1/\varepsilon = 1/(\epsilon_0 \epsilon_r) \) as proportionality factor.

- The generalized Faraday’s law of induction:

  \[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (2.2) \]

  Every time-dependent magnetic flux density \( \vec{B} \) is accompanied by an electric field which does not need the existence of charges. It manifests itself either in closed loops (vortices) or reach to infinity.
• The Gauss’s law for magnetism\(^1\):

\[
\nabla \cdot \vec{B} = 0
\]

(2.3)

There is no divergence of the magnetic flux density \(\vec{B}\), which means there exist no magnetic monopoles. The field lines manifest themselves in closed loops. In integral notation it states that the magnetic flux density through a closed surface is zero, since the same amount of field lines which leave the enclosed volume also reenters it.

• The Ampère’s circuital law with the addition from Maxwell:

\[
\nabla \times \vec{B} = \mu_0 \mu_r \left( \vec{J} + \epsilon_0 \epsilon_r \frac{\partial \vec{E}}{\partial t} \right)
\]

(2.4)

The original Ampère’s circuital law states that an electric current density \(\vec{J}\) generates a magnetic flux density around the current with the absolute permeability \(\mu = \mu_0 \mu_r\) as proportionality factor. Maxwell’s addition is the displacement current density \(\vec{J}_D = \epsilon_0 \epsilon_r \frac{\partial \vec{E}}{\partial t}\), originating from a time-dependent electric field which leads to a magnetic flux density, too, without the need of an electric current.

From Equ. 2.2 and Equ. 2.4, we see that a time-dependent magnetic and electric field influences each other. This property allows self-sustaining electromagnetic waves which do not need any medium to propagate through space.

\[\text{2.2 Electromagnetic waves}\]

The spectrum of electromagnetic waves is divided into several regions where visible light and the infrared region is only a small fraction of it [29, 40, 41]. From Maxwell’s equations one can derive the wave function for an electric field in free space as following: First, we use the rotation on both sides of equation 2.2 which corresponds to the second derivative

\[
\nabla \times (\nabla \times \vec{E}) = \nabla \times \left( -\frac{\partial \vec{B}}{\partial t} \right)
\]

(2.5)

\[\text{Note: The name for this equation is given in Ref. 26 while it is often referred without any name.}\]
CHAPTER 2. THEORETICAL BACKGROUND

Since we have a cross product of a cross product on the left side of this equation, we can use the general operator identity (based on the Graßmann identity) [42–44]

\[ \nabla \times (\nabla \times \vec{A}) = \nabla(\nabla \cdot \vec{A}) - \Delta \vec{A} \]  
(2.6)

where \( \Delta = \nabla \cdot \nabla = \nabla^2 \) is the Laplace operator and \( \vec{A} \) a vector field. For free space, the charge density \( \rho \) is zero and Equ. 2.1 can be set to \( \nabla \cdot \vec{E} = 0 \). For the right side of Equ. 2.5 we can place Equ. 2.4 with \( \vec{J} = 0 \) (since there are no electric currents in free space) and \( \mu_r = \epsilon_r = 1 \) (vacuum).

\[ \nabla \times \left( -\frac{\partial \vec{B}}{\partial t} \right) = -\frac{\partial}{\partial t} \left( \nabla \times \vec{B} \right) = -\mu_0 \epsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} \]  
(2.7)

Thus, Equ. 2.5 results in the wave equation for the electric field in free space:

\[ \Delta \vec{E} = \mu_0 \epsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} \]  
(2.8)

With similar steps one can derive the wave equation for the magnetic flux density in free space

\[ \Delta \vec{B} = \mu_0 \epsilon_0 \frac{\partial^2 \vec{B}}{\partial t^2} \]  
(2.9)

From general wave equations it is known that nearly all of them can be described in this general form

\[ \Delta \psi = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2} \]  
(2.10)

with a general function \( \psi \) and speed of propagation (phase velocity) \( v \). Thus, in vacuum the speed of electromagnetic waves is derived as \( c = 1/\sqrt{\epsilon_0 \mu_0} \) where \( \epsilon_0 \) is the vacuum permittivity and \( \mu_0 \) the vacuum permeability. A possible solution for Equ. 2.10 is a harmonic plane wave

\[ \psi(\vec{r}, t) = Ae^{i(\omega t - \vec{k} \cdot \vec{r} + \varphi)} \]  
(2.11)

with the amplitude \( A \) and the phase angle \( \varphi \).

With Equ. 2.2 one can show that an electromagnetic plane wave in vacuum is a transversal oscillation of an electric field \( \vec{E} \) with a time-dependent perpendicular magnetic flux density \( \vec{B} \). Both propagate along the wave vector \( \vec{k} \). In that case, the electric field as well as magnetic flux density are orthogonal to the wave vector \( \vec{k} \).
and to each other (see Fig. 2.1). Via \( k = |\vec{k}| = 2\pi/\lambda \) the wavelength is related to the wave vector. The direction of the energy flux is described by the Poynting vector

\[
\vec{S} = \frac{1}{\mu_0} \vec{E} \times \vec{B} = c^2 \varepsilon_0 \vec{E} \times \vec{B} \tag{2.12}
\]

and its absolute value gives the power (radiant flux) per area (SI units: \([S] = \frac{1}{m^2} = W/m^2\)). The averaged Poynting vector over an interval \( T' \) gives the irradiance which is commonly called intensity. For harmonic fields like a plane wave, this results in

\[
I = \langle S \rangle_{T'} = \frac{1}{2} c^2 \varepsilon_0 \left| \vec{E}_0 \times \vec{B}_0 \right| = \frac{1}{2} c \varepsilon_0 E_0^2 \tag{2.13}
\]

while the factor 1/2 originates from the harmonic approach \( \langle \cos(\vec{k} \cdot \vec{r} - \omega t)^2 \rangle_{T'} = 1/2 \) as long as the measured interval is much larger than the period \( T \) of the electromagnetic wave \( (T' \gg T) \). \( \vec{E}_0 \) and \( \vec{B}_0 \) are the amplitudes of the electric field and magnetic flux density, respectively.

### 2.2.1 Electromagnetic waves in matter

For an optically isotropic and homogeneous dielectric medium, the speed of electromagnetic waves is defined via

\[
c_m = \frac{1}{\sqrt{\varepsilon \mu}} = \frac{1}{\sqrt{\varepsilon_0 \varepsilon \mu_0 \mu}} \tag{2.14}
\]
The ratio of the speed in vacuum to the one in the medium defines the real part of the complex refractive index as

\[ n = \frac{c}{c_m} = \sqrt{\epsilon_r \mu_r} \]  

(2.15)

which reduces simply to \( n = \sqrt{\epsilon_r} \) for non-magnetic materials. The different phase velocity also affects the wave vector to

\[ k = \frac{2\pi n}{\lambda} . \]  

(2.16)

A further consequence is given by the conservation of energy \((E = h\nu)\): the frequency \(\nu\) of an electromagnetic wave is not affected by the material but its wavelength. The relation is given by

\[ \nu = \frac{c}{n\lambda} . \]  

(2.17)

For monochromatic linear polarized electromagnetic waves, Equ. 2.13 for the irradiance can be simply modified to

\[ I = \frac{1}{2} c n \epsilon_0 E_0^2 . \]  

(2.18)

### 2.2.2 Absorption through media

Up to now, we only had a look on the basic definitions and relations for vacuum and isotropic, homogeneous, dielectric materials. Such materials are basically transparent for electromagnetic waves. For other non-magnetic materials where absorption effects cannot be neglected, the frequency-dependent refractive index gets complex and is defined via

\[ N(\omega) = n(\omega) + i\kappa(\omega) = \sqrt{\epsilon_{r1}(\omega) + i\epsilon_{r2}(\omega)} , \]  

(2.19)

with the complex permittivity \( \epsilon_r(\omega) = \epsilon_{r1}(\omega) + i\epsilon_{r2}(\omega) \), where \( \omega \) is the angular frequency \( \omega = 2\pi\nu \). The absorption effect is covered by the imaginary part \( \kappa \) which is called extinction coefficient, while the real part \( n \) only provides the ratio of reduced phase velocity. The closer the frequency to the energy of a resonance—which origins

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2Note: In literature two definitions \( N = n \pm i\kappa \) with different sign can be found, depending on the sign of the imaginary part \( \kappa \) [26, 40, 41, 45].
from ionic, dipolar, atomic, or electronic transitions—the stronger the absorption. Thus, when an atom absorbs an electromagnetic wave or a photon with the energy \( E = h\nu \), it means that the atom gains energy. Whether this energy dissipates in heat or emittance of a photon depends on the system.

By taking the harmonic wave ansatz (Equ. 2.11) for the electric field in one dimension (\( x \)) with phase angle \( \varphi = 0 \) and the relation \( k = 2\pi/\lambda = N\omega/c \), one gets

\[
\vec{E} = \vec{E}_0 e^{-\omega|\kappa|x/c} \cos(\omega(t - nx/c)) \quad .
\] (2.20)

Therefore, an electromagnetic wave through an absorbing material has an oscillating part and an amplitude which is exponentially decreasing with the distance propagating inside the material.

For the irradiance—which is proportional to the squared time-averaged electric field—following relation\(^3\) can be derived:

\[
I(d) = I_0 \cdot e^{-\alpha d} = I_0 \cdot e^{4\pi\kappa \lambda d}
\] (2.21)

with the initial irradiance \( I_0 \), the attenuation coefficient\(^4\) \( \alpha \) and the distance \( d \). The attenuation coefficient itself is a function of the extinction coefficient \( \kappa \) and the wavelength \( \lambda \). By neglecting losses at the interfaces, the ratio

\[
T_{\text{bulk}} = \frac{I(d_{\text{bulk}})}{I_0} = e^{-\alpha d_{\text{bulk}}}
\] (2.22)

gives the portion of energy which is transmitted through the bulk material.

From the attenuation coefficient, the penetration depth is defined via

\[
\lambda_p = \frac{1}{\alpha} \quad .
\] (2.23)

At this depth, the intensity is decayed to \( 1/e \cdot I_0 \). Whether a materials looks transparent or not depends on the thickness compared to the penetration depth\(^5\) for the respective wavelength.

\(^3\) Also known as Lambert-Beer’s law.

\(^4\) Also known as absorption coefficient.

\(^5\) If the penetration depth is high compared to the sample thickness, the material looks transparent.


2.2.3 Electromagnetic waves at interfaces

When an electromagnetic wave passes a boundary between two isotropic and homogeneous media, at the interface, one part is reflected into the same medium where it comes from with a refractive index of $N_i$ and another one is transmitted into the next medium with a refractive index $N_t$ (see Fig. 2.2). In such media, the wave front oscillates perpendicular to the energy flux, while the latter one propagates on a straight line. Due to that property, one typically speaks of rays, which can be drawn in the same direction as the wave vector $\vec{k}$.

**Reflexion**

For a reflected ray as depicted in Fig. 2.2, which has a reflection angle of $\theta_r$ to the surface normal, following relation is valid

$$|\theta_r| = |\theta_i| \quad ,$$

(2.24)
where $\theta_i$ is the incident angle. The incident and reflected ray span the so called *plane of incidence*. In literature, Equ. 2.24 is typically found as $\theta_r = \theta_i$ [26, 29, 46] without usage of absolute values. In this thesis, all angles which are located in the 2nd and 4th quadrant—with respect to the surface normal—will have a negative sign while all the others possess a positive one. Fig. 2.3 provides a definition for the quadrants related to the surface and its normal vector (see also Sec. 5.3).

**Refraction**

For isotropic and homogeneous media, the refracted rays propagate in the same plane as the incident and reflected rays. Thus, $\vec{k}_i$, $\vec{k}_r$, and $\vec{k}_t$ are coplanar. The different phase velocities between the two media cause the refraction angle $\theta_t$, which can be calculated via Snell’s law

\[
n_i \sin(\theta_i) = n_t \sin(\theta_t) \quad .
\]

Equ. 2.25 is only valid for materials where the absorption i. e. the imaginary part $\kappa$ of the complex refractive index is small. Otherwise, the generalized Snell’s law has to be utilized [47–49]. In the latter case, planes of constant phase and planes of constant amplitude exhibit not the same direction anymore. In case of a transition from an optical dense to a less dense material ($n_i < n_t$), one speaks of inner reflection. Here, when the angle exceeds the total reflection angle

\[
\theta_c = \arcsin \left( \frac{n_i}{n_t} \right) \quad ,
\]

no ray is refracted, and all the energy is reflected instead. Incidentally, this is also the scenario where evanescent waves appear [26, 29].
2.2.4 Fresnel’s equations

With the law of reflection and refraction, the corresponding angles can be determined. The fraction of the amplitude of the reflected and refracted electric field can be calculated via Fresnel’s equations 2.27 to 2.30:

\[ r_s = \frac{N_i \cos(\theta_i) - \frac{\mu_{r,i}}{\mu_{r,t}} N_t \cos(\theta_t)}{N_i \cos(\theta_i) + \frac{\mu_{r,i}}{\mu_{r,t}} N_t \cos(\theta_t)} \] (2.27)

\[ r_p = \frac{N_t \frac{\mu_{r,i}}{\mu_{r,t}} \cos(\theta_i) - N_i \cos(\theta_t)}{N_t \frac{\mu_{r,i}}{\mu_{r,t}} \cos(\theta_i) + N_i \cos(\theta_t)} \] (2.28)

\[ t_s = \frac{2N_i \cos(\theta_i)}{N_i \cos(\theta_i) + \frac{\mu_{r,i}}{\mu_{r,t}} N_t \cos(\theta_t)} \] (2.29)

\[ t_p = \frac{2N_i \cos(\theta_i)}{N_t \frac{\mu_{r,i}}{\mu_{r,t}} \cos(\theta_i) + N_i \cos(\theta_t)} \] (2.30)

Here, \( r \) and \( t \) are the complex reflection and transmission coefficients for vertical (s) and parallel (p) polarized light (see also Fig. 2.2). The particular indices \( i \) and \( t \) for the angle \( \theta \), the complex refractive index \( N \), and the relative permeability \( \mu_r \) refer to the incident and transmitting material, respectively. For the materials investigated in this thesis, one can set \( \mu_{r,i} \approx \mu_{r,t} \approx 1 \) [50]. By utilizing Snell’s law (Equ. 2.25) with only the real part of the complex refractive indices, we can express \( \theta_t \) as

\[ \theta_t = \arcsin \left( \frac{n_i}{n_t} \sin(\theta_i) \right), \] (2.31)

which is set into Fresnel’s equations. Thus, in this approximation, those equations are functions depending on the refractive indices and incident angle only.

With the presented coefficients, the reflectance \( R \) and transmittance \( T \) can be calculated via

\[ R_j = \left| \frac{E_{0,r,j}}{E_{0,i,j}} \right|^2 = r_j \cdot \bar{t}_j \] (2.32)

and (as long as \( \mu_i = \mu_t = \mu_0 \))

\[ T_j = \left| \Re \left( \frac{N_i \cos(\theta_i)}{N_i \cos(\theta_i)} \right) \right| \left| \frac{E_{0,t,j}}{E_{0,i,j}} \right|^2 = \left| \Re \left( \frac{N_i \cos(\theta_i)}{N_i \cos(\theta_i)} \right) \right| \cdot t_j \cdot \bar{t}_j \] (2.33)
with the complex conjugates \( r_j \) and \( t_j \), where \( j = s, p \). For unpolarized light, one uses

\[
R = \frac{1}{2}(R_s + R_p) \tag{2.34}
\]

and

\[
T = \frac{1}{2}(T_s + T_p) \tag{2.35}
\]

In Fig. 2.4, the reflectance and transmittance for a dielectric and absorbing material is depicted. Here, one can identify Brewster’s angle where the parallel polarized light has zero reflectance and maximum transmittance. The Brewster’s angle can be determined via

\[
\theta_B = \arctan \left( \frac{n_t}{n_i} \right) \tag{2.36}
\]

For absorbing materials, the Pseudo-Brewster’s angle \( \theta_{PB} \) gains an offset which results in a minimum with finite value in reflectance and a maximum below 1 in transmittance.

### 2.3 Polarization

The polarization of a transverse electromagnetic wave is the orientation of its oscillating electric field. Up to this point, this field was handled as linearly polarized. Every amplitude of an electromagnetic wave can be divided into its projections to the vertical (s) and parallel (p) plane with respect to an incident plane, as shown in
Fig. 2.2. The ratio of the corresponding projected amplitudes determine the orientation $\beta$ of the linear polarized wave (see Fig. 2.5 a)). As long as the phase difference is $\Delta \varphi = 0 \pm n \cdot \pi$, the resulting wave is linearly polarized, no matter how the ratios of the projected amplitudes look like. When the amplitudes of the electric fields have the same value ($E_{0,s} = E_{0,p}$) and the phase difference is $\Delta \varphi = -\pi / 2 \pm n \cdot 2\pi$ with $n \in \mathbb{N}_0$, the result is a right circular polarization (Fig. 2.5 b)). For the same case but with $\Delta \varphi = \pi / 2 \pm n \cdot 2\pi$, it is a left circular polarization. Both, linear as well as circular polarization are special cases of elliptical polarized light (see Fig. 2.5 c)). Another type is unpolarized light. In that case, no specific state of polarization can be determined, because it consists of many fast changing polarization states. However, in principle there is no real unpolarized light, it is rather weakly or partially polarized.

The polarization state can be influenced in its kind and direction, for instance by polarizers, $\lambda/2$, and $\lambda/4$ wave plates$^6$.

### 2.4 Ellipsometry

Ellipsometry is a powerful tool to analyze the reflectance and the scattering behavior of a material$^7$. Contrary to infrared spectroscopy, where reflected intensities are analyzed, in ellipsometry, relative changes in polarization of reflected$^8$ light are analyzed. A benefit of the latter type of analysis is that there is no need of a Kramers

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$^6$Also known as retarder.

$^7$For more details than given here, see Ref. [45, 51, 52].

$^8$Also possible for transmittance.
Kronig analysis in order to gain the physically related quantities e.g. the complex refractive index $N$. The fundamental equation in ellipsometry is

$$\frac{r_p}{r_s} = \tan(\Psi) \cdot e^{-i\Delta},$$

(2.37)

with the reflection coefficients for perpendicular $r_s$ and parallel $r_p$ polarized light, while $\Psi$ and $\Delta$ define the two ellipsometry parameters\(^9\) [45]. For these parameters,

$$\Psi = \arctan\left(\frac{|r_p|}{|r_s|}\right) = \arctan\left(\sqrt{\frac{R_p}{R_s}}\right)$$

(2.38)

is related to the amplitude ratio and

$$\Delta = \varphi_p - \varphi_s$$

(2.39)

to the phase difference between p- and s-polarization [45].

The Cauchy-Urbach dielectric function model is utilized in order to fit the ellipsometric parameters $\Psi$ and $\Delta$ and is typically applied to insulators [45, 53]. From this model, the complex refractive index $N$ can be extracted. The real part $n$ and the imaginary part $\kappa$ are calculated via following fitting functions:

$$n(\lambda) = A + B \frac{1}{\lambda^2} + C \frac{1}{\lambda^4},$$

(2.40)

$$\kappa(\lambda) = \alpha e^{12400\beta}\left(\lambda^{-1}-\gamma^{-1}\right)$$

(2.41)

$A$, $B$, $C$, $\alpha$, and $\beta$ are fitting parameters, while $\gamma$ represents the band edge [53].

In addition, the effect from the surface roughness of a sample to the optical properties is handled as a further fitting parameter with an effective medium theory (EMT) [54].

### 2.4.1 Effective medium approximation

For somehow heterogeneous media (inclusions of small particles in a homogeneous medium), porous materials, or rough surfaces, EMTs or effective medium approximations (EMAs) are often used to describe some sort of effective optical properties e.g. $N_{\text{eff}}$ [20]. The Maxwell Garnett and the Bruggeman effective medium theories

\(^9\)The minus sign in $e^{-i\Delta}$ corresponds to the definition of the refractive index: $N = n + ik$. 
are the most common ones [45, 55–57]. The Maxwell Garnett theory assumes small spherical nanoparticles—smaller than the wavelength—which are included in a dielectric homogeneous medium with small filling factors [55]. An improved EMT is the Bruggeman EMT where even high concentrations of extrinsic ellipsoidal particles can be modeled [55]. For materials with different void morphologies, the general effective media approximation delivers better results [58].

2.5 Scattering

When an electromagnetic wave interacts with an atom, it first absorbs and then emits (in the wave image) a spherical electromagnetic wave. For dense media, the waves in all directions—except the forward one—interfere destructively with each other and only the contribution in forward direction is left over, which leads to the macroscopic description of reflectance and transmittance. For single particles, the wave is scattered in all directions. The denser the material gets, the more the forward scattering dominates [26].

The basic theory which describes scattering phenomena is the Mie theory where its lower limit in size compared to the wavelength is described by Rayleigh scattering.

2.5.1 Mie theory

In 1908, Gustav Mie\(^\text{10}\) developed—based on Maxwell’s equations—a theory for scattering of light on spherical gold particles with sizes smaller or in the same range as the wavelength [59–61]. For these particle sizes, the law of refraction and reflection

\(^{10}\)His full name: Gustav Adolf Feodor Wilhelm Ludwig Mie.
cannot be applied anymore. In his theory, he also considered the conductivity of the particles and he knew that dipole radiation dominates for particles which are much smaller than the wavelength; this is the regime of Rayleigh scattering, which will be summarized in the next section [59]. In Mie’s theory, scattered light is partially polarized and rotationally symmetric with respect to the incident direction [59] (see also Fig. 2.6). Mie concluded that with increasing particle size, forward scattering is enhanced. Additionally, the wavelength dependence is rather weak compared to Rayleigh scattering [26]. The strength of the Mie scattering is typically expressed by the relative scattering cross section

\[ K = \frac{\sigma_{\text{tot}}}{\pi r^2} \]  \hspace{1cm} (2.42)

with the total scattering cross section \( \sigma_{\text{tot}} \) and the particle radius \( r \). The relative scattering cross function is a function of the size parameter

\[ a = \frac{2\pi r}{\lambda} \]  \hspace{1cm} (2.43)

and oscillates around a value of 2 while the amplitude decreases with increasing size parameter. The total scattering cross section can be calculated via

\[ \sigma_{\text{tot}} = 2\pi \int_0^\pi \sigma_M \sin(\xi) \, d\xi \]  \hspace{1cm} (2.44)

with Mie’s scattering function \( \sigma_M \) and the scattering angle \( \xi \) [60]. The relative scattering cross section gives the enhancement of attenuation caused by scattering of a parallel beam compared to the pure shadowing caused by the cross section of the particle itself [60].

Mie scattering effects are important for atmospheric research where sun light is scattered at molecules and dust. Even though in the early beginning of the theory, only spherical particles could be described by Mie’s theory, as time went by it was managed to extent the theory to non-spherical particles as well [59]. Since solving the mathematical equations for Mie’s theory needs quite a bit of computational power, it took quite a long time until it could be actually utilized to simulate physical systems. Nowadays, a variety of free available programs exist, which are able to solve the equations for spherical particles [62–64]. In Fig. A.1, one example is provided for three different particles sizes. The presented results in Fig. A.1 were simulated with Ref. 62.
2.5.2 Rayleigh scattering

For non-interacting particles much smaller than the wavelength ($< \lambda/15$ [26]) and with sufficient distance to each other (no interaction between them), the scattering of light can be described by Rayleigh scattering. Rayleigh scattering can appear on particles in the air, but also at extrinsic atoms or domains in a solid body [59]. Because of the phase relation between incident and scattered light, the particles have to be distributed irregularly—e.g. by density fluctuations [59]. Due to the statistically random localization of the scattering centers, Rayleigh irradiation is incoherent light [59]. Therefore, the scattered intensities can be simply summed up. The differential scattering cross section (sometimes also called intensity [65]) for a macroscopic volume $V$ of a vapor medium in air is given by

$$
\sigma(\xi) = \frac{2\pi^2V}{N_N\lambda^4} \left( n^2(\lambda) - 1 \right)^2 \left( 1 + \cos(\xi) \right)^2
$$

with the scattering angle $\xi$, the particle density $N_N$, and the refractive index $n$ [59]. From the scattering cross section, we can see that the scattered intensity is

$$
I_{\text{Scat}} \propto \frac{1}{\lambda^4}.
$$

As a consequence, the wavelength dependence in the region of Rayleigh scattering is much stronger than for bigger particle sizes where the Mie effect describes the scattering behavior. The scattered light consists of a parallel $I_p$ and a perpendicular part $I_s$. The latter one is independent of $\xi$, thus the $(1 + \cos(\xi)^2)$ factor in Equ. 2.45 results in 1, while $I_p$ depends on $\xi$. Fig. 2.6 a) and A.1 a) depicts this characteristic. By integrating Equ. 2.45 over all scattering angles $\xi$, the total scattering cross section results to

$$
\sigma_{\text{tot, Rayleigh}} = \frac{8\pi^3V}{3N_N\lambda^4} \left( n^2(\lambda) - 1 \right)^2
$$

The degree of polarization shown in Fig. A.1 is calculated via

$$
P(\xi) = \frac{I_s(\xi) - I_p(\xi)}{I_s(\xi) + I_p(\xi)}
$$

2.5.3 Single scattering events

Single scattering events can be well described with the Mie theory. A relationship between incident and scattered light is provided by the Müller calculus, where the Mie
theory determines the Müller matrix (scattering matrix) for spherical particles [20, 66, 67]. It is based on the Stokes parameters, which describe the polarization state of an electromagnetic wave in a four-dimensional vector [66]. Single scattering events exhibit stronger polarization effects than multiple scattering events [45].

2.5.4 Multiple scattering events

Multiple scattering events of photons can be described by a random walk [66] e. g. through a porous material. The state of polarization continuously changes along the scattering path and—after some scattering events—the light is typically depolarized, while for paths in the material which are only short, there remains a residual state of polarization [20].

For scattering in backward direction, the emitted intensity has a cosine depen-

Figure 2.7: Sketch of the coherent backscattering. For $\xi \rightarrow 0$, the two paths are exactly the same and since they can be obtained from each other by time inversion they constructively interfere. Adapted from Ref. 68.
tendency with respect to the surface normal \([20]\), better known as *Lambert’s law* (see Sec. 2.5.5). In direct backscattering direction, one can observe higher intensities which is called coherent backscattering cone and origins from coherent interference effects \([20, 66, 68–73]\).

In Fig. 2.7, a sketch of a path is illustrated, which causes coherent backscattering. When the incident light is a plane wave and photons follow the path \(S_1 \rightarrow S_2 \rightarrow \ldots \rightarrow S_n\) as well as its conjugated path \(S_n \rightarrow S_{n-1} \rightarrow \ldots \rightarrow S_1\), they fulfill the theorem of reciprocity\(^\text{11}\) where they can interfere (at \(\xi \rightarrow 0\) constructively) \([20, 66]\). Thus, the directly backscattered intensity is enhanced. In general, for directions off direct backscattering, the phase difference for the two paths is \(\vec{k}_o \vec{r} - (-\vec{k}_i \vec{r})\). As a consequence, the intensities oscillate with the scattering angle \(\xi\) because of interference effects. However, this is canceled out by the amount of different paths which also result in different values for \(\vec{r}\); except for \(\xi \rightarrow 0\) \([20, 68]\). The resulting peak in direct backscattering direction is normally very narrow (in most cases smaller than 1°\(^\text{12}\) \([68]\)), however, absorption by the material prevents long paths, which results in a broadening of the peak and the spiky tip gets rounded \([20, 66]\). At this point it is worth mentioning that the coherent backscattering peak can be also observed from rough surfaces \([74–78]\).

Additionally to the coherent backscattering peak, an asymmetric peak with negative polarization\(^\text{13}\) occurs if the incident light is unpolarized. The negative polarization exhibit a minimum at a small phase angle\(^\text{14}\) \([71, 73]\). This effect is called polarization opposition effect (POE) \([71]\).

Another effect which leads to a backscattering peak—also called hot-spot or opposition effect—is shadow hiding\(^\text{15}\). Shadow hiding occurs for structures which are much larger than the wavelength \([78, 81–86]\). In this case, for observing angles which deviate from the direct backscattering angle, the detector collects less intensity due to shadows caused by the roughness and therefore, results in lower signals. For low albedo materials, this effect is mostly dominated by single scattering events \([81, 87]\). For astronomical objects like the moon, both effects, coherent backscattering and shadow hiding seem to be present \([87]\).

\(^{11}\)The scattering matrix of one path is the transposed scattering matrix of the other path.

\(^{12}\)For white paint also 10° could be observed \([68]\).

\(^{13}\)Negative polarization: \(I_p > I_s\), following Equ. 2.48.

\(^{14}\)Angle between incident and scattering direction \([71]\).

\(^{15}\)There are simulations where near-field effects also play a role for materials with low albedo and densely packed structures \([79, 80]\).
2.5.5 Lambert’s law

A consequence of multiple scattering events is given by Lambert’s law. If light is scattered inside the material, the probability that it leaves the material from a depth $h$ without being scattered again decreases with the observing angle $\theta$ by $e^{\frac{-h}{l \cos(\theta)}}$ where $l$ is the mean free path between two scattering events [68]. By integrating $h$, Lambert’s law results in first approximation [68]. This law describes an angular dependence of the diffuse reflected intensity which is cosine-like

$$I = I_0 \cdot \cos(\theta),$$

(2.49)

with the intensity $I_0$ scattered into the zenith direction, and the angle $\theta$ to the surface normal [88]. While the irradiance (intensity) varies with the observing angle, the radiance\footnote{Note: Unit of radiance: $W \text{sr} \text{m}^{-2}$.} $L$ stays constant. In our daily life we can see this effect very nicely on a sheet of white paper. No matter at which angle one looks at it, it exhibits roughly always the same brightness because it is close to a Lambertian scatterer. Additionally, a lot of scattering events occur for Lambertian scattering, which lead theoretically to unpolarized diffuse reflected light [89].

2.6 Diffuse scattering

Most materials and objects diffusely reflect incident light, otherwise we would only see the them in specular direction with respect to the incident light. The scattering behavior of any material is described by the bidirectional scattering distribution function (BSDF) [21]. It includes the scattered light after transmission through the material via the bidirectional transmittance distribution function (BTDF), as well as the scattered light on the incident light side via the bidirectional reflectance distribution function (BRDF) [21–23].

The BRDF is defined as the ratio of the reflected radiance $L_r$ and the irradiance $E_i$ for a parallel beam [22, 90]

$$BRDF = f(\theta_i, \phi_i, \theta_r, \phi_r, \lambda) = \frac{dL_r(\theta_i, \phi_i, \theta_r, \phi_r, \lambda)}{dE_i(\theta_i, \phi_i, \lambda)},$$

(2.50)
which depends on the wavelength $\lambda$, the zenith $\theta_j$ and azimuth $\phi_j$ angle of the incident and observing direction of light (index $j = i, j = r$ respectively). Schaepman-Strub et al. explicitly show in their publication that the usage of the BRDF terminology is often handled incorrectly in literature [22]. The BRDF is a function of infinitesimal quantities and therefore cannot be measured directly [22].

For that reason, the reflectance factor is typically measured which is defined as the reflected radiant flux $\Phi_r$ and the reflected radiant flux from an ideal diffuse surface $\Phi_r^{\text{ideal}}$ (Lambertian surface), while the conditions of irradiation have to be the same for sample and reference. There exist different types of reflectance factors depending on the beam geometry [22]. The most general one is the bidirectional reflectance factor (BRF) from a surface area $dA$:

$$BRF = R(\theta_i, \phi_i, \theta_r, \phi_r, \lambda) = \frac{d\Phi_r(\theta_i, \phi_i, \theta_r, \phi_r, \lambda)}{d\Phi_r^{\text{ideal}}(\theta_i, \phi_i, \lambda)}$$ (2.51)

It can be applied, as long as the geometry includes a single illumination and parameters like viewing angle as well as surface area stay the same for sample and reference. Since the BRDF of a lossless Lambertian surface is $1/\pi\text{sr}^{-1}$, the BRF of any surface is directly linked to the BRDF via $BRDF = BRF \cdot 1/\pi\text{sr}^{-1}$ [22, 91]. Following the strict description in Ref. 22, the results presented in this thesis rather correspond to the biconical reflectance factor (CCRF). However, since our utilized light cones are rather narrow compared to the other dimensions, the angle-dependent results are referred to the BRF. In literature, also the term relative bidirectional reflectance factor (RBRF) is sometimes used for such cases [92]. For measurements on a certain zenith and azimuth angle of interest, the term reflectance factor is used in this thesis. The total reflectance of such a sample can be calculated by integrating the BRDF over the upper hemisphere [21]

$$R_{\text{tot}}(\theta_i, \phi_i, \lambda) = \int_0^{2\pi} \int_0^{\pi/2} f(\theta_i, \phi_i, \theta_r, \phi_r, \lambda) \cos(\theta_r) \sin(\theta_r) \, d\theta_r \, d\phi_r .$$ (2.52)

**Solid angle**

The solid angle is defined as

$$\Omega = \frac{A}{r^2} ,$$ (2.53)

---

17 Unit of the BRDF: sr$^{-1}$.
18 Similar to the geometric albedo (see also Sec. 9.2.1).
19 Also an infinitesimal quantity.
where $A$ is a spherical surface area and $r$ is the radius of the corresponding sphere. In spherical coordinates, it can be calculated via

$$\Omega = \int_{\phi_1}^{\phi_2} \int_{\theta_1}^{\theta_2} \sin(\theta) \, d\theta \, d\phi$$

with the azimuth angle $\phi \in [0, 2\pi]$ and the zenith angle $\theta \in [-\pi/2, \pi/2]$. The solid angle of the unit sphere is $4\pi$ sr. For only a fraction of the unit sphere:

$$\Omega = 2\pi \left( 1 - \cos \left( \frac{\omega_{sa}}{2} \right) \right)$$

(2.55)

gives a relation between the opening angle $\omega_{sa}$ of the cone and the solid angle [43].

### 2.6.1 Surface scattering

In principle, there are only two processes which lead to diffuse reflected light. One of them is the scattering on rough surfaces. When the wavelengths are smaller than the roughness, geometric optics can be applied to determine the scattering. In that case, the surface can be modeled via small mirrors with randomly distributed normal vectors (see Fig. 2.8 a)) [23, 93]. Thus, Fresnel’s equations can be applied at each interface.

![Figure 2.8: Sketch of surface a) and volume scattering b). The dashed blue lines in b) indicate further reflecting and transmitting processes, while the colored areas are supposed to illustrate different domains. Adapted from Ref. 94.](image-url)
2.6.2 Volume scattering

The other mechanism for diffuse reflection is volume scattering (see Fig. 2.8 b)) [23]. Most natural materials are inhomogeneous, consisting of domains with different complex refractive index $N$. Light which is transmitted into such a material gets reflected and transmitted at each interface between domains with different refractive index. Therefore, the fraction of light which escapes the material—after many scattering events—is diffusely scattered into all directions. Thus, even perfect flat polished surfaces of materials, which possess volume scattering, reflect light diffusely. For instance, a polished piece of polytetrafluoroethylene (PTFE) or white granite looks white from all directions, while in specular direction one can see the effect of the flat surface.

2.7 Drude Lorentz model

The Drude Lorentz model describes the electrodynamic properties of metals and semiconductors. Since our investigated samples possess many phononic contributions, the model is briefly explained by following Ref. 41 and is similar to Ref. 95.

2.7.1 Drude model

The Drude model is applied to describe intraband transitions and corresponds to a metal-like behavior. Electrons are treated as particles within a classical gas without accounting any Coulomb interactions in this model. They only interact in form of collisions. From this assumption, a relaxation time $\tau$ is derived, which is the average time between two collisions where the equation of motion results in

$$
m \frac{d^2 \vec{r}}{dt^2} + \frac{m}{\tau} \frac{d\vec{r}}{dt} = -e \vec{E}_{\text{ext}}(t),
$$

with the external electric field $\vec{E}_{\text{ext}}$, the position $\vec{r}$, the time $t$, the charge $e$, and the electron mass $m$. By applying the harmonic ansatz $\vec{E}_{\text{ext}}(t) = \vec{E}_0 e^{-i\omega t}$, a solution for Equ. 2.56 expressed in terms of the optical conductivity is provided by

$$
\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = \frac{Ne^2}{m} \frac{1 + i\omega t}{1 + \omega^2\tau^2},
$$

(2.57)
Figure 2.9: Isolated Drude (a-c) and Lorentz (d-f) contribution for the reflectivity (a, d), optical conductivity (b, e), and refractive index (c, f). The Drude term has a damping of $1/\tau = 60 \text{ cm}^{-1}$ and a dc conductivity of $\sigma_{dc} = 100 \Omega^{-1}\text{cm}^{-1}$. It results a plasma frequency $\omega_p = 600 \text{ cm}^{-1}$ which is marked with a green dashed line. The Lorentzian has a permittivity at zero frequency ($\nu \rightarrow 0 \text{ cm}^{-1}$) of $\epsilon_0 = 1000$, a center frequency of $100 \text{ cm}^{-1}$, and a damping of $1/\tau = 100 \text{ cm}^{-1}$. In a), the reflectivity decreases with increasing frequency. At the plasma frequency a sharp drop appears. The inset highlights the Hagen-Rubens regime where the red dashed line represents the fit from its relation. The reflectivity for the Lorentzian in d) is rather constant for low frequencies, increases at the center frequency and drops similar to the Drude model at $\omega_p$. In b), the inflection point in $\sigma_1$ and the maximum in $\sigma_2$ can be utilized to identify the damping $1/\tau$ (purple dashed line). For a Lorentzian in e), the center frequency (wine dashed line) can be identified by the maximum in $\sigma_1$ and the inflection point in $\sigma_2$. In c), the absolute values of $n$ and $\kappa$ are identical for low frequencies and split up with increasing frequency. At $\omega_p$ it is again $|n| = |\kappa|$. For the Lorentzian in f), the absolute values of $n$ and $\kappa$ are only equal at $\omega_0$ and $\omega_p$.

with the charge carrier density $N$ and the angular frequency $\omega$. For $\omega = 0 \frac{1}{s}$, Equ. 2.57 yields the zero frequency conductivity

$$\sigma_{dc} = \frac{N e^2 \tau}{m} = \frac{1}{4\pi \omega_p^2 \tau} \quad (2.58)$$
where $\omega_p$ is the plasma frequency (compare Fig. 2.9). For $\omega \ll 1/\tau$, the real part of $\sigma(\omega)$ dominates and $\sigma_1(\omega) \approx \sigma_{dc}$. This frequency range is called Hagen-Rubens regime where the reflectivity can be modeled via

$$R(\omega) \approx 1 - \sqrt{\frac{2\omega}{\pi \sigma_{dc}}} = 1 - \sqrt{\frac{2e\omega}{\sigma_{dc}}}.$$  \hspace{2cm} (2.59)$$

Between $1/\tau < \omega < \omega_p$, the imaginary part of $\sigma(\omega)$ dominates and the reflectivity is nearly constant. This frequency range is called relaxation regime. For $\omega > \omega_p$, the electrons are too inert to follow the external electric field. Therefore, the material exhibits no absorptions and is transparent.

In 1933, Sommerfeld improved the Drude model with a quantum mechanical extension by considering the Fermi surface, which leads to an effective electron mass $m^*$. The effective mass of an electron depends on the curvature of the Fermi surface within this modified model [41]. This assumption affects the mean free path $l$, which depends on the Fermi velocity $v_F$ in this case ($l = v_F \tau$), instead of the average thermal velocity $\bar{v}_h$ of two electrons.

### 2.7.2 Lorentz model

While the Drude model treats electrons like free charges, they are considered as harmonic oscillators with a damping of $1/\tau$ in the Lorentz model. This model is able to describe interband transitions, absorptions, phonons or ionic transitions. The equation of motion looks similar to the one of the Drude model:

$$m \frac{d^2 r}{dt^2} + m \frac{dr}{dt} + m \omega_0^2 \vec{r} = -e \vec{E}_{ext}(t) \hspace{2cm} (2.60)$$

where $\omega_0$ is the resonance frequency of the Lorentzian. With $\vec{E}_{ext}(t) = \vec{E}_0 e^{-i\omega t}$ and $\vec{r}(t) = \vec{r}_0 e^{-i\omega t}$ one obtains the solution

$$r(\omega) = -\frac{e}{m \omega_0^2 - \omega^2 - i\omega/\tau} \vec{E}_{ext}(\omega)$$ \hspace{2cm} (2.61)$$

which is again a complex quantity. In Ref. 41, it is elaborated that from this result the optical conductivity results in

$$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = \frac{N e^2}{m} \frac{\omega}{i(\omega_0^2 - \omega^2) + \omega/\tau} = \frac{\omega_p^2}{4\pi} \frac{\omega}{i(\omega_0^2 - \omega^2) + \omega/\tau}$$ \hspace{2cm} (2.62)$$

27
where $\omega_p$ is again the plasma frequency (compare Fig. 2.9).

For low frequencies $\omega < (\omega_0 - 1/\tau)$, nearly no absorptions occur, similar to the Drude model. Close to $\omega_0$, the electromagnetic radiation can excite electrons, therefore, strong absorptions can be measured. These absorptions also lead to a strong contribution of the real part of the optical conductivity. For $(\omega_0 + 1/\tau) < \omega < \omega_p$ the reflectivity exhibits highest values, which can be in the order of reflection from metals. When $\omega > \omega_p$, the material gets transparent, exactly as in the Drude model.

### 2.8 Kramers Kronig relation

To be able to calculate the optical conductivity or the refractive index from reflectivity measurements, one needs the optical phase shift $\phi(\omega)$ as well. However, this is only possible for techniques like ellipsometry or time domain spectroscopy [96]. Since the causality condition is valid for all optical constants, the Kramers Kronig relation\(^{20}\) can be applied in order to calculate the phase shift:

$$\phi(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\ln(|r(\omega')|)}{\omega'^2 - \omega^2} d\omega'$$

(2.63)

where $\mathcal{P}$ denotes the Cauchy principle value and $|r|$ is the complex reflection coefficient (amplitude) [97, 98]. From this equation it is obvious, that relation 2.63 only works for an infinite frequency range. Therefore, it is important to measure a very broad frequency range and to properly extrapolate the reflectivity data to very low and high frequencies.

### 2.9 Surface roughness

The investigated samples within this thesis possess macroscopic roughness values. There exist several definitions for determining a quantity to express the roughness of a sample. The notations given here follow DIN EN ISO 4287.

The most general one is the maximum height $R_t$ of the profile which is given by the highest peak and the deepest valley for a measured distance $L_t$ (see Fig. 2.10 a)) [99–

\(^{20}\)For the mathematical framework have a look at Ref. 41, Ref. 97, and Ref. 98.
Figure 2.10: Sketch of different definitions for surface roughness. In a), the maximum height $R_t$ and the arithmetical mean roughness value $R_a$ are illustrated. The green line $L_m$ is at a height $z$ where the blue and the red area are equal. In b) the averaged smoothing depth $R_z$ is calculated from five sections. Adapted from Ref. 99.

The arithmetical mean roughness value $R_a$ gives the averaged deviation from the mean line $L_m$ which is calculated via

$$R_a = \frac{1}{L_t} \int_{0}^{L_t} |z(x) - L_m| \, dx ,$$

while $z(x)$ is the measured profile and the mean line results from $L_m = \frac{1}{L_t} \int_{0}^{L_t} z(x) \, dx$. A disadvantage of $R_a$ is that it cannot distinguish between peaks and valleys. Thus, many different kind of profiles result in the same value for $R_a$. However, since $R_a$ is based on a broad averaging, its reproducibility is very good [100]. When single peaks and valleys are supposed to have a stronger impact on the roughness value, the quadratic arithmetical mean roughness delivers better results, which is defined as

$$R_q = \sqrt{\frac{1}{L_t} \int_{0}^{L_t} (z(x) - L_m)^2 \, dx} .$$
CHAPTER 2. THEORETICAL BACKGROUND

The averaged surface roughness $R_z$ (depicted in Fig. 2.10 b)) reacts more sensitive to changes in the surface structure and is defined as the sum over five equidistant sections $L_r$

$$R_z = \frac{1}{5} \sum_{i=1}^{5} R_{z,i}$$  \hspace{1cm} (2.66)

where $R_{z,i}$ is the maximum height of its section (highest peak minus deepest valley) [100]. The parameters $R_t$, $R_a$, $R_q$, and $R_z$ do not provide any information whether the roughness consists predominately of peaks or valleys. For both cases, different surface roughness configurations could be found where the mentioned parameters would deliver the same result. For such cases, the averaged peak height $R_p$ and the averaged valley depth $R_v$ help to distinguish between these two cases. They are defined very similar as the averaged surface roughness $R_z$. For each of the five segments, the vertical distance $p_i$ between the mean line $L_m$ and the highest peak for $R_p$—or $v_i$ for the lowest valley of $R_v$ respectively—are summed up and averaged:

$$R_p = \frac{1}{5} \sum_{i=1}^{5} p_i$$  \hspace{1cm} (2.67)

$$R_v = \frac{1}{5} \sum_{i=1}^{5} v_i$$  \hspace{1cm} (2.68)

By establishing the ratios $R_p/R_z$ and $R_v/R_z$, it is possible to make conclusions about different surface profiles [100].

2.10 Water

Although water has a very simple molecular structure, novel physical properties are still discovered. Examples are the emergence of superconductivity in doped ice X with a critical temperature $T_c$ of 60 K at 150 GPa [10], the experimental evidence for a ferroelectric soft mode in confined water [9], or novel phases like superionic water ice [12] or $\beta$-XV ice [11]. Since water possesses a very rich phase diagram with at least 16 experimentally proven phases [102–104], there will be for sure more fascinating properties discovered in future, maybe even more phases.

For the atmospheric and astrophysical research, detailed and accurate optical behavior for water, ice, and snow is very important in order to create appropriate models [105–107]. Under ambient pressure, the ice phase is the so called Ih phase.
with a simple hexagonal crystal structure. Even for this phase, spectroscopic measurements for obtaining its physical properties like the complex refractive index are tricky. Air bubble enclosures affects the measurements, which is the reason why very clear ice is favorable for comparative studies about the pure ice properties—e.g. by producing it via the freeze-pump-thaw technique [108, 109]. Additionally, depending on the spectral region, the thickness of such ice samples is an important factor e.g. in transmission measurements, which has to be either very thin [110] or very thick [111]. These parameters make the sample preparation even more difficult. The optical properties of snow depend strongly on the grain size [112] and the shape of the flakes, which is also influenced by the age of the snow. Typical optical investigations are performed during field tests [113–115]. However, also whole laboratories are cooled down in order to get reliable spectra [112].

Spectroscopic measurements on liquid water have some difficulties, too. For instance the real part of the complex refractive index is typically determined by Abbe refractometers. This, however, needs a re-treatment with correction terms. The imaginary part of the refractive index is then measured with a different setup by utilizing liquid cells [25].

### 2.10.1 Vibrational modes

<table>
<thead>
<tr>
<th>State</th>
<th>Vapor [7, 116–118]</th>
<th>Liquid [118][[7]]</th>
<th>Solid [118][[7]]</th>
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<tbody>
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<td>3049</td>
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<tr>
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<tr>
<td>$\nu_3$ (cm$^{-1}$)</td>
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<td>3615</td>
<td>3490</td>
</tr>
</tbody>
</table>

Table 2.1: Energies of the fundamental vibrations of molecular water (vapor), liquid water (bulk) and solid water (bulk ice). $\nu_1$ is the symmetric stretch, $\nu_3$ the asymmetric stretch, and $\nu_2$ the bending mode. Since literature gives slightly different values, two typical ones are listed here.

In this thesis, especially the combination bands and overtones of water are investigated in the near-infrared (NIR) region. The fundamental vibrational modes are located in the mid-infrared (MIR) and are all infrared active, while the librations are rather located in the THz and far-infrared (FIR) region [8].
By passing through the phase diagram from vapor to the solid state at ambient pressure, the excitation energies of the symmetric \( \nu_1 \) and asymmetric stretching mode \( \nu_3 \) decrease \[119\], while the one for the bending mode \( \nu_2 \) increases (see Tab. 2.1). In Fig. 2.11, the three fundamental vibrational modes and librations are illustrated. The librations originate from restricted rotations due to the influence of hydrogen bonding in the liquid phase \[8\]. The small moment of inertia with respect to rotations lead to a very rich vibrational-rotational spectrum in the vapor phase. Therefore, for spectroscopic measurements, humidity is avoided especially in the THz range by utilizing a nitrogen atmosphere or vacuum. The very narrow absorption lines in the vapor phase broaden in the liquid phase, leading to an overlap of absorption features \[8\]. The earlier mentioned shifts of absorptions in Tab. 2.1 are caused by hydrogen bonds \[8, 119, 120\]. In water, the molecules are arranged dynamically without any specific order. Therefore, the influence of hydrogen bonds can vary strongly, which makes it difficult for an exact specification of the absorption modes\[21\]. In the NIR region, the first and second overtones as well as combination bands of the fundamental modes are present. Essentially, these are \( \nu_1 + \nu_3, \nu_1 + 2\nu_2, \nu_3 + 2\nu_2, \nu_1 + \nu_2 + \nu_3, \nu_1 + 2\nu_3, \) and \( 2\nu_1 + \nu_3 \) \[8, 121–123\].

\[21\] In solutions, the modes can also shift, because dissolved molecules have an influence on the hydrogen bonds, too \[120\].
Snow consists of ice crystals and air. A simple single snow flake is transparent, only the amount of snow flakes in total or fine structures like in dendrites lead to its white appearance.

Snow flakes appear in a lot of different shapes and sizes [125, 126]. An intense study about the morphology of snow crystals was performed by Nakaya et al. [127]. These studies lead to a morphology diagram, which is often called Nakaya diagram (see Fig. 2.12) [128]. In this diagram, depending on the temperature and supersaturation, the resulting shapes of snow flakes are illustrated. There are two main categories: plates and columns, both based on the hexagonal shape originating from the Ih group of ice. For a temperature range between 0 °C and −35 °C, there can be four different regions allocated: down to approximately −4 °C plates, between −4 °C and −10 °C columns, between −10 °C and −22 °C again plates, and below −22 °C a mixture of both [124, 129]. The supersaturation (\( \rho = m/V \)) with the water
mass $m$ and the volume $V$ [126]) determines the complexity of the shapes. If the humidity is really high, the crystal growth is fast. The fast growth together with diffusive instabilities [128] lead to complex, fractal dendrite structures, which we typically have in our mind when we think about snow flakes [124].

The reflectance or albedo of snow depends a lot on the grain size [112, 130]. Since the grains get bigger and less fine structured by aging, older snow exhibit less reflectance [131].
3 Asphalt

In this section, a small introduction into roads or asphalt in particular will be presented. Especially its components and nomenclature will be examined. A road consists of many layers, where its top layer is typically 4 cm thick [132]. Since optical experiments—mainly in the NIR region—are performed in this thesis and the penetration depth is way shorter than this thickness of this layer, the introduction concentrates on this top layer.

3.1 Brief introduction

The existence of roads can be traced back to several thousand years BC [133]. The Romans are known to be the first who used a large network of roads to connect even distant locations [134]. The quality of some roads were really high, so that some of them even survived until today. In our modern world—with a high traffic volume—a lot of improvements were achieved in the field of road construction. Nevertheless, in the past as well as nowadays, roads are made up from several layers [135], where each possesses its own specific properties to fulfill the demanded requirements—e. g. high durability or low noise generation.

3.2 Structure

Depending on their usage (rural, urban, highways, etc.) and the load they have to endure, roads consist of different amount of layers\(^1\), with their thickness also varying dependent on their type [132, 136, 137]. In Fig. 3.1, a cross section of a typical road is illustrated. Depending on the stability of the ground beneath a road, it can stay as it is or—if it is too unstable—the ground has to be reinforced. The subgrade is

\(^1\)Determined by the Richtlinien für die Standardisierung des Oberbaus von Verkehrsflächen (RStO).
**CHAPTER 3. ASPHALT**

Figure 3.1: Schematic of a road cross section. On the left side a general cut through a road with its three main sections. On the right side, a zoom into the different layers of the superstructure. Common thickness values of these layers are provided while the white dashed lines represent the corresponding lower value. The relative scale of the schematic (right side) fits to its values. Adapted from Ref. 133.

Typically there to stabilize the road and to reach a desired height. The superscript consists of several layers, each with its own task. For regions where frost can occur, a frost protection layer is needed. The material itself has to be permeable for water, resistant against frost, and its grains have to be rather coarse with low content of small grains [133]. The bulkhead or gravel base course belongs to the base layers and consists only of grains, without any binding material. Its ability to withstand load mainly originates from internal friction between the grains [133]. The asphalt base course is the first layer which possesses a binding material (bitumen). This layer has to be at least 8 cm thick and varies dependent on the construction class\(^2\). It is supposed to distribute the vertical load to the underneath layers which is the reason why this layer has to be very stable. The typical lifetime of this layer is 50 years [133]. The highest shear stress from deceleration and acceleration appears

\(^2\)For roads with low workload, this layer can be even omitted.
in the asphalt binder course. Therefore, this layer has to consist of high quality asphalt material. It is crucial that this layer has an even surface, because it is hard to correct an unevenness with the asphalt wearing course [133]. The latter course is the last layer and thus, simply called upper or top layer in this thesis. It is directly exposed to weather conditions, sun light and the traffic. The stone components of this layer need to have high enough resistance against polishing effects caused by the tires, because the road has to guarantee a certain friction coefficient. However, this is only one of many requirements for the top layer. There exist many different types which are used in different locations, dependent on the local circumstances. The typical thickness of this layer is 4 cm (compare Fig. 3.1), while there are slight deviations possible, depending on the used grain sizes. The lifetime of this layer is the shortest one from all of the layers. Therefore, it has to be frequently replaced to guarantee a long lifetime of the whole road [133].

For the ensemble of various top layers, there exist short notations which will be also used in this thesis and are thus shortly explained in the next subsection.

### 3.2.1 Nomenclature

The following expression is one short notation of an asphalt wearing course, which is investigated in this thesis:

\[ \text{SMA} \underline{8} \underline{S} \underline{25/55 - 55} \underline{A} \]

**Type**

The type specifies the class of the wearing course. Some of the most general used types are shortly described in the following:

- Asphalt Concrete (AC)
  
  It is one of the most frequently utilized asphalt types. The name “concrete” is related to the process how the grains are sieved. From the sieving process, there results a steady grading of grain sizes, thus, the void content is quite small with 3 Vol.-% to 5 Vol.-% [133]. Big grains are surrounded by smaller ones [133, 138]. Nowadays, for roads with heavy workload (Bk_{100} and Bk_{32} [132]), the AC-type is not used anymore [133, 138]. The surface of this kind of top layer has a rather fine structure due to high content of sand and small grains (\( \leq 2 \text{ mm} \)) [133].
• Stone Mastic Asphalt (SMA)
The SMA consists of roughly 70% to 80% of double-crushed chips with more bitumen and filler material than the AC-type [133]. The double-crushed chips are nearly cube-shaped. In the sieving process, the smaller grains are filtered out, thus the big grains touch each other and stabilize themselves [133, 138]. They build a stable structure with low deformability. The gaps are filled by a bitumen-filler-mixture, so that in the end it has a void content of roughly 3 Vol.-% to 5 Vol.-% [133]. The high content of bitumen makes it necessary to add stabilizers (usually cellulose fibers) which hold the bitumen together during the construction. The mixture of bitumen, filler and stabilizers is called mastic [133].

• Mastic Asphalt (MA)
AC and SMA belong to the group of roller-compacted asphalts which have to be directly compressed by rolling after putting them on the ground. The MA is liquid-like when it is heated up and can be poured. There is no further compression necessary and there is no significant void content. The liquid mixture consists of coarse stone grains, sand, filler, and a hard type of bitumen. The latter one is the major stabilizer for this kind of asphalt. In Germany, the amount of MA is rather low in road constructions [133].

• Porous Asphalt (PA)
In Germany, the porous asphalt is better known as “Wasserdurchlässiger Asphalt (water permeable asphalt) (WDA)”\(^3\). For this kind of asphalt, all layers are permeable to water and therefore, the water can directly percolate into the ground. The void content of this type is between 13 Vol.-% and 20 Vol.-% [133].

• Open Porous Asphalt (OPA)
This type of asphalt is also known as drainasphalt and was initially only used at airport runways. Since it additionally reduces the noise of rolling tires, it is also known as a “whispering asphalt”. Compared to all other asphalts, the void content is very high with around 22 Vol.-% to 28 Vol.-%. In addition, since there are exist only big grains, the voids are physically connected with each other, which allows water to drain through the asphalt [133, 139]. While in PA-type, the water can directly percolate into the ground, at the OPA,

\(^3\)Note: In literature, the differentiation between OPA and PA is not very strict and the OPA is often called PA [138].
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the water is guided to the sides, since the binder course is impermeable to
water [133].

- Noise Optimized Asphalt (LOA)
  The LOA possesses a special surface structure with an optimized distribution
  of the rather small grain size, which leads to a significant noise reduction [139].
  The layer consists of dense packed grains with low amount of fine material
  and a void content between 4 Vol.-% to 9 Vol.-% [138]. For the noise optimized
  effect, it is crucial that the layer is very even. This type of asphalt is not very
  robust, therefore it is normally used in urban areas [138].

**Grain size**

The number provided behind the type represents the main grain size in mm [24].
Depending on the type, there are also smaller grains present, which act as filler or
stabilizer. For the given example it means that the main grain size is 8 mm.

**Identifier**

In Germany only, the first letter after the grain size is an identifier for the layer,
while the second letter represents a hint about the stress it can handle. In Tab. 3.1,
the letters and their meaning are summarized [140]. For asphalt types which are

<table>
<thead>
<tr>
<th>1. letter</th>
<th>Meaning</th>
<th>2. letter</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Base course (Asphalttragschicht)</td>
<td>S</td>
<td>Heavy load</td>
</tr>
<tr>
<td>B</td>
<td>Binder course (Asphaltbinderschicht)</td>
<td>N</td>
<td>Normal load</td>
</tr>
<tr>
<td>D</td>
<td>Wearing course (Asphaltdeckschicht)</td>
<td>L</td>
<td>Low load</td>
</tr>
<tr>
<td>TD</td>
<td>Combined base and wearing layer (Asphalttragdeckschicht)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: On the left side, the first letter and on the right side the second letter is
assigned.

only used for the wearing course e. g. SMA, the first letter is neglected. Thus, the
given example is suitable for heavy loads.

**Bitumen**

The numbers which follow the identifiers characterize the bitumen. The first two
numbers are determined via the needle penetration test [133, 141, 142] and represents
the hardness of the bitumen.
• Needle penetration test:
  In this test, the bitumen sample is thermally stabilized at 25°C. For 5 s, a standardized needle is vertically pressed inside the bitumen with in total 100 g. The resulting penetration depth is measured in 1/10 mm [133, 142]. For a very soft bitumen, where the penetration depth is more than 33 mm, the temperature is reduced to 15°C [133, 142]. The test is done several times on different spots. The lower and upper value provides the range of the penetration depths and so determines the hardness of the bitumen.

For our example, a bitumen with a hardness/penetration depth between 2.5 mm and 5.5 mm is used. It is a quite hard bitumen, which is typically utilized for highways. The third number results from the softening point and is a measure for the elasticity. In general, it is only noted for a polymer modified bitumen (PmB).

• Ring and ball method:
  This method is an additional measurement procedure to characterize bitumen and results in the softening point\(^4\). Here, a ring filled with bitumen is placed inside a vessel full of water or glycerol. On top of the bitumen a small steel sphere (diameter: 9.5 mm [143]) is placed. The vessel is slowly and constantly heated. The sphere will bend the bitumen and at the temperature where the ball is lowered by (25 ± 0.4) mm [143], the experiment stops. This temperature provides then the softening point in °C [133].

Thus, the bitumen utilized in this example has a softening point of 55°C.

**Polymer**

The last letter indicates which type of polymers (consistent of natural rubber and synthetic polymers) are used to influence the viscoelastic properties of the bitumen [133]. An A represents a modification with elastomers, while a C represents plastomers [140]. In Germany, usually the elastomer modified bitumen is utilized [140].

\(^4\)In German: Erweichungspunkt Ring und Kugel (EP RuK).
3.3 Composition

3.3.1 Main material – stones

Except for the bitumen part, asphalt consists mainly of locally available stones as long as the kind of stone material is suitable for roads [24]. In other cases, the material is delivered. For instance, asphalt in northern Germany has a high content of stones from Scandinavia, which are mainly igneous rocks (e.g. granodiorite) [144]. For dark stones like basalt, brighteners (natural and artificial) are added into the asphalt mixture to reach a certain brightness of the road. Roads in Baden-Württemberg are mainly made of moraine from the Alps. Moraine is debris originating from glaciers. In case of asphalt samples investigated in this thesis, the moraine contains a mixture of limestone, rhyolite, feldspar, quartz and other stones or minerals [24]. In the following, a closer look at the rocks and minerals is presented:

• Limestone:
  Limestone belongs to the family of sedimentary rocks. It consists mainly (at least 50 %) of the mineral calcite (CaCO$_3$). Other components are for example small amount of quartz, feldspar, and other minerals [145].

• Rhyolite:
  Rhyolite is very quartz-rich stone, made up from very small grains, and belongs to the igneous rocks [146]. Except of quartz, it contains also of types of feldspar (plagioclase and sanidine) with additional traces of [146]
  – hornblende:
    Mineral with a generalized chemical composition of
    \[(\text{Ca}, \text{Na})_{2-3}(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Si}, \text{Al})_8 \text{O}_{22}(\text{OH}, \text{F})_2\] [147]
    and
  – biotite:
    Mineral with a generalized chemical composition of
    \[\text{K}(\text{Mg}, \text{Fe})_{2-3}\text{Al}_{1-2}\text{Si}_{2-3}\text{O}_{10}(\text{OH}, \text{F})_2\] [148].

• Feldspar:
  This mineral represents a large group of rock-forming silicates. All feldspar minerals are similar in structure, physical properties and chemical composition. The chemical compositions of common feldspars are: $\text{KAlSi}_3\text{O}_8$, $\text{NaAlSi}_3\text{O}_8$, etc.
and CaAl$_2$Si$_2$O$_8$ with the generalized chemical composition $X(\text{Al, Si})_4\text{O}_8$ where $X$ can be replaced by the ions $K^+$, $Na^+$, $Ca^{2+}$, $Ba^{2+}$, $Rb^+$, $Sr^{2+}$, and $Fe^{2+}$ [149].

- **Quartz:**
  This mineral is present in nearly every type of rocks and has a chemical composition of SiO$_2$ [150].

- **Granodiorite:**
  Granodiorite is an igneous rock, very similar to granite with main contributions of around 76 wt% SiO$_2$ and 14.5 wt% Al$_2$O$_3$ [151]. The darker the rock, the higher the mineral contribution from plagioclase (special types of feldspar, ranging from albite Na(AlSi$_3$O$_8$) to anorthite Ca(Al$_2$Si$_2$O$_8$) [152]), biotit, and hornblende [153].

- **Greywacke:**
  Greywacke is a sandstone [154] and belongs to the clastic sedimentary rocks with main contributions of feldspar (mainly plagioclase) and quartz [153].

- **Brightener:**
  A natural brightener used in some of the investigated samples is Lysit, which is white granite gravel. An artificial brightener is Luxovite, consisting of sintered flint [154].

### 3.3.2 Bitumen

Bitumen is in most cases a waste product from crude oil refinery [133, 155, 156]. It consists mainly of combinations of alkanes, cycloalkanes, and aromatics [157]. Additionally, it contains few other atoms despite carbon and hydrogen, for instance oxygen, nitrogen, sulfur and traces of metals [155–158]. Bitumen is a complex mixture of molecules and it is difficult to divide it in all its components [155]. By a separating method called SARA (saturates, aromatics, resins and asphaltenes), it was proven that even bitumen can exhibit a microstructure [159].

In roads, around 2% to 6% of the mass is bitumen [133]. The elastic and viscous properties which strongly dependent on the temperature [133] have to be considered for local usage in roads.
## Table 3.2: List of investigated asphalt types with their name, a short description about the condition, peculiarities, and the surface roughness $R_t$ (see Sec. 4.6). For the “PA 15” and “SMA 8 S” there is no information about the bitumen. The “II” and “new” (see also later in the text) helps to distinguish between the asphalts as long as they cannot be distinguished by their condition.
3.4 List of investigated asphalt samples

Tab. 3.2 presents a list with the investigated asphalts during this thesis. There are three different aging states, namely: untreated, sandblasted, and drilling core. The untreated asphalt samples still have their bitumen layer on top. They are newly made samples (26 cm times 32 cm) in a laboratory and were never built into a road. Another group was made the same way, however, the surface got sandblasted in order to remove the upper bitumen coating. This group represents the first aging step. At a road, this is achieved by the tires of the vehicle, which remove this coating as well. The last group are samples which were actually already built into a road. These are drilling cores with a typical diameter of 15 cm. This type of sample represents the highest aging phase investigated here. Load of the vehicle compressed the top layer and so slightly changed their surface structure.

The samples investigated within this thesis are from TPA Gesellschaft für Qualitätssicherung und Innovation GmbH, Ingenieurbüro Thomas Voll, and the university of Minho in Portugal.

The top layer SMA 8 LA 40/100-65 A is an SMA type, which is noise optimized (LA – “lärarm”). Compared to the other SMA types, it contains some amount of smaller grains [139] and therefore, a more porous surface structure (void content between 9 Vol-% and 14 Vol-%) which is responsible for the reduction of noise [138].

3.5 General optical properties

Optical investigations on asphalt samples are not a totally new topic. For example, Puttonen et al. made some field observations on different asphalts of the AC-type in southern Finland [91]. In their analysis they reduced the angular dependence of the BRDF from the incident azimuth angle $\phi_i$ and the azimuth angle in reflecting direction $\phi_r$ to only one azimuth angle $\phi_d$, which is the difference between both angles. They establish this approximation because they assume asphalt samples as flat and isotropic enough. Compared to our oldest aging state, they were able to go one step further, since vehicles with studded tires lead to even more wear; thus leading to a stronger aging effect. The metal parts of the tires (studs) lead to a rougher surface while this surface is additionally polished by the studs. The loosen particles stick to the surface, together with dust and dirt, which lead to a

---

5Studded tires are common for northern countries like Finland.
dull appearance of the asphalt [91]. For older samples, they could resolve a peak in
direct backscattering direction of the BRF, while new samples did not exhibit this
peak. Additionally, their older samples displayed two to three times larger brightness
compared to the new ones. Polarization-dependent measurements showed different
magnitudes dependent on the age of the samples [91], which is in good agreement
with our results\(^6\), as we will discuss in Sec. 6.2.2.

\(^6\)For results from polarization-dependent measurements, the interested reader is referred to the
master thesis of Christoph Müller [160].
4 Experimental setups

In this chapter, the utilized setups are introduced and important aspects for the measurement procedure are explained. It begins with a short mapping of the infrared (IR) range, together with an overview about the utilized sources and detectors. Afterwards the different setups are introduced. Since one of the setups was also used during my master thesis, some parts will be similar or just linked to Ref. 95.

4.1 Infrared region

![Figure 4.1: Overview about the energy range of the IR region. Four units are presented which are common within various scientific communities. The green area (far-infrared (FIR) to visible (VIS)) marks the range which is covered with the Fourier-transform infrared (FTIR) spectrometer, while the brown part (part of the near-infrared (NIR)) is covered with the grating spectrometer. The light blue area (far far-infrared (FFIR)) together with the green one displays the possible measurement range of our FTIR spectrometers.](image)
Within the community of infrared spectroscopy, the observed energy range is typically given in CGS units (cm$^{-1}$ – spoken: wavenumber). For other communities, providing the energy in eV (electron volts), frequency (THz), or wavelength is more common. In this thesis, primary wavelength and frequency in wavenumber is utilized. Fig. 4.1 helps to categorize the different units to the desired one. An exact conversion between the presented units can be achieved with following relation:

\[ \omega = 2\pi \nu = 2\pi \frac{c}{\lambda} = 2\pi c\vartheta, \]  

(4.1)

where \( c \) is the speed of light, \( \omega \) the angular frequency in \( 1/s \), \( \nu \) the frequency in Hz, \( \lambda \) the wavelength, and \( \vartheta \) the frequency (wavenumber). The FTIR spectrometers from the 1. Physikalisches Institut are able to cover a range between 10 cm$^{-1}$ and 25000 cm$^{-1}$, which is part of the THz, the complete IR, and the visible (VIS) range. Even though the different infrared regions are defined in part 7 of DIN5031 [161], the regions are rather coupled to the sources and detectors in the IR community. Therefore, Tab. 4.1 provides a definition on how the different terms for the IR regions are used within this thesis. As consequence of this kind of definition, the regions slightly overlap. The FIR region is typically dominated by intra- and interband transitions (Drude response), while the MIR, NIR, and VIS region are dominated by interband transitions. Phonons can basically occur in all the regions.

<table>
<thead>
<tr>
<th>Region</th>
<th>Energy (meV)</th>
<th>Frequency (THz)</th>
<th>Wavelength (μm)</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIR</td>
<td>8.7 – 86.8</td>
<td>2.1 – 21</td>
<td>143 – 14.3</td>
<td>70 – 700</td>
</tr>
<tr>
<td>MIR</td>
<td>93 – 744</td>
<td>22.5 – 180</td>
<td>13.3 – 1.7</td>
<td>750 – 6000</td>
</tr>
<tr>
<td>NIR</td>
<td>248 – 1240</td>
<td>60 – 300</td>
<td>5 – 1</td>
<td>2000 – 10000</td>
</tr>
<tr>
<td>VIS</td>
<td>992 – 3100</td>
<td>240 – 749</td>
<td>1.25 – 0.4</td>
<td>8000 – 25000</td>
</tr>
</tbody>
</table>

Table 4.1: The spectral regions according to our sources and detectors. In this thesis, a range from the FIR to the VIS is covered. Note: For measurements which utilize the grating spectrometer, the range spans from 840 nm to 1650 nm, which is also referred as NIR range.

4.1.1 Sources – FTIR spectrometer

As already mentioned, there are several light sources used to cover a broad frequency range, where each one has a limited spectral range. The sources are all blackbody
radiators, which ideally have no sharp peaks or dips. Since the spectra depend strongly on the temperature, depending on the source, it needs quite some time until they are stable, if at all. The utilized sources are shortly described in the following.

**MIR source – Globar**

A Globar lamp covers a range from $\sim 50 \text{ cm}^{-1}$ to $6000 \text{ cm}^{-1}$ (see Fig. 4.2). It is made of silicon carbide (carborundum) in form of a rod and is operated at $1200^\circ \text{C}$ [163]. This source is used in combination with a Mylar\(^1\) (FIR) and KBr (MIR) beam splitter. The latter one is sensitive to humidity, which has to be considered by storing this type of beam splitter. The lifetime of a Globar source is rather long, around 25000 hours [164]. The source normally runs continuously since switching it off and on reduces its lifetime. When it is switched on, it needs at least one to two hours to stabilize. It is important that the source is constantly cooled either by water or air, depending on the type and spectrometer, otherwise it is damaged quite fast [95].

**NIR/VIS source**

The IR-source is a 50 W tungsten lamp and is operated with 12 V. The lamp can cover a frequency range between $2000 \text{ cm}^{-1}$ and $25000 \text{ cm}^{-1}$ (see Fig. 4.2). It needs two different CaF\(_2\) beam splitters to cover this range, with one of them being used for the NIR and the other one for the VIS range. Since its lifetime is rather short with approximately 2000 hours [164], it should always be switched off when not utilized. It takes around 30 min after switching it on until it is stable enough to start the measurements. Similar to the Globar lamp, the tungsten lamp has to be cooled, either with a water cooling system or by air [95].

\(^{1}\text{A trademarked name for a biaxially-oriented polyethylene terephthalate (BoPET) foil.}\)
4.1.2 NIR source – grating spectrometer

The grating spectrometer utilizes a 5 V halogen lamp within a special metal housing. The housing guarantees a good thermal connection to the surrounding heat sink. Its spectrum resembles the NIR source from the FTIR spectrometer (see Fig. 4.2).

4.1.3 Detectors – FTIR spectrometer

In the following, the different detectors are introduced, which are applied with the FTIR and grating spectrometer. The different types of detectors strongly determine some measurement parameters which influence the signal-to-noise ratio (SNR).

**FIR detector**

As FIR detector, we typically use a bolometer which is able to cover a range between some cm$^{-1}$ and 700 cm$^{-1}$. A very sensitive thermistor is cooled down to 4.2 K with liquid helium$^2$ in order to decrease the thermal background as much as possible [166]. An additional chamber filled with liquid nitrogen reduces thermal radiation to the helium chamber from the outside, which decreases the evaporation rate of the helium. This helps to increase the possible measurement time. The outer vacuum chamber (OVC) has to be at very low pressure ($\sim 10^{-6}$ mbar) in order to aid a long measurement time and to operate the device in a safe manner. With a proper handling of the bolometer, one helium filling lasts more than 24 hours [166].

The incident IR radiation slightly heats up the thermistor whereupon it changes its resistant, which is detected and analyzed as a signal. During the measurements, the helium recovery line should be removed from the bolometer, since pressure oscillations in the recovery system can influence the measurement. For a proper handling and filling procedure, the interested reader is referred to Ref. 95.

**MIR detector**

A photovoltaic detector$^3$ is used for the MIR range, which belongs to the class of mercury cadmium telluride (MCT) detectors. It works on the principle of the photoelectric effect [167]. Thus, it consists of a semiconductor where photons from

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$^2$For a source and sample with a strong signal, a Deuterated Triglycine Sulfate (DTGS) detector can be used, which has a worse signal-to-noise ratio and lower sensitivity than a bolometer. This type of detector can be operated at room temperature [165].

$^3$Manufacturer identifier: KV100.0.25 B7/190 from Kolmar Technologies.
the incident light excite electrons to the conduction band. The transition leads to a detectable current flow. By varying the cadmium content, the size of the band gap can be controlled. Our photovoltaic detector covers a range between 800 cm\(^{-1}\) and 8000 cm\(^{-1}\). The detector has to be cooled down with liquid nitrogen and due to stability reasons, one should not start the measurements too early. A delay between filling with liquid nitrogen and start of the measurement of 60 min is a good compromise. Before, the signal drifts significantly. Such MCTs possess good signal-to-noise ratios and a high sensitivity. For high intensities, one has to consider a possible non-linear response from the detector [95].

**NIR detector**

The detector for the MIR range works on the same principle as the photovoltaic detector. However, the material is indium antimonide (InSb)\(^4\). It is linear over a broad signal range and covers a frequency range between 2000 cm\(^{-1}\) and 12000 cm\(^{-1}\). The detector is also cooled down with liquid nitrogen and needs the same hold time as the MIR detector [95].

**VIS detector**

For the VIS range, a silicon diode is utilized as detector. It belongs to the DTGS type\(^5\) and does not need to be cooled down for operating. It works on the basis of the pyroelectric effect. The semiconductor of the detector has an asymmetric crystal structure with an electric dipole moment [168]. Incident radiation causes an expansion of the crystal, resulting in a change of its dipole moment and therefore, a change in voltage. This voltage change is proportional to the incident radiation [168]. Typically, DGTS are able to cover a broad frequency range; in this case, the detector works in a range between 8000 cm\(^{-1}\) and 25000 cm\(^{-1}\) [95].

### 4.1.4 Detector – grating spectrometer

In Fig. 4.3, the detector unit (polychromator) is illustrated. The optical fiber is connected at the SMA connector. An aperture guarantees the necessary illumination of the collimator lens. Higher energy contributions (shorter wavelengths) are filtered from the collimated beam at the high-pass filter before the grating splits

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\(^4\)Manufacturer identifier: D413/6 from InfraRed Associates.

\(^5\)Manufacturer identifier: ID510/8 Si-diode.
up the beam into its different wavelengths. The split wavelengths are focused on the different elements of the InGaAs photodetector array. The array in the utilized spectrometer (see Sec. 4.3.1) has 256 elements, which are all cooled down to 4°C by a Peltier element and a fan. Prior each measurement session, the shutter located directly after the aperture blocks any incident light for a dark measurement. During this measurement, the dark current of the InGaAs photodetector for each pixel is determined and considered automatically for following measurements.

### 4.2 Broadband spectroscopy

Two types of spectrometers are utilized within this thesis. A Fourier-transform infrared (FTIR) and a grating spectrometer. In the next two subsections, the concept of both types are introduced.

#### 4.2.1 Michelson interferometer

The heart of every FTIR spectrometer is a Michelson interferometer. There are several variations in construction/arrangement possible. Fig. 4.4 displays a general sketch of a Michelson interferometer. Light from a coherent light source is split up
4.2.2 FTIR spectrometer

Compared to disperse spectrometers, FTIR spectrometers have the advantage that they are capable to measure a broad frequency range with a very good resolution. The whole frequency range is measured simultaneously at the same time, which is called Multiplex or Fellgett advantage [170]. The Michelson interferometer inside the FTIR spectrometer provides an intensity-interferogram \( I(s) \) of a broad frequency range. \( I(s) \) depends on the position \( s \) of the movable mirror (scanner), which is displaced from an original position. At \( I(s) = \text{max} \), the two beam paths exhibit exactly the same length and all frequencies within the observed range interfere constructively. The frequency-dependent spectrum \( S(\nu) \) is obtained by applying a Fourier transformation (see Fig. 4.5). The position \( s \) is determined by another Michelson
Figure 4.5: Interferogram and resulting spectrum after Fourier transformation. The dense packed lines in the spectrum are caused by absorptions in air.

interferometer in combination with a HeNe laser (vacuum wavelength: 632.9 nm). For a single frequency, the interferogram $I(s)$ is a simple sinusoidal signal. Here, each zero crossing $I(s) = 0$ provides a single measurement point. Therefore, it is crucial that the laser frequency is very stable, because it determines the frequency accuracy of the spectrometer. Since $\Delta \nu \propto 1/(\Delta s)$, high precision—0.01 cm$^{-1}$ and better—is typically achieved (Connes advantage [170]) with these kind of spectrometers. The utilized software is very important for the quality of the obtained data, since it has to perform a discrete Fourier transformation (DFT) where it has to overcome several issues like leakage or aliasing [95, 170].

4.2.3 Bruker VERTEX 80v

The Bruker VERTEX 80v has an attached Hyperion 1000 microscope. With these two devices, the spectrometer is able to cover a frequency range between 20 cm$^{-1}$ and 25000 cm$^{-1}$. In this thesis, all measurements were performed with the microscope, which limits the lower end of this range to around 100 cm$^{-1}$ to 200 cm$^{-1}$ (depending on the used aperture). In Fig. 4.6, a sketch of the spectrometer and microscope is provided with the beam path highlighted for reflection measurements. The spectrometer itself has two light sources, the Globar and NIR lamp which are both cooled by air. The external source is typically a mercury lamp$^6$ which is needed for frequencies below 100 cm$^{-1}$. From the source, the beam path first passes the aperture and then reaches the Michelson interferometer part. Four beam splitters can be placed

$^6$More details to the mercury lamp in Ref. 95.
Figure 4.6: Sketch of the Bruker VERTEX 80v and Hyperion 1000 microscope. In orange, the beam path is highlighted for reflection measurements at the microscope. Inside the spectrometer, a DGTS at position D1 and an MCT at position D2 enable measurements under weak vacuum. For the Hyperion 1000 microscope at position D3, different MCTs for the MIR, an InSb for the NIR, and a DGTS detector for the VIS region can be mounted, while a bolometer at D4 enables measurements in the FIR region. Depending on the chosen detector, the mirror arrangement is changed automatically. Sketch for the Bruker VERTEX 80v and Hyperion 1000 microscope adapted from Ref. 171 and Ref. 172.

inside the spectrometer. Among these beam splitters, one is selected, while this can be done without venting the spectrometer. It is easy to exchange certain beam splitters when the spectrometer is vented. The scanner is mounted on two rods, which possess a nitrogen gas bearing in order to guarantee minimal friction and a smooth movement of the scanner. Due to the nitrogen bearing, the pressure which is reached inside the spectrometer is roughly 3 mbar. After the Michelson interferometer, the beam is guided to the microscope. The window between spectrometer and the non-pumped microscope has to be adapted according to the desired frequency range. In the microscope, two visible lamps provide a possibility of pre-alignment. By looking through the ocular, the stage is moved up or down until one gets a sharp image of the sample’s surface. Afterwards, the beam path is changed to the IR light, which is highlighted in Fig. 4.6. Detector position D4 (bolometer) is utilized for the FIR range and detector position D3 is utilized for the MIR to VIS range.
4.2.4 Measurement procedure

An overview about the different parameters like the type of beam splitter is provided for the different frequency ranges in Tab. 4.2. In this thesis, measurements are only performed at room temperature. The sample and reference mirror are placed each on top of one mechanical alignment stage. Each alignment stage possesses two axes, which can tilt the stage in two directions. Mirror and sample are aligned by signal after they were pre-aligned with the visible light. The investigated samples are compressed pellets with 1 cm in diameter. Even though the surface of the pellets is quite flat, it reflects the incident light diffusely. Therefore, the signal from the samples—which is only the specular part—is very small. For that reason, the aperture wheel at the microscope were at the position open for all measurements.

<table>
<thead>
<tr>
<th>Range</th>
<th>Source</th>
<th>Beam splitter</th>
<th>Window</th>
<th>Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIR</td>
<td>Globar</td>
<td>Mylar</td>
<td>Polypropylene</td>
<td>4.2 K bolometer</td>
</tr>
<tr>
<td>MIR</td>
<td>Globar</td>
<td>KBr</td>
<td>KBr</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>NIR</td>
<td>Tungsten</td>
<td>Si/CalF₂</td>
<td>KBr</td>
<td>InSb</td>
</tr>
<tr>
<td>VIS</td>
<td>Tungsten</td>
<td>UV/CalF₂</td>
<td>Quartz</td>
<td>Si-Diode</td>
</tr>
</tbody>
</table>

Table 4.2: Overview about the optical parameters, which are used to measure the different frequency ranges.

4.2.5 Obtaining the reflectivity

A measurement signal contains time-dependent optical information about the source \( I_Q(t) \), the beam splitter \( I_B \), all mirrors \( I_M \), the detector \( I_D(t) \), and the sample \( I_S \). The information from the source and detector may drift over time, while the information from the other objects are estimated as time-independent. It is rather challenging to calibrate the whole spectrometer in a way that all the unwanted optical information (for instance from the mirror) is dropped. For that reason, a reference with well-known optical reflectance has to be measured frequently in between to achieve the same result: information about the sample alone. In general, a mirror (typically gold for the FIR to NIR and protected silver mirror for the VIS and UV) serves as the reference, which exhibit a signal \( I_R \) close to unity. The reflectivity of the sample is then given by

\[
R_S = \frac{I}{I_{\text{ref}}} \frac{R_R}{R_R} = \frac{I_Q(t_1)I_BI_MI_D(t_1)I_r(t_1)I_S}{I_Q(t_2)I_BI_MI_D(t_2)I_r(t_2)I_R} \approx \frac{I_S}{I_R} \frac{R_R}{R_R}, \tag{4.2}
\]
where $I_{\text{ref}}$ is the total signal of the reference measurement, $R_R$ the reflectivity of the reference mirror, and $I_i$ other contributions like absorptions of air. In this relation, it is assumed that the time interval between sample and reference measurement is rather short, that one can simplify $t_1 = t_2$. This is typically verified by measuring the sample and reference twice. If both measurements provide the same result, the interval between the measurements is short enough.

### 4.2.6 Fitting procedure

For the investigated pellets, spectra are available in the range between $\sim 100 \text{ cm}^{-1}$ and $\sim 20000 \text{ cm}^{-1}$. It is not possible to gain the total (hemispherical) reflectance with the utilized setup, because the samples reflect in a diffuse manner. Thus, only relative values are available, which is sufficient for identifying intra- and interband transitions, phonons, and other contributions. Nevertheless, a Kramers Kronig analysis is performed to obtain a relative optical conductivity and refractive index. For this analysis, the reflectivity data is extrapolated. Since the samples are insulators, the low frequency part is extrapolated with a constant value. For the high frequency region (up to $10^6 \text{ cm}^{-1}$), several approaches are utilized and compared (see Sec. 6.1.2 Kramers Kronig analysis on page 104). With the program Windows automatic spectrum fitters (WAsf), the reflectivity and optical conductivity is fitted with Drude (if necessary) and Lorentz contributions. Afterwards these fits are utilized for a new extrapolation of the low and high frequency part. This procedure is repeated several times until the fit matches well with the data. A good indication for an appropriate fit is a smooth transition at the boundary between the extrapolation part and the real data part in the optical conductivity.

### 4.3 Near-infrared spectroscopy

This thesis focus on NIR spectroscopy on real macroscopic asphalt samples. For these measurements, a grating spectrometer is utilized together with a home-built setup from Marco Werz [173] which got an upgrade (enable BRF measurements) from Simon Amann [21].
4.3.1 Grating spectrometer

A grating spectrometer belongs to the family of disperse spectrometers. A grating splits up the light into its different frequencies (compare Sec. 4.1.4). The frequency separation of the signal can be achieved by using either a detector array or a slit located after the grating. At the input of the detector unit, an aperture is necessary to guarantee the correct illumination, however, this leads to a power loss at the slit and thus to a worse signal-to-noise ratio compared to FTIR spectrometers [174]. In order to cover a broad frequency range with a grating spectrometer, the device needs to be either quite large or possess many elements in the detector array, which would be very expensive. Additionally, the lattice spacing of the grating has to be very narrow to be able to achieve a high resolution. The grating spectrometer used during this work is from Polytec (see inset of Fig. 4.8). It includes an illumination and detection module. The measurement range is between 840 nm and 1650 nm with a resolution of roughly 3 nm.

4.3.2 Reflectance factor

In this thesis, the reflectance factor is defined as the ratio between a sample signal $I_S(\lambda, \theta_i, \theta_r)$ and a reference signal $I_R(\lambda, \theta_i, \theta_r)$:

$$RF = \frac{I}{I_{ref}} = \frac{I_Q(t_1)I_F I_L I_D(t_1)I_r(t_1)I_S(\lambda, \theta_i, \theta_r)}{I_Q(t_2)I_F I_L I_D(t_1)I_r(t_2)I_R(\lambda, \theta_i, \theta_r)} = \frac{I_S(\lambda, \theta_i, \theta_r)}{I_R(\lambda, \theta_i, \theta_r)} \quad (4.3)$$

with the wavelength $\lambda$, the incident angle $\theta_i$, the observing angle $\theta_r$, information of the source $I_Q(t)$, the fibers $I_F$, the lenses $I_L$, the detector $I_D(t)$, and other disturbances like absorptions in air $I_r(t)$. It is defined very similar to the reflectivity in Sec. 4.2.5. The source and detector from the utilized grating spectrometer were shown to be very stable [173]. Therefore, the assumption $t_1 = t_2$ holds for longer time intervals than at the FTIR spectrometer. The reference is a white Zenith Polymer reflectance standard (here simply called white standard (WS)) from SphereOptics with 99% reflectance, which has similar properties as Spectralon [19]. It exhibits a diffuse reflection behavior, which is close to the ideal Lambertian theory. As already mentioned, the definition of the reflectance factor is very close to the reflectivity shown in Sec. 4.2.5. However, while for a perfectly specular reflecting surface, the reflectivity is equal to the reflectance, the reflectance factor has to be integrated over the whole hemisphere to gain the reflectance.
4.3.3 Setup

Figure 4.7: Home-built setups for NIR measurements. The setup in a) shows the BRF setup, where the incident and observing angle can be adjusted independently. The reference standard is placed on top of the metal block close to the asphalt. With the setup displayed in b), reflectance factors at specific angles can be measured, where incident and observing angle are nearly identical. The brown circled inset shows the lens holder of the BRF setup with only one mounted lens, while the red circled inset shows the lens holder for the reflectance factor measurements with two mounted lenses. The inset with the green circle shows the metal pin for positioning the sample at a certain spot. 3D models from the setups are taken from Ref. 21.

The home-built setup for BRF measurements is illustrated in Fig. 4.7 a) while the setup for “normal” measurements under a specific incident and observing angle is illustrated in Fig. 4.7 b). Two separately rotatable arms are mounted at the BRF setup, where one represents the incident and the other the observing channel. Both utilize the same collimation lens with a focal length of 10 mm. The lenses are connected to the spectrometer via optical fibers. The fibers are from Ocean Optics with low OH silica cores. Since the fibers have a length of 2 m, the low OH content is particular important to guarantee minor absorptions inside the core for the NIR range. The core diameter for the detector channel has typically a diameter
of 400 µm, while the one for the illumination channel has 1000 µm. This combination provides a good signal with less loss of intensity at the aperture (slit) located inside the detector chamber of the spectrometer. Measurements with repetitious accuracy of a specific position are achieved via a metal pin and a metal ruler (see inset of Fig. 4.7). The pin is positioned at the corner of a metal plate, which itself in turn is mounted on two linear translators, both fixed on the base plate. This combination enables a one dimensional alignment of the sample position. The arm for the observing angle in Fig. 4.7 a) and for both angles (incident and observing) in Fig. 4.7 b) is attached to the electric rotary stage DMT 130N from Owis. This stage allows a relative angular accuracy of better than one angular minute. The arm for the incident angle in Fig. 4.7 a) is adjusted by hand with a small digital goniometer. The lens holder for this arm can be pushed backwards to avoid a collision between the two arms. For the setup in Fig. 4.7 b), the intention is to have the incident and observing angle as close as possible together. The red circled inset shows the utilized lens holder, where only a small angle of 4° is present between illumination and detection lens. In this configuration, the centers of the lenses are 15 mm apart from each other. For both setups, the center of rotation is chosen in a way that the distance between sample surface and lens is 20 cm.

Dominika Penkala designed and tested adapters for the lens holders of both setups during her student research project. These adapters enable polarization-dependent measurements. The polarizers are sheet polarizers (OIR2500) for the NIR from Knight Optical Ltd., which can be trimmed to a desired size by hand. Trimming the polarizers is necessary due to the lack of space between the lenses—especially for the lens holder of the setup illustrated in Fig. 4.7 b). The orientation of each polarizer is adjusted by hand via two small 3D-printed gears. Even though everything is so compact, the polarization angle can be set with an accuracy better then ±5°.

### 4.3.4 Measurement procedure

For BRF as well as simple reflectance factor measurements (both setups in Fig. 4.7), it is important that the measurement geometry does not change between sample and reference measurement. To achieve that, the sample surface has to be at the same height as the center of rotation from the measurement arms. The reference is automatically at the correct height due to the matched metal block. Special care is necessary for the BRF setup, so that the two arms do not collide; there should be some buffer between incident and observing angle. For measurements with water on
top of asphalt, the asphalt sample is placed inside a box which is shown in Fig. 4.7 b). The WS is measured for any angle at the beginning of every measurement session, which is then also measured on the sample. In case that the sample is measured with the same angle at different spots, the stability of the spectrometer allows that the WS needs to be measured only once.

4.4 Freezer Modification

Figure 4.8: Modified freezer setup for measurements below 0°C. The gloves enable the surface preparations even at low temperatures. The inset in the green circle shows the measurement stage, which is placed inside the freezer. At the upper right side, the grating spectrometer is depicted.

In order to measure a pure snow or ice-covered asphalt surface, it is necessary to perform the measurements below 0°C. This is typically achieved by extensive field measurements [113–115, 175, 176] which, however, depend strongly on the weather conditions. Another group even cooled down a whole laboratory or room in order to optically investigate snow [112, 177]. Especially the latter method is expensive and challenging for measurement devices to work properly. In solid state
physics, the sample is typically put into an evacuated cryostat for temperature-dependent measurements. However, generally this procedure is avoided for liquid samples as they can lead to damage and dangerous blockings of the thin capillaries. To overcome these challenges, a commercial top opening freezer from Bosch (GCM34AW30) is modified in a way that it is possible to perform these kinds of measurements efficiently at small spaces, so they are comparable in their conditions to field experiments. Fig. 4.8 shows the modified freezer, the measurement stage, and the spectrometer. A new top was made of two 6 mm thick acrylic plates. These plates have feedthroughs for two gloves and for the optical fibers. An original sealing is mounted on the acrylic plates, which improves the temperature conditions. The freezer itself is big enough so that in addition to the measurement stage, also a box with snow and various tools like weights for snow compression can be placed inside. Unfortunately, the electric rotary stage is not specified for temperatures below \(10^\circ\text{C}\). Therefore, the arm with the lens holder is screwed to a vertical metal plate, which allows to choose currently between three different pre-defined angles, \(0^\circ\), \(\pm 20^\circ\), and \(\pm 40^\circ\). In case that other angles are from interest, one can easily produce and exchange the appropriate vertical metal plate. The lens holder is the same as in the red circled inset of Fig. 4.7). The reference standard, optical fibers, and lenses are applicable for temperatures down to \(40^\circ\text{C}\). Still, for the optical fibers, it is necessary to cool down or heat up slowly to prevent any damage of the core. As already mentioned, a box of snow is placed inside the freezer. With a strainer, the asphalt samples can be smoothly coated, which—at least for the eyes—resembles an actual coating from snow fall.

4.4.1 Characterization

Since the freezer is modified with a top made of two 6 mm thick acrylic plates, which possesses two holes for gloves and one for the fibers, it is important to know how the temperature inside develops with time. For that reason, four temperature sensors are placed inside (compare inset Fig. 4.9). The temperatures are logged with a Testo 177-T4 logger.

The first test was performed with the original top to get a general idea about the temperature’s behavior. The freezer has six different options for cooling. Each was tested for several hours. Fig. 4.9 shows mode ECO1 and ECO6. For ECO1 to ECO5, the freezer does not reach a stable temperature, since in these modes the freezer seems to use an on-off controller. Only for ECO6, a stable temperature
Figure 4.9: Temperature development inside the freezer with the original top over time for mode ECO1 a) and ECO6 b).

is reached after roughly 6 hours. Solely channel 3 (Ch3) deviates from the other channels, as this sensor is directly located at the wall where the cooling elements are placed behind. Therefore, this sensor reads lower temperatures when the freezer is cooling. In Tab. 4.3, the maximum and minimum values for each mode at the stable condition are provided for the important channels (Ch1 and Ch2).

<table>
<thead>
<tr>
<th>Temp.</th>
<th>ECO1</th>
<th>ECO2</th>
<th>ECO3</th>
<th>ECO4</th>
<th>ECO5</th>
<th>ECO6</th>
</tr>
</thead>
<tbody>
<tr>
<td>max (°C)</td>
<td>-13</td>
<td>-13.7</td>
<td>-14.7</td>
<td>-17</td>
<td>-19.4</td>
<td>-30.5</td>
</tr>
<tr>
<td>min (°C)</td>
<td>-20</td>
<td>-19.7</td>
<td>-20</td>
<td>-22</td>
<td>-23.9</td>
<td>-30.5</td>
</tr>
</tbody>
</table>

Table 4.3: Maximum and minimum temperature reached at Ch1 and Ch2 for every possible cooling mode from the freezer.

at ECO6 mode, a stable temperature is reached, which is necessary for our studies. Therefore, together with the modified top, another cooling run is performed in the ECO6 mode in order to check the influence of the acrylic top to the temperature inside the freezer. The result is presented in Fig. 4.10. It takes again roughly six hours to cool it from room temperature to a stable temperature at around \(-20°C\) (Ch1 and Ch2). The modified top is barely isolated, thus, the minimum temperature reached is roughly 10 K higher than with the original top. However, this temperature is perfectly fine for the desired measurements. Unlike in previous measurements with the original top, Ch4 only reaches \(\sim 16°C\), corresponding to a weak temperature gradient inside the freezer located close to the top (compare position of Ch1 and Ch2). At \(\sim 140\) min, the narrow peaks correspond to turbulences caused by usage of the gloves. Here, channel 4 (Ch4) displays the biggest impact. Since this sensor is
placed directly below the acrylic top, which is far away from the actual location for
the optical measurements, the temperature influence is not crucial at all. The air
inside the freezer is significantly warmer than the cooling elements behind the walls.
Therefore, all the humidity freezes out at the walls and not on the warmer parts.
Thus, the optics do not have to be protected further in order to prevent damage or
disturbances of the measurements.

4.4.2 Measurement procedure

With the freezer, snow and ice-covered samples are measured. For measuring
snow-covered samples, the asphalt, strainer, and other tools are placed inside the freezer
before it starts to cool down. It is also very important that the fibers are connected to
the lens holder inside the freezer from the beginning of the cooling run to guarantee
a slow cooling of the fibers. For checking the temperature at the asphalt surface,
a Testo 735 temperature logger is utilized, which constantly logs the temperature
with a measurement rate of typically one point per minute. As soon as the stable
temperature is reached, the box of snow is placed inside the freezer. By using the
gloves, the asphalt is covered with snow via the strainer. Here it is important that
the strainer has a temperature below 0 °C, otherwise the snow will melt at the mesh and block the holes of the strainer.

For ice-covered samples, there are several possibilities. One option is to first cool down everything without water and as soon as a stable temperature is reached, the water is poured on top of the already cold asphalt, while the asphalt itself is again placed inside a box. Another possibility is to put the water on top before the freezer starts to cool down. This enables temperature-dependent measurements and the investigation of the phase transition from liquid to solid H₂O. Via a spray bottle, a cold asphalt surface can be coated with a very thin layer of ice. For the spray bottle method, there is no need to put the asphalt in a box, since the water directly freezes out. Depending on the measurements, the reference is measured at room temperature or at the low, stable temperature.

4.5 Ellipsometry

Ellipsometric measurements on asphalt pellets are performed in the NIR and VIS region with a variable angle spectroscopic ellipsometer (VASE) from J. A. Woollam. The schematic of this ellipsometer is shown in Fig. 4.11. A xenon lamp enables measurements for wavelengths between 200 nm and 2200 nm. The spectrum of the lamp is split and selected inside the monochromator with a turnable grating. Via a fiber, the selected wavelength is guided to the illumination unit. Here, first the light gets linearly polarized at a Glan-Taylor polarizer, which is then again transformed into circular polarized light at the retarder (λ/4 plate) and reflected at the sample. The reflected circular polarized light gets polarized by a rotating analyzer (calcite) and is finally detected by the detector. The detector itself consists of a Si photodiode, which detects wavelengths up to 1100 nm and an InGaAs photodiode for λ > 1100 nm. At the illumination unit, it is also possible to connect LEDs via fibers instead of the monochromator. For the samples investigated in the framework of this thesis, the LEDs a favored, because the samples exhibit only low and diffuse reflectance. The drawback of this is that only a few wavelengths are available (more in the VIS than NIR range). Without focusing probes, the collimated light spot has a diameter of roughly 3 mm at the sample. Theoretically, reflection measurements can be performed for angles between θ_i = −θ_r = 15 ° and θ_i = −θ_r = −80 ° to the surface normal, however, for our weak reflecting samples, 7There is only a little temperature-dependent change in signal at the reference standard.
Figure 4.11: Schematic of the ellipsometer setup. At the monochromator, the desired wavelength is filtered and guided to the illumination unit. Here, first a polarizer linearly polarizes the light, which gets then nearly circular polarized at the retarder (λ/4 plate). A rotating analyzer enables the detection of the necessary polarization states.

the bigger the angle, the better the signal. The angles are automatically changed as desired by the software with an accuracy better than ±0.01° [55]. The ellipsometer is also able to be used as scatterometer. Here, the observing angle can be changed independently from the incident angle. This mode is used by Christoph Müller in his master thesis to investigate the diffuse reflecting properties of our asphalt pellets [160].

### 4.6 Sand-patch method

The average surface texture depth \( h_R \) in mm of asphalt samples can be determined via the *sand-patch method* [178]. This method is described in DIN EN 13036-1 [179]. The norm states that \( V = 25 \text{ ml} = 25 \text{ cm}^3 \) of quartz sand is flattened circularly on
the surface without applying any pressure. When the diameter of the sand-covered part stays constant (all pores within the sand radius filled), the diameter \( d \) in cm is measured. The average surface texture depth is then calculated via

\[
h_R = \frac{4 \cdot V}{\pi \cdot d^2}.
\]  

(4.4)

By subtracting \( h_R \) from the upper surface, the resulting value resembles the profile mean line \( L_m \) introduced in Sec. 2.9. To translate this value into a roughness, one can relate \( h_R \) to the maximum height \( R_t \)

\[
R_t \approx 2h_R.
\]  

(4.5)

In this thesis, the sample sizes are limited, therefore less volume of quartz sand is utilized to determine \( h_R \), which can cause a slightly enhanced error in \( h_R \).
5 Simulations

In this thesis, ray tracing-based simulations are developed and utilized in order to model the optical response of the layered H$_2$O/asphalt system. Our ray-tracing method utilizes the Monte Carlo approach, which is based on working with probabilities. The simulations are in 2D and written in MathWorks Matlab. Besides real measurements, simulation results for liquid water on top of asphalt are also compared to 3D simulations from Simon Amann who utilized Zemax for his simulation during his master thesis [21].

5.1 Monte Carlo ray tracing approach

Normally, at any interface—for example air/ice (snow flake)—an incident ray is split up into one reflecting and one transmitting ray. The intensities of both rays are determined by the initial ray, $R$, and $T$. This splitting occurs at each interface$^1$. For simulations with a high number of interfaces, one can imagine that this splitting process would exceed storage capacity as well as computation time, especially since every split ray is an incident ray by its own. Thus, for the water/ice simulations in Sec. 5.2.2 as well as for the snow simulations in Sec. 5.3, $R$ and $T$ are treated as a probability whether a ray—with all its intensity—is reflected or transmitted at the interface. This procedure is the Monte Carlo ray tracing approach [180] and enables the usage of any standard computer for the here presented simulations.

5.2 Water, ice and dry

The goal for the simulations is to be simple in structure but still physically correct. Therefore, a 2D-based approach is utilized. In this section, the framework of the simulations are explained, while the results are presented in the next chapters.

$^1$In this example: for air/ice as well as for ice/air.
Fig. 5.1 shows the higher level flow chart for the simulations covering dry, wet, and icy asphalt. Since water and ice layers differ only in their complex refractive index, their main flow chart is identical. The input contains all necessary parameters like: incident angle, spot size, field of view (FOV), amount of rays, initial intensity, lens parameters, height of the water/ice layer, light polarization, ground parameters, and more. Here it is also decided whether a dry, water, or ice-covered system is supposed to be simulated. It is possible to choose between three different modes\(^2\) how the ground reflects the incident rays:

![Flow chart for the header of the dry, wet, and icy asphalt system. There are two trees (one for the dry condition), because even though they do the same, the programming and analysis of the intensity is different. The red box refers to the flow chart in Fig. 5.3 and the green one to the flow chart in Fig. 5.4.](https://example.com/flowchart.png)

\(^2\)This is linked to the blue boxes in Fig. 5.3 and Fig. 5.4.
1. Lambert:
The reflection angle is a random value between $-90^\circ$ and $90^\circ$ with respect to the surface normal, while the random values follow a cosine distribution (compare Fig. 5.2 a)). It is calculated via

$$\theta_r = \sin^{-1}(-1 + 2\eta)$$  \hspace{1cm} (5.1)

where $\eta$ represents a random number between 0 and 1. The reflected intensity does not depend on the incident or reflected angle.

2. Fresnel:
This approach should be better called pseudo Fresnel. The reflecting angle is the incident angle times $-1$ (law of reflection), while the reflected intensity corresponds to the defined reflectance value of the ground (angle-independent). This intensity behavior arises from the absence of a simple refractive index for asphalt (for more details see Sec. 6.1.2).

3. Mix of Lambert and Fresnel:
The reflection angle $\theta_r$ is again specified by a cosine distributed probability. However, at each reflection process, a random value $\eta_r$ between 0 and 1 is computed and compared to an appropriate fraction of specular reflection $\zeta_s$. Each time when $\eta_r < \zeta_s$, the ray is reflected specularly ($\theta_r = -\theta_i$). The reflected intensity is again independent from the incident angle.

For the simulation of a dry, rough ground, the right side of the flow chart in Fig. 5.1 is activated. In the first step, each facet of the ground gets typically a reflecting parameter of 0.1, which is roughly the reflectance of an asphalt. Afterwards, the main program (see Sec. 5.2.1) for the dry simulation is called, which returns the resulting data for the sample and saves them into a table. Later on, an even ground is computed, where the reflected angle is again determined via Equ. 5.1, while its reflectance is 1. This flat ground is the reference and equivalent to the white standard mentioned earlier. The stored data from the sample and reference contain every last intersection point before leaving the sample and the slope of each ray. A detector unit—consisting of a 1 mm long detector and a lens with the parameters\(^3\) from the spectrometer—is step by step positioned around the sample between $-90^\circ$ and $90^\circ$.

\(^3\)Distance lens to detector: 9.95 mm, curvature radius: $\sim$ 5.05 mm, lens diameter: 5 mm, lens thickness: 2.7 mm, and a refractive index of BK7 glass.
Figure 5.2: Histogram for the reflection angle a) and a schematic for one part of the search algorithm b). In a), 80,000 random numbers are computed and apply the cosine distributed probability function (Equ. 5.1). The solid line depicts an actual cosine function. In b), the potential amount of facets—which might have an intersection with the incident ray—are limited, in this case to three (green line).

For each observing angle, it is computed which rays hit the detector within its full acceptance angle of $25.4^\circ$. Only the amount of reflection processes for each ray is important to compute the final intensity of a ray, because there is no attenuation caused by a medium.

At each observing angle, the received intensity from the sample is divided by the received intensity of the reference. The mentioned parameters for the surface roughness in Sec. 2.9 are computed and saved in an Excel file, together with the analyzed intensity data. At the very end of the simulation, a sheet with the essential plots$^4$ is returned (see Fig. A.2 in the Appendix).

For water or ice-covered samples, the same kind of analysis is done, where first the sample is simulated, then the reference. Afterwards, the result of the simulated sample is normalized by the one from the reference. While for the dry case, the absence of an intermediate layer makes it possible to calculate the final intensity at the very end of the simulation, for water and ice-covered samples, the intensity of each ray is already computed during the different steps inside the main program (due to the attenuation inside the water/ice). In order to improve the comparability to real measurements, the wavelength-dependent reflectance value of the ground facets can be adapted until the result of the dry run (reflectance factor) matches the one

$^4$For instance: angle-dependent BRF, wavelength-dependent albedo (integrated reflectance factor), surface roughness parameters, ground profile, etc.
CHAPTER 5. SIMULATIONS

from the actual dry measurement\textsuperscript{5}. By this, the layered (water/ice) simulations can be better compared with the actual measurements. The correction factor for the ground facets’ reflectance obviously depends on the surface roughness. For an even ground, a Lambertian response means that the measured reflectance factor is equal to the reflectance of the ground.

5.2.1 Main program – dry

When the main program mentioned in Fig. 5.3 is executed, first the ground is generated according to the ground parameters form the header input. Those parameters determine the expansion in $x$ and $y$ direction. For the $x$ direction, an equidistant step size is chosen, while the values for the $y$-direction are random values within a desired range. The resulting ground consists of many facets, where each orientation can be described by its normal vector. The coordinate points are saved in a separate file. This file enables the usage of the same ground for many simulation runs, for instance, different polarization states or different types of layers on top (water/ice). Within the input information, the program can be told whether it should use already available ground data. In this case, it skips the ground generation.

Finding the correct intersection point between the rays and a rough ground is not as simple as for an even ground. In principle, each facet can be described by a linear equation ($y = mx + b$). The straight forward method is to calculate the intersection points between any ray and each linear equation of the facets. Afterwards, for all found intersection points it has to be examined, which intersection point is within the boundaries of each facet. Even here, it is possible to have more than one solution per ray (for instance a ray with a flat incident angle). Therefore, the intersection points have to be filtered by looking for the smallest distance between the initial start of the ray and the intersection point. One can imagine that this needs a lot of computational time.

Therefore, a slightly different method is chosen to improve the efficiency of the simulation. The possible intersections are narrowed down by using the maximum ($y = y_{\text{max}}$) and minimum ($y = y_{\text{min}}$) height of the ground. For each ray, the intersection points are calculated at $y_{\text{max}}$ and $y_{\text{min}}$. Calculating these intersection points basically needs no time, because this process can be computed for all rays at once.

\textsuperscript{5}Note: All facets possess the same reflectance. When adapting the value, they are adapted for all facets at the same way.
Figure 5.3: Simplified flow chart for the simulation of a dry ground. The reflection angle (blue box) depends on the chosen option of reflection mentioned at the beginning of the chapter. The gray area highlights the main loop which is iterated until no new intersections with the sample are found anymore.

For each ray, exactly two intersection points\(^6\) result, which can be interpreted as a narrowed window, where an intersection point exists between the ray and the ground. For the schematic example given in Fig. 5.2 b), this window includes only three facets. Within this window, the earlier described straight forward method is then processed in order to find the real intersection point for each ray.

As this has to be computed separately for each ray, the code is written in a way that

\(^6\)Except the ray has a slope of \(m = 0\).
it allows the usage of multiple cores, which significantly improves the computational time consumption. When all the intersection points for the rays are found, the reflection angle for each ray is computed at once (blue box in Fig. 5.3). It depends on the input information, whether the ground should act as Lambertian scatterer or whether there is a specular fraction involved.

Now, the program executes a loop (gray area in Fig. 5.3) which is repeated until no ray possesses a new intersection with the ground anymore. This is done as follows:

- The new possible intersection points with the ground are again narrowed down, which is one more time computed at once in order to save time. Then, within a for-loop, the program searches again for the real intersection points for each ray separately on multiple cores. If there is no intersection point found, the program checks whether the ray leaves the sample sideways in direction of the ground or into the upper hemisphere. For both cases, the last intersection point and reflection angle is written into a buffer. Logging the rays which are lost due to the boundaries helps to decide whether the sample dimensions are too small. When the next intersection points are found for all rays, the same procedure is repeated for any ray, which did not leave the sample yet. If there are no rays left to compute, the buffered data is sent back to the header section, which was already introduced in Sec. 5.2.

### 5.2.2 Main program – water or ice

When the main program mentioned in Fig. 5.4 is executed, first—like described in the section before—the ground is generated and saved if there is no intention to use already existing ground data. The given water or ice layer thickness respectively is added to the minimum ground value $y_{\text{min}}$. The program then splits up into two cases: $d_{\text{layer}} > y_{\text{max}}$ and $d_{\text{layer}} \leq y_{\text{max}}$, with the latter case being the computational more complex one.

**Layer level > $y_{\text{max}}$ (see Fig. 5.4, left)**

As a first step, the intersection points from each ray with the layer (water or ice) surface is calculated, which can be done for all rays at once. Afterwards, Fresnel’s equations are solved for each ray. Since the Monte Carlo ray tracing approach is used—already explained in more detail in Sec. 5.1)—the resulting reflection coefficient is compared with a random generated value. Depending on this comparison,
Figure 5.4: Simplified flow chart for the water and ice-covered system. The reflection angle (blue box) depends on the chosen option of reflection mentioned at the beginning of the chapter.
the program decides whether a ray is either transmitted or reflected with all its intensity. Afterwards, each ray is computed separately\(^7\).

- **In case of reflection:** The ray is reflected specularly and the current intersection point, intensity, as well as the reflection angle is written into a buffer.

- **In case of transmission:** The intersection with the ground is calculated, following the same procedure as introduced for the dry case in Sec. 5.2. The calculation of the reflection angle depends on one of the three possible options how the ground behaves (see Sec. 5.2). With the resulting reflection angle, the next intersection point between ray and ground is calculated. If an intersection point exists, the last two steps (reflection angle $\rightarrow$ intersection point with the ground) are repeated until there is no more intersection within the boundaries of the ground (inside: no). In this case, it is checked whether an intersection point at $y = 0$ exists. If yes (layer surface: no), the data (intersection point, intensity, and reflection angle) are written into a separate buffer for rays which are out of boundaries. Otherwise, an intersection point with the surface of the water or ice layer exists and is calculated.

For the surface, again Fresnel’s equations are solved and the resulting reflection coefficient is compared to a random number, which decides whether the ray is reflected or transmitted (see gray area of Fig. 5.4).

- For the latter case, the ray leaves the sample into the upper hemisphere and the resulting data is written into the buffer.

- If the ray is reflected instead, the intersection with the ground is calculated again and checked whether this point exists or if it is out of boundaries. If it is beyond the sample dimensions, the data is written again into the separate buffer. For an existing intersection point with the ground, the whole procedure starting from point 2 is repeated until the ray either leaves the sample. Every time when the data of a ray is written into a buffer or saved, the process starts again from point 1.

Unlike for the pure dry simulation, an intermediate layer with a non-zero imaginary part of the refractive index $N$ is present. Therefore, the intensities of the rays have to be calculated during the simulation and not as before for the very last step. Each path through the H$_2$O layer and each reflection on the ground is immediately considered by recalculating the current intensity of the ray.

\(^7\)This process is again capable to use multi core analysis.
Layer level $\leq y_{\text{max}}$ (see Fig. 5.4, right)

For the case when the water or ice level is below $y_{\text{max}}$, the flow chart gets more complex. In the first step, the intersection points of each ray with the H$_2$O surface is calculated at once. Afterwards, the rays are computed separately\(^8\). Additionally, from the same starting point (light source), the intersection point of a ray with the (dry) ground is calculated via the introduced searching algorithm (see Sec. 5.2). The verification whether the ray leaves the sample into the upper hemisphere or whether it is out of bounds is skipped for the first run at each ray, since it is not of importance at this point. However, for later loops, it is necessary to check this condition and write the data into the appropriate buffer. Back to the initial rays, by knowing the intersection point with the H$_2$O surface and the ground for one ray, it can be evaluated whether the physical correct intersection is with the layer or the ground.

- If it is the ground, the reflection angle depends again on one of the three earlier mentioned options how the ground behaves (see Sec. 5.2). Starting from this point, the next intersection with the ground and the H$_2$O surface is calculated. Afterwards, the process jumps back to point 4 where the procedure continues.

- Fresnel's equations are solved, when the first intersection is not with the ground, but with the H$_2$O surface (layer). By comparing the reflection coefficient with a random number, it is decided whether the ray is transmitted or reflected.
  - In case of a reflection: The next intersection point with the ground is calculated and—in case it exists—the process jumps back to point 4 for further computation. If the intersection point does not exist, the ray leaves the sample and the data (intensity, last intersection point, and reflection angle) is written into a buffer in order to begin with the next ray.
  - When the random number leads to a transmission at the H$_2$O surface, an intersection point with the ground is computed. However, when this intersection does not exist, the ray has to be automatically out of boundaries and the resulting data is written into the separate buffer. For the case that the intersection with the ground exists, the reflection angle at

\(^8\)The process is capable to run on multiple cores.
the ground is computed and the potential next intersections with the ground as well as with the H$_2$O surface are calculated. If the correct next intersection point is with the ground, the process jumps back to point 5, while Fresnel’s equations are solved, when the true intersection is the H$_2$O surface.

By comparing the reflection coefficient with a random number, the decision whether the ray is reflected or transmitted is determined (see the light blue area in Fig. 5.4).

* For the former case of a reflection, the program calculates the next intersection with the ground. If the intersection exists, the process jumps back to point 5; if not, the ray is out of boundaries and the corresponding data is written into the separate buffer.

* In case of transmission, the next intersection with the ground is computed and the process jumps back to point 4. Every time a ray ends, the next ray starts at point 3 until all rays are computed.

Like before, each path through the H$_2$O layer and each reflection on the ground is immediately considered by recalculating the current intensity of the ray, since an intermediate layer with a non-zero imaginary part of the refractive index $N$ is present.

5.3 Snow

In literature, much effort is taken in order to simulate the optical behavior of snow. Different approaches exist, each with its own advantages and disadvantages with respect to the physics, complexity and computational extensiveness [70, 181–188]. The self-written ray-tracing simulation presented here has its focus on the simplicity of the model. The simulated spectral response is compared to measurements—which are performed inside of our modified freezer—and to literature.

We take advantage from the fact that snow can be simply described by a mixture of randomly orientated ice crystals or ice structures, which are divided from each other by air. In literature, it is suggested to treat snow flakes as large bodies, which can be simply described by geometric optics [189, 190]. Indeed, the snow flakes are much larger than the wavelength in most cases. Therefore,—as long as the size parameter $a = 2\pi r/\lambda$ is not smaller than approximately 20 [191]—effects from Mie
scattering are negligible. While the authors in Ref. 49 include diffraction effects into their simulations, they are neglected in our simulations, because measurement and simulation results already match quite well to each other, as can be seen in Ch. 9. In the atmospheric conditions on earth, water typically crystallizes in the Ih symmetry group when it freezes to ice [102]. Therefore, on earth nearly all snow flakes are based on a hexagonal shape, which can be distorted with time and during the growth processes (compare to Sec. 2.10.2). On the ground, the flakes are randomly oriented as bulk snow.

Considering all the mentioned points, the presented simulation handles snow as 2D stacked layers of randomly oriented hexagonal shaped particles. Each hexagon is treated as an ice crystal and possesses a complex refractive index $N_{\text{ice}}$. For $N_{\text{ice}}$, literature data are utilized which were measured by Warren et al. [192]. An exemplary image of such a sample is shown in Fig. 5.5. Even though the typical particle shape is a hexagonal pattern, other polygonal shapes are simulated as well, to investigate the influence of the shape to the optical response. As the main focus of the snow simulations are thick snow samples, the ground is not important for the optical response of the snow/asphalt system. Therefore, the ground is handled as a flat surface with a complex refractive index $N_{\text{asphalt}}$, which originates from broad-band ellipsometric measurements on an asphalt pellet.

How the ray tracer works can be derived from the simplified flow chart in Fig. 5.6. At the input, all the important parameters like: sample size ($x$ and $y$ direction), amount of sides for the polygons, amount of rays, grain size, incident angle, dimensions of
Figure 5.6: Simplified flow chart for the snow simulation.
the light spot, threshold intensity $\epsilon$, and more are defined. The threshold intensity $\epsilon$ is important, because a ray could be trapped inside the sample and unnecessarily blow up the computation time. Therefore, as soon as a ray reaches a certain level of intensity, the computation for this ray stops and its intensity is written into a buffer. By changing the amount of sides of the polygons, one can directly observe the impact of the flake shape to the optical response of the snow system. In the following, we assume a hexagonal snow flake for the explanation.

When the simulation starts, first the intersection point with the virtual zero—which is the surface of the snow layer—is calculated (1st intersection). From the intersection point with the virtual zero, only the nearest neighbored polygons have to be considered in order to find the correct polygon, which is hit by the ray. Each polygon consists of $n$ sides, which can be described by linear functions. For each hexagon considered within the nearest neighbors, all intersection points between the ray and each side—in this case six sides—have to be calculated. If the first step of calculating the intersection with the virtual zero would be dropped, a lot of polygons would have to be considered, taking too much time. In case that the nearest neighbors do not deliver the correct intersection, the next nearest or even further neighbors are considered, until the correct polygon is found.

Once the identification of the correct polygon is achieved, the incident angle is computed with respect to the normal of the hit side. By solving Fresnel’s equations, the reflectance $R$ and transmittance $T$ is determined. In Sec. 5.1, the Monte Carlo ray tracing approach was already introduced. Like for the simulations of water or ice-covered asphalt, this approach provides a significant advantage regarding computational requirements, especially since there exist many air/ice interface within these snow simulations.

After calculating $R$ and $T$, a random number between 0 and 1 is generated, which is compared to $R$. If the random number is higher than $R$, the ray is transmitted, otherwise reflected. For the latter one, the reflection angle and thus, the direction of the ray propagation is calculated. With these parameters, the subsequent intersection with another polygon is calculated. For the case that a subsequent intersection with a polygon exists, the program jumps back to point 2 and the procedure starts again.

---

As long as the “correct polygon” actually exists, otherwise, the ray hits the ground without interacting with one single snow flake.
In case there is no intersection found, one of the following three cases can occur:

1. The ray hits the sample boundary:
   The computation of the ray is terminated. The intensity is written into a buffer, which is saved on a separate table at the end of the simulation. If the summed up intensity of the table content exceeds a certain limit (for example 1%), the sample dimensions should be expanded and the simulation be rerun.

2. The ray hits the ground:
   At the ground, the ray is reflected and its intensity is determined by Fresnel’s equations from the air to asphalt interface. From the intersection point at the ground, the reflection angle is calculated and the program jumps back to point 1 where the search for the next intersection with a polygon begins.

3. The ray leaves the snow sample:
   The ray leaves the sample into the upper hemisphere. Its last intersection point, slope, and intensity is written into a buffer. When the simulation for all rays is done, the buffer is transferred into a table where the data can be analyzed afterwards.
   
   In case that the ray is transmitted into the polygon, the refraction angle is determined via Snell’s law with respect to the normal of the polygon’s side. The refraction angle together with the angle of the normal determines the slope of the ray.
   
   Inside the polygon, the intensity is attenuated according to Lambert-Beer’s law. The next intersection point within the polygon is computed, and Fresnel’s equations again determine whether the ray is reflected or transmitted. For the latter one, the program jumps to point 3 and computes the intersection with the next polygon. In case that the ray is reflected inside of the polygon, the next intersection within the polygon is searched. This is repeated until the ray leaves the polygon or its intensity decreases below $\epsilon$. 
6 Dry asphalt

In this chapter, the results from optical measurements on dry asphalts are presented and discussed. It starts with an overview about pellets made from asphalt samples and is directly followed by their broadband investigations. Here, it gets clear why the NIR range is favorable when building any type of optical sensor. After the pellet analysis, results from the macroscopic asphalt samples are discussed, which starts with the determination of an appropriate light spot size and is followed by the discussion about the diffuse reflecting properties of various dry asphalt samples. Some of the results are already published in Ref. 193 and Ref. 194.

6.1 Pellet samples

Our setups for broadband spectroscopy as well as for ellipsometry are not suited to handle big heavy samples like our asphalts. Additionally, the light spot sizes are too small compared to the grain size (several µm to roughly 2 mm), because the typical samples which are investigated are in general homogeneous and very small, up to some mm [195–198]. Therefore, we utilize pellets in order to achieve a general insight into the broadband optical response of asphalt by covering a range between \(\sim 400\) nm and \(\sim 100000\) nm. Additional tests regarding the comparability between asphalts and their pellets can be found in the master thesis of Christoph Müller [160].

6.1.1 Pellets – Overview

Fig. 6.1 presents a direct comparison between the macroscopic asphalt sample and its corresponding pellet. Without the scale and just by looking at the image, it is hard to distinguish between the actual asphalt sample and the pellet. The asphalt sample in Fig. 6.1 has a diameter of 150 mm, while the pellet is only 10 mm in diameter. Interestingly, it seems like that the grains are scaled down in the same
Figure 6.1: Macroscopic asphalt sample (left) compared to its pellet (right). The asphalt and pellet shown here are the AC 11 DS 50/70.

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Bitumen</th>
<th>KBr content</th>
<th>Data available</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC 11 DS 50/70</td>
<td>✓</td>
<td>0 %</td>
<td>FIR–VIS</td>
</tr>
<tr>
<td>AC 14 surf 35/50</td>
<td>✓</td>
<td>0 %</td>
<td>FIR–VIS</td>
</tr>
<tr>
<td>OPA 8 40/100-65</td>
<td>✓</td>
<td>0 %</td>
<td>FIR–VIS</td>
</tr>
<tr>
<td>EloMinit</td>
<td>×</td>
<td>0 %</td>
<td>FIR–VIS</td>
</tr>
<tr>
<td>“White”</td>
<td>×</td>
<td>5 %</td>
<td>MIR–VIS</td>
</tr>
<tr>
<td>“Mix”</td>
<td>×</td>
<td>5 %</td>
<td>MIR–VIS</td>
</tr>
<tr>
<td>Rhyolite</td>
<td>×</td>
<td>5 %</td>
<td>MIR–VIS</td>
</tr>
<tr>
<td>Sandstone</td>
<td>×</td>
<td>5 %</td>
<td>MIR–VIS</td>
</tr>
<tr>
<td>“Typical”</td>
<td>×</td>
<td>5 %</td>
<td>MIR–VIS</td>
</tr>
</tbody>
</table>

Table 6.1: Overview about the available pellets from asphalts and some raw materials. The ones with bitumen content are highlighted and the observed optical ranges are provided. For some pellets made of raw materials, 5% KBr had to be added as a stabilizer.

ratio as the outer diameter. In Sec. 6.2.1 it is shown that the light spot has to have a certain diameter in order to average the different grains. Since the grains in the pellets are much smaller, the ratio of the light spot diameter compared to the grain size stays roughly the same for measurements on the macroscopic asphalt samples with our grating spectrometer and measurements on the pellets with the broadband setups (see Tab. 6.2). An overview about the investigated pellets is provided in
CHAPTER 6. DRY ASPHALT

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spot size $L_d$</th>
<th>Grain size $G_d$</th>
<th>Ratio $L_d/G_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellets</td>
<td>250 µm</td>
<td>75 µm - 200 µm</td>
<td>1.3 - 3.3</td>
</tr>
<tr>
<td>Asphalts</td>
<td>20 mm</td>
<td>5 mm - 15 mm</td>
<td>1.3 - 4.0</td>
</tr>
</tbody>
</table>

Table 6.2: Overview about the ratio of light spot size and grain size between the pellet and asphalt samples.

Figure 6.2: Overview about the raw material of typical AC asphalt. The grains are sorted to their appearance and divided into five categories (from left to right): white, typical, mixture of all, sandstone-like stones and rhyolite.

Tab. 6.1. For the pellets, pieces of asphalt or grains of raw material are pestled with a mortar to a very fine powder. Afterwards, roughly 300 g to 400 g of each powder is pressed into a pellet in a hydraulic press at roughly 70 kN for 15 min. The raw material for typical AC types and their resulting powders are illustrated in Fig. 6.2.

6.1.2 Measurements at small incident angle

In this subsection, the results which are obtained from measurements at 0° incident angle are presented and discussed. In Fig. 6.3, the optical reflectivity spectra are presented for raw materials of typical AC type asphalts with 5% KBr content. The covered range spans from the MIR to the VIS. All the spectra look very
Figure 6.3: Broadband results for typical raw materials of an AC type asphalt. Single reflecting spectrum for each kind of sample from a) to e), and a direct comparison between them in f).

similar, only some small differences can be recognized in the appearance and strength of the modes (see Fig. 6.3 f)). For example, the mode at $\sim 1465$ cm$^{-1}$ is quite strong in the mixture as well as in the sandstone-like grains, while the mode at $\sim 1100$ cm$^{-1}$ is rather strong in rhyolite and the white grains. Between $\sim 1570$ cm$^{-1}$
and $\sim 3674$ cm$^{-1}$, the absolute values deviate less between the different types of stone, while for $> 3674$ cm$^{-1}$, the differences increase again. Interestingly, there is no distinct mode present above $\sim 3700$ cm$^{-1}$. A broad electronic transition defines this energy region. A closer look reveals around $\sim 7100$ cm$^{-1}$ (insets in Fig. 6.3) a very weak dip in the spectra of the rhyolite, sandstone, typical stones, and mixture sample corresponding to the $\sim 1410$ nm dip of the $-\text{OH}$ overtone [199, 200].

**Mode detection – nonbituminous samples**

In general, absorption bands which are located in the region between 400 cm$^{-1}$ and 1500 cm$^{-1}$ typically appear from specific bending vibrations within the different molecules and are referred to as fingerprint region [201]. Absorption bands located between 1500 cm$^{-1}$ and 4000 cm$^{-1}$ originate typically from functional groups (for instance C=O, $-\text{OH}$, N$-\text{H}$, CH$_3$, and more) [201].

The samples corresponding to Fig. 6.3 contain no bitumen, therefore, the modes of pure stone contributions can be identified. Since the samples consist of a broad variety of minerals and rocks, the exact identification is challenging. In Sec. 3.3, the general chemical composition of asphalt is provided. This knowledge helps to classify the different optical features, however, the modes can be shifted in its frequency compared to the pure minerals, due to the complex molecular environment. As could be already seen, biotite and hornblende are complex compounds. In literature, for biotite, following contributions are verified: SiO$_2$, Al$_2$O$_3$, FeO, Fe$_2$O$_3$, MgO, TiO$_2$, MnO, K$_2$O, CaO, Na$_2$O, and even more traces of other molecules and atoms [202–205]. For hornblende, SiO$_2$, Al$_2$O$_3$, TiO$_2$, FeO, MnO, MgO, CaO, Na$_2$O, K$_2$O, and Cr$_2$O$_3$ are essential elements, which is very similar to biotite [203].

Additionally, minerals like CaCO$_3$ can occur in a variety of different crystal structures, for instance calcite (space group $R\bar{3}C$), aragonite (space group $Pmcn$) and vaterite$^1$ [207]. The similar case accounts for SiO$_2$ with the additional effect of glass-like structures, which broaden the modes in the optical spectra [208]. Nevertheless, the overtone and combination bands in quartz (SiO$_2$) have highly characteristic modes, e. g. a group at $\sim 1790$ cm$^{-1}$, $\sim 1870$ cm$^{-1}$, and $\sim 2000$ cm$^{-1}$, which are stronger in quartz than in other silicates [209]. Carbonate (CO$_3^{2-}$) exhibit modes which overlap with some of the quartz modes [209]. Therefore, the coexistence of CO$_3^{2-}$ and quartz might result in a more developed feature in the spectra. Different types of feldspar—for instance albite and ortoclase—have similar features

$^1$The space group of this mineral is not known [206].
between $\sim 375 \text{ cm}^{-1}$ and $\sim 650 \text{ cm}^{-1}$, $\sim 700 \text{ cm}^{-1}$ and $\sim 800 \text{ cm}^{-1}$, $\sim 900 \text{ cm}^{-1}$, and $\sim 1200 \text{ cm}^{-1}$ [210].

In Fig. 6.3 a), for the pellet made of white/transparent rocks, following features appear:

- $\sim 739 \text{ cm}^{-1}$: Even though this frequency is at the edge of the measurement range, a sharp mode can be identified. There are several possible vibrations, which contribute to this mode. Most probably it originates mainly from carbonate ions ($\text{CO}_3^{2-}$) with its $\nu_4$ mode$^2$ at $\sim 727 \text{ cm}^{-1}$ [210]. The carbonate ion contributes for instance in variations of CaCO$_3$. These are the in-plane bending mode of calcite at $\nu_4 \approx 712 \text{ cm}^{-1}$ [207, 211, 212], aragonite at $\nu_4 \approx 713 \text{ cm}^{-1}$, and vaterite at $\sim 745 \text{ cm}^{-1}$ [207]. It can also appear in dolomite (CaMg(CO$_3$)$_2$) at $\nu_4 \approx 730 \text{ cm}^{-1}$ [207]. Another vibrational mode, which contribute to this mode is from aluminum compounds. For example the Al–O–Al stretching in muscovite at $\sim 748 \text{ cm}^{-1}$ [213], the Al–O band stretch (octahedrally) between $\sim 500 \text{ cm}^{-1}$ and $\sim 750 \text{ cm}^{-1}$ [214], and the condensed tetrahedra stretch Al–O$_4$ at $\sim 739 \text{ cm}^{-1}$ [215]. A mode of TiO$_2$ at $\sim 729 \text{ cm}^{-1}$ [216] and a longitudinal optical (LO) band of MgO at $\sim 737 \text{ cm}^{-1}$ [217] might also contribute to the observed feature.

- $\sim 776 \text{ cm}^{-1}$: Most probably, this optical feature corresponds to the Si–O symmetric stretching mode of $\alpha$-quartz ($\text{SiO}_2$) at $\sim 780 \text{ cm}^{-1}$ [210, 218, 219]. However, contributions of biotite, for instance the MgFeOH deformation band at $\sim 762 \text{ cm}^{-1}$ [213] and the Al–O–Si mode at $\sim 766 \text{ cm}^{-1}$ [205], could also contribute to this feature.

- $\sim 796 \text{ cm}^{-1}$: Another sharp mode which corresponds to the response of silicates. For instance, the symmetric Si–O–Si stretch of several SiO$_2$ compounds ($\alpha$-cristobalite, coesite, tridymite, vitreous silica (glass like SiO$_2$), quartz) are all$^3$ located between $\sim 790 \text{ cm}^{-1}$ and $\sim 813 \text{ cm}^{-1}$ [202, 210, 214, 218, 220, 221]. Even the Si–O deformation in muscovite at $\sim 800 \text{ cm}^{-1}$ [213] is located at this frequency. The same accounts for the SiO$_4$ symmetric stretch at $\sim 800 \text{ cm}^{-1}$ [208], the SiO$_4$ tetraherda Si–O symmetric stretch ($\nu_1$) between

$^2$There exists also a report, which locates the $\nu_4$ mode for pure CO$_3^{2-}$ at $\sim 680 \text{ cm}^{-1}$ [211].

$^3$Only Müller et al. report a broader range between $\sim 670 \text{ cm}^{-1}$ and $\sim 830 \text{ cm}^{-1}$ for quartz [208].
CHAPTER 6. DRY ASPHALT

\[ \sim 780 \text{ cm}^{-1} \text{ and } \sim 800 \text{ cm}^{-1} \] [222], and the SiO\(_6\) octahedral stretch between \[ \sim 750 \text{ cm}^{-1} \text{ and } \sim 850 \text{ cm}^{-1} \] [223]. However, for this frequency, also rutile (TiO\(_2\)) at \[ \sim 828 \text{ cm}^{-1} \] [224] and a mode in MgO at \[ \sim 800 \text{ cm}^{-1} \] [225] might contribute to the observed feature.

- \[ \sim 874 \text{ cm}^{-1} \]: Carbonate (CO\(_3^{2-}\)) has a very distinct mode at this frequency, which is the \( \nu_2 \) out-of-plane bend at \[ \sim 875 \text{ cm}^{-1} \] [199, 209–211]. Therefore, CaCO\(_3\) in its different structures gives rise to this mode. For calcite, the mode is reported at \( \nu_2 \approx 877 \text{ cm}^{-1} \), for aragonite at \( \nu_2 \approx 858 \text{ cm}^{-1} \), and for vaterite at \( \nu_2 \approx 876 \text{ cm}^{-1} \) [207, 209, 212, 225, 226]. Again, the carbonate ion in dolomite (CaMg(CO\(_3\))\(_2\)) with its mode at \( \nu_2 \approx 882 \text{ cm}^{-1} \) could also contribute to the observed feature [207]. At the same frequency, the LO \( \nu_3 \) mode of Al\(_2\)O\(_3\) is located at \[ \sim 875 \text{ cm}^{-1} \] [227–229]. It cannot be excluded that MgO and TiO\(_2\) also contribute to this mode, since they appear in the material and possess a mode at \[ \sim 885 \text{ cm}^{-1} \] [225] and an LO mode at \[ \sim 876 \text{ cm}^{-1} \] [230], respectively.

- \[ \sim 1090 \text{ cm}^{-1} \]: The strongest feature in the spectrum. Like the previous modes, it is dominated by different structures of SiO\(_2\). For example the Si–O stretching mode of \( \alpha \)-cristobalite at \[ \sim 1100 \text{ cm}^{-1} \] [218, 221], \( \beta \)-cristobalite (2SiO\(_2\)) at \[ \sim 1087 \text{ cm}^{-1} \] [221], the Si–O stretching mode of coesite between \[ \sim 1040 \text{ cm}^{-1} \text{ and } \sim 1098 \text{ cm}^{-1} \] [218], the asymmetric Si–O stretch of albite between \[ \sim 1000 \text{ cm}^{-1} \text{ and } \sim 1250 \text{ cm}^{-1} \] [223], the Si–O stretching mode of tridymite at \[ \sim 1109 \text{ cm}^{-1} \] [218], the Si–O stretching mode of vitreous silica (glass like SiO\(_2\)) at \[ \sim 1108 \text{ cm}^{-1} \] [218], and the asymmetric stretching mode Si–O–Si of quartz (also for natural quartz) at \[ \sim 1090 \text{ cm}^{-1} \] [208, 210, 219, 220]. In biotite, the asymmetric stretch of Si–O–Si is very broad and might overlap with the Si–O stretch at \[ \sim 1005 \text{ cm}^{-1} \] [202, 205, 213, 215, 219], while the Si–O (apical) stretch is reported at \[ \sim 1063 \text{ cm}^{-1} \] [213]. For alumino-silicate, a lattice vibration near \[ \sim 1020 \text{ cm}^{-1} \], and fundamental O-Si-O stretching at \[ \sim 1080 \text{ cm}^{-1} \] is reported [209], which might contribute to the broadening of the mode\(^4\). The asymmetric Si–O stretch (\( \nu_3 \)) of tetrahedra SiO\(_4\) is also located at \[ \sim 1085 \text{ cm}^{-1} \] [222]. Again, CaCO\(_3\) has a similar \( \nu_1 \) mode, which is IR active but weak in aragonite at \[ \sim 1082 \text{ cm}^{-1} \] and in vaterite.

\(^4\)In literature it is also found that the Si–O stretching can be observed near \[ \sim 1000 \text{ cm}^{-1} \] [231].
at $\sim 1090 \text{ cm}^{-1}$ [207, 225].

- $\sim 1167 \text{ cm}^{-1}$: Close to the strongest mode, this feature can be assigned again to an SiO$_2$ contribution. For $\alpha$-quartz, the Si–O stretching mode is located at $\sim 1150 \text{ cm}^{-1}$, for $\alpha$-cristobalite at $\sim 1160 \text{ cm}^{-1}$, for coesite at $\sim 1170 \text{ cm}^{-1}$, and for tridymite at $\sim 1175 \text{ cm}^{-1}$ [218].

- $\sim 1412 \text{ cm}^{-1}$: This feature can be assigned to the fundamental $\nu_3$ vibration (asymmetric C–O stretch) of CO$_3^{2-}$, which is located between $\sim 1400 \text{ cm}^{-1}$ and $\sim 1429 \text{ cm}^{-1}$ [199, 210, 211]. An Al–O mode close to $\sim 1356 \text{ cm}^{-1}$ might explain why the observed feature is rather broad [219].

- $\sim 1450 \text{ cm}^{-1}$: This feature probably belongs to the in-plane asymmetric stretching ($\nu_3$) mode of CO$_3^{2-}$, which is normally shifted to higher frequencies in calcite and observed for carbonate at $\sim 1450 \text{ cm}^{-1}$ [209]. Depending on the surrounding material, it is reported between $\sim 1407 \text{ cm}^{-1}$ and $\sim 1450 \text{ cm}^{-1}$ [207, 212, 213, 225]. A mode of Mg(OH)$_2$, which is located at $\sim 1436 \text{ cm}^{-1}$ [232] might explain why there are so different allocations for the $\nu_3$ mode$^5$ of CO$_3^{2-}$. Huang et al. also reports that the mode of MgO and CaO are located at $\sim 1429 \text{ cm}^{-1}$ [225], while for Na$_2$CO$_3$ it is reported at $\sim 1450 \text{ cm}^{-1}$ [225]. The fundamental C–H stretch at $\sim 1470 \text{ cm}^{-1}$ might also contribute to this feature [219].

- $\sim 1600 \text{ cm}^{-1}$: Even though the H$_2$O $\nu_2$ bend is located at $\sim 1630 \text{ cm}^{-1}$ [199, 202, 213, 214, 219, 233], the observed feature can be attributed to this fundamental OH bend which is affected by a chemical shift. For instance, in an SiO$_2$ environment like in biotite, the OH bend is affected by Si–O stretch bands and thus, located at $\sim 1600 \text{ cm}^{-1}$ [205, 233]. Also for Mg(OH)$_2$, the OH bending is rather located near $\sim 1600 \text{ cm}^{-1}$ [231, 232].

- $\sim 1682 \text{ cm}^{-1}$: The following two modes can be attributed to this feature: First, H$_2$O inclusions in KBr, which result in a mode at $\sim 1667 \text{ cm}^{-1}$ [225]. Second,

$^5$An OH mode typically results as a dip in the spectrum in reflection measurements.
H-feldspar (HAlSi$_3$O$_8$) possess a feature at $\sim 1630$ cm$^{-1}$ [234].

- $\sim 1797$ cm$^{-1}$: This feature is caused by a combination of the $\nu_1$ and $\nu_4$ mode of CaCO$_3$ in its different crystal structures (aragonite, calcite, and even dolomite), which is located between $\sim 1800$ cm$^{-1}$ and $\sim 1818$ cm$^{-1}$ [207, 209, 225]. Quartz (SiO$_2$) has three very characteristic combinations and overtone bands at $\sim 1790$ cm$^{-1}$, $\sim 1870$ cm$^{-1}$, and $\sim 2000$ cm$^{-1}$ [209]. For the observed sample, all three features are present, therefore, a contribution of quartz is highly probable. A possible contribution of Al$_2$O$_3$ at $2\nu_3 \approx 1730$ cm$^{-1}$ cannot be neglected [229].

- $\sim 1875$ cm$^{-1}$: This is another feature of the three combination and overtone bands from quartz at $\sim 1870$ cm$^{-1}$ (combination of $\sim 1080$ cm$^{-1}$ and $\sim 800$ cm$^{-1}$) [209]. The observed feature in H-feldspar (HAlSi$_3$O$_8$)—which contains a high content of SiO$_2$—at $\sim 1840$ cm$^{-1}$ [234] confirms this allocation.

- $\sim 1937$ cm$^{-1}$: This feature is assigned to the third characteristic overtone and combination band triple of quartz at $\sim 2000$ cm$^{-1}$ [209].

- $\sim 2135$ cm$^{-1}$: The assignment of this feature to a specific mineral is hard, however, it nicely fits to a $-\text{C}=$CH, $-\text{S}-\text{C}=\text{N}$, $-\text{N}_2$ mode, $-\text{N}=\text{C}=\text{N}$, or a $>\text{C}=$C=O mode [235]. Since the minerals have a lot of carbon bonds, it is very likely that the feature corresponds to a mixture of all mentioned ones. Additionally, the Si–H stretching is also located between $\sim 2100$ cm$^{-1}$ and $\sim 2250$ cm$^{-1}$ [236], which leads again to a silicon compound.

- $\sim 2234$ cm$^{-1}$: The same accounts for this feature. It might relate to a $-\text{C}=\text{C}$ triple bond, $-\text{C}=\text{N}$, $-\text{N}_2^+$ or to a $-\text{NCO}$ mode [235]. Like the mode before, it can also originate from an Si–H stretching.

- $\sim 2515$ cm$^{-1}$: This feature can be mainly attributed to a combination of the IR inactive $\nu_1$ and the IR active $\nu_3$ mode in CaCO$_3$ between $\sim 2500$ cm$^{-1}$ and
~ 2600 cm$^{-1}$ [207, 209, 225]. For H-feldspar (HAlSi$_3$O$_8$), an OH absorption at ~ 2485 cm$^{-1}$ might also contribute to this feature [234].

• ~ 2876 cm$^{-1}$: Pure calcite (CaCO$_3$) has an optical feature at ~ 2880 cm$^{-1}$ [209]. Since many C–H bonds are present in the samples, their stretching mode at ~ 2855 cm$^{-1}$ might also influence this feature [219].

• ~ 2985 cm$^{-1}$: Several bands contribute to this feature. For instance, the second overtone of $\nu_2 = 1450$ cm$^{-1}$ from CO$_3^{2-}$ at $2\nu_2 \approx 2900$ cm$^{-1}$, which is slightly shifted in pure calcite to ~ 2988 cm$^{-1}$ [209], the C–H stretching at ~ 2920 cm$^{-1}$ [219], the alkyl-CH$_2$ between ~ 2850 cm$^{-1}$ and ~ 2930 cm$^{-1}$ in soil organic matter [237], and the OH absorption at ~ 3000 cm$^{-1}$ for H-feldspar (HAlSi$_3$O$_8$) [234].

• ~ 3401 cm$^{-1}$: The dip in the spectrum can be attributed to the symmetric OH stretching mode $\nu_1$ of H$_2$O, which is located around ~ 3445 cm$^{-1}$ [199]. In the vicinity of other materials, this mode is also reported between ~ 3405 cm$^{-1}$ and ~ 3445 cm$^{-1}$ [202, 205, 213, 219].

• ~ 3628 cm$^{-1}$: The dip is dominated by the asymmetric stretching of O–H at ~ 3650 cm$^{-1}$ [203]. Depending on the different compounds, the exact position in the spectrum can vary. For example the Si–OH stretch is located between ~ 3858 cm$^{-1}$ and ~ 3730 cm$^{-1}$ [233, 238], in Mg$_2$FeOH at ~ 3594 cm$^{-1}$ [213], in MgFeOH at ~ 3562 cm$^{-1}$ [213], the Al–O–H at ~ 3640 cm$^{-1}$ [219, 237], for crystalline hydroxyl between ~ 3622 cm$^{-1}$ and ~ 3698 cm$^{-1}$ [199, 209, 214, 219, 231, 233], for Ca(OH)$_2$ at ~ 3628 cm$^{-1}$ [239], and in biotite at ~ 3792 cm$^{-1}$ [205].

• ~ 3934 cm$^{-1}$: This feature can be allocated to the combination $\nu_1 + 2\nu_3$ of CaCO$_3$ at ~ 3921 cm$^{-1}$ [199].
• $\sim 4279\text{ cm}^{-1}$: The overtone $3\nu_3$ of CaCO$_3$ at $\sim 4255\text{ cm}^{-1}$ [199] is very likely causing this dip in the spectrum.

• $\sim 5141\text{ cm}^{-1}$: The combination of the stretching and bending mode of fluid H$_2$O and Si–OH is located at $\sim 5200\text{ cm}^{-1}$ [233]. They give rise to the observed dip. Similarly, the combination of the OH $\nu_2 + \nu_3$ mode is located at $\sim 5263\text{ cm}^{-1}$ [200]. For pure water, the $\nu_2 + \nu_3$ mode is located at $\sim 5333\text{ cm}^{-1}$ and for water inclusions in rocks it is shifted to $\sim 5263\text{ cm}^{-1}$ [199]. So the mode is dominated by OH combinations bands. However, the overtone combination $\nu_1 + 3\nu_3$ at $\sim 5263\text{ cm}^{-1}$ and $2\nu_1 + 2\nu_3$ at $\sim 5000\text{ cm}^{-1}$ of CaCO$_3$ [199] lead to similar features. Both, the OH and CaCO$_3$ overtone combinations, cause likely the observed dip.

One can summarize that the white/transparent stone material is dominated by SiO$_2$ with intermediate contributions of CO$_3^{2−}$. The region between $\sim 2000\text{ cm}^{-1}$ and $\sim 4000\text{ cm}^{-1}$ is strongly influenced by OH stretching modes, which lead to strong absorptions.

For the mixed material, there are some additional features and the strength of the different features differ from the white/transparent rocks. For example the feature at

• $\sim 1050\text{ cm}^{-1}$: This is most probably an absorption from albite (Na[AlSi$_3$O$_8$]), which belongs to the group of feldspars and is located at $\sim 1037\text{ cm}^{-1}$[223].

• $\sim 3570\text{ cm}^{-1}$: This feature corresponds to an OH stretching mode, too. Since there are many different hydroxyl groups present, the mode can be shifted.

• $\sim 7076\text{ cm}^{-1}$: The dip in the spectrum can be assigned to the combination band of the fundamental $\nu_1 + \nu_3$ mode of OH as inclusions in rocks, which is located at $\sim 7143\text{ cm}^{-1}$ [199, 200]. For pure water the band appears at $\sim 7246\text{ cm}^{-1}$ [199].

Thus, in this mixture the optical features from SiO$_2$ compared to other features are clearly weaker and the features from CO$_3^{2−}$ are the strongest. Obviously, the exact locations of the different peaks and dips vary a few cm$^{-1}$, compared to the
white/transparent rock sample.

For the reddish rock sample (probably rhyolite), following additional features can be observed:

- \( \sim 1535 \text{ cm}^{-1} \): It might fit to a aromatic nitrate mode, which is located at \( \sim 1520 \text{ cm}^{-1} \) [219]. However, these kind of molecules are rather rare in nature, therefore, it is more likely that it originates from an absorption of H-feldspar (\( \text{HAlSi}_3\text{O}_8 \)), which spans from \( \sim 1500 \text{ cm}^{-1} \) to \( \sim 2000 \text{ cm}^{-1} \) [234].

- \( \sim 1990 \text{ cm}^{-1} \): In the white/transparent stone sample, this feature is located at \( \sim 1937 \text{ cm}^{-1} \); thus, it is quite shifted. In this sample, it is closer to the reported \( \sim 2000 \text{ cm}^{-1} \) and thus, it can be assigned to the third characteristic overtone and combination band triple from quartz (\( \text{SiO}_2 \)) [209].

- \( \sim 3619 \text{ cm}^{-1} \): This feature can be attributed to OH oscillations [203, 214, 219], for example the Si–OH stretch at \( \sim 3650 \text{ cm}^{-1} \) [233]. Depending on the material, the exact location can vary a lot, for example in biotite at \( \sim 3792 \text{ cm}^{-1} \) [205], in \( \text{Mg}_2\text{FeOH} \) at \( \sim 3594 \text{ cm}^{-1} \), in \( \text{MgFeOH} \) at \( \sim 3562 \text{ cm}^{-1} \) [213], and in \( \text{Al–O–H} \) at \( \sim 3640 \text{ cm}^{-1} \).

- \( \sim 4496 \text{ cm}^{-1} \): This absorption results from a combination of the fundamental stretching and bending mode of fluid \( \text{H}_2\text{O} \) and Si–OH, respectively, at \( \sim 4500 \text{ cm}^{-1} \) [233, 238]. In albites, a combination of the OH stretch and AlOH bend leads to the same feature between \( \sim 4348 \text{ cm}^{-1} \) and \( \sim 4545 \text{ cm}^{-1} \) [200]. The combination and overtone bands of \( \text{CaCO}_3 \), for instance the \( \nu_1 + 2\nu_3 + \nu_4 \) and \( 3\nu_1 + 2\nu_4 \) lead to a similar absorption at \( \sim 4630 \text{ cm}^{-1} \) [199].

For rhyolite, a high quartz content is reported [146], which is in good agreement with the observed spectrum, where the \( \text{SiO}_2 \) features are the strongest ones.

For the sandstone-like stones, there are again new features:

- \( \sim 1739 \text{ cm}^{-1} \): This weak feature results from a feldspar mineral. For instance, Na-feldspar (\( \text{NaAlSi}_3\text{O}_8 \)) has an absorption around \( 1760 \text{ cm}^{-1} \) and sanidine ((\( \text{K,Na}\))AlSi_3O_8) at \( \sim 1760 \text{ cm}^{-1} \) [234]. A contribution of the \( 2\nu_3 \) overtone of
Al₂O₃ at ∼ 1730 cm⁻¹ [229] may be possible.

- ∼ 4434 cm⁻¹ and ∼ 4524 cm⁻¹: This double feature corresponds to the different contributions from a broad mode, which was already described for the rhyolite sample around ∼ 4496 cm⁻¹.

It seems that the sandstone-like stones possess a higher contribution of feldspar. For the typical stone type—which represents the most frequent type of stone in our raw material sample—only one additional feature can be identified:

- ∼ 3815 cm⁻¹: This feature can be attributed to the asymmetric OH stretch, which is already assigned for the white/transparent stone, where it is located at ∼ 3628 cm⁻¹. Thus, it originates from the Si–OH stretch, which is located between ∼ 3858 cm⁻¹ and ∼ 3730 cm⁻¹ [233, 238].

In total, the optical spectra of nearly all the stones investigated here are dominated by either SiO₂ or CO₃²⁻. While for the mixed and the typical stone type, the SiO₂ features are rather weak, the CO₃²⁻ impact is rather strong. The vice versa case accounts for the white/transparent, rhyolite, and sandstone-like stones.

EloMinit (furnace slag) is the raw material for the OPA 8 40/100-65 asphalt. Since its chemical composition varies a lot dependent on the slag composition, it is hard to identify specific modes. In Fig. 6.4, both pellets, from raw material and asphalt, are compared to each other. In the direct comparison, it can be already seen that the chemical composition of the investigated EloMinit cannot be identical to the one used in the investigated asphalt. The pure EloMinit sample possesses a higher metal

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Vibration</th>
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<tbody>
<tr>
<td>100 to 750</td>
<td>M—X stretching</td>
</tr>
<tr>
<td>600 to 800</td>
<td>M—H bending</td>
</tr>
<tr>
<td>850 to 1010</td>
<td>M—O stretching</td>
</tr>
<tr>
<td>875 to 1020</td>
<td>M—N stretching</td>
</tr>
<tr>
<td>1700 to 2250</td>
<td>M—H stretching</td>
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Table 6.3: Stretching and bending modes for inorganic, diatomic molecules [236]. M and X are the replacements for metal and halogen atoms respectively.
Figure 6.4: Comparison between EloMinit and OPA 8 40/100-65 asphalt. At low frequencies, the EloMinit exhibits an increasing reflectivity with decreasing frequency, indicating a Drude contribution. The arrow in the inset marks the potential C=O stretching mode at $\sim 1700 \text{ cm}^{-1}$.

content, which can be identified in the low frequency regime. While the asphalt exhibits a rather constant reflectivity below $300 \text{ cm}^{-1}$, the reflectivity of the EloMinit sample rises with decreasing frequency. The latter case fits to a Drude contribution, while the first one is rather described by a Lorentz oscillator. In addition, not all modes that appear in the EloMinit sample, also appear in the asphalt sample. For EloMinit, following modes can be found in the spectrum:

- $\sim 157 \text{ cm}^{-1}$ and $\sim 226 \text{ cm}^{-1}$: These mode are of unknown origin. They probably originate from inorganic, diatomic molecules.

- $\sim 278 \text{ cm}^{-1}$: It corresponds to a TiO$_2$ transverse optical (TO) mode located at $\sim 279 \text{ cm}^{-1}$ [240].
• ~ 512 cm\(^{-1}\): This mode can be assigned to an Al\(_2\)O\(_3\) LO mode located at ~ 512 cm\(^{-1}\) [227, 228].

• ~ 875 cm\(^{-1}\): A mode which might be again an Al\(_2\)O\(_3\) LO mode located at ~ 871 cm\(^{-1}\) [227, 228].

• ~ 975 cm\(^{-1}\): It probably corresponds to an LO stretching mode of Al–O located at ~ 968 cm\(^{-1}\) [215] or an absorption of MgO located at ~ 985 cm\(^{-1}\) [232].

• ~ 1535 cm\(^{-1}\): A mode which is challenging to assign, however, H-feldspar (HAlSi\(_3\)O\(_8\)) possess absorptions between ~ 1500 cm\(^{-1}\) and ~ 2000 cm\(^{-1}\) [234] any may be the origin of this mode.

• ~ 1749 cm\(^{-1}\): The 2\(\nu_3\) overtone of Al\(_2\)O\(_3\) located 1730 cm\(^{-1}\) [229] can be assigned to this mode.

• ~ 1797 cm\(^{-1}\): This mode is likely originating from Na-feldspar (NaAlSi\(_3\)O\(_8\)), which has an absorption around 1760 cm\(^{-1}\) [234]. Another feldspar, sanidine ((K, Na)AlSi\(_3\)O\(_8\)) has a mode located at ~ 1760 cm\(^{-1}\) [234].

• ~ 3547 cm\(^{-1}\): An –OH asymmetric stretching for example in in Mg\(_2\)FeOH at ~ 3594 cm\(^{-1}\) [213] or in MgFeOH at ~ 3562 cm\(^{-1}\) [213].

The stone materials also contain traces of halogen atoms like fluorine. Therefore, most of the observed low frequency features, can probably be assigned to diatomic, inorganic molecules which include a metal and halogen atom. In Tab. 6.3, regions of IR-active vibrations of inorganic, diatomic molecules are listed.

For the OPA 8 40/100-65, there are more and also different features present, than in the EloMinit sample:

Identical or similar modes compared to the EloMinit sample are at ~ 225 cm\(^{-1}\), ~ 532 cm\(^{-1}\), ~ 1795 cm\(^{-1}\), and ~ 3623 cm\(^{-1}\). Modes which are hard to assign are at ~ 372 cm\(^{-1}\), ~ 394 cm\(^{-1}\), and ~ 429 cm\(^{-1}\). All of them are within the range of Tab. 6.3 for bending modes of metal-containing molecules. The other modes might arise due to the bitumen content.

**Mode detection – bituminous samples**

Many reports exist about FTIR measurements on bitumen samples, which investigate vibrational stretching and bending modes in the FIR to MIR [201, 241–254].
The composition of bitumen depends a lot on its origin and the manufacturing process at the fabrication [242]. Typically, it consists of around 85% carbon, 10% hydrogen, and heteroatoms such as sulfur (0% to 9%), nitrogen (0% to 2%), and oxygen (0% to 2%), as well as traces of metals such as iron, nickel, and vanadium [156].

In bitumen, a typical C–O stretching mode from carbonyl compounds is located at \( \sim 1700 \text{ cm}^{-1} \) [201, 241, 243, 245, 247–249, 253, 254], however, in our samples, there is no feature observed at this frequency or it is hidden within a broader feature, indicated by a slight, broad dip in the OPA 8 40/100-65 sample (see the inset of Fig. 6.4).

Another very distinct feature is located at 1030 cm\(^{-1}\), which is assigned to the S–O stretch in sulfoxides [201, 241, 243, 247–249, 254]. The latter mode can be seen at the OPA sample, while for the AC sample in Fig. 6.5 it might be hidden within the SiO\(_2\) mode. The oxides are an indicator for aging. The stronger the oxidation level, the older the asphalt and the stronger the optical feature [201].

One of the modes from the C–C double bond in aromatics—located at 1600 cm\(^{-1}\)—nearly overlaps with the H\(_2\)O bending mode [201, 245, 249].

In butadiene, one mode of C=C double bonds is located at \( \sim 965 \text{ cm}^{-1} \) [245, 247]. For the investigated samples, it might lead to a slight broadening of the peak located at \( \sim 1000 \text{ cm}^{-1} \), which is mainly caused by SiO\(_2\).

The absorptions caused by methyl (CH\(_3\)) and ethylene groups (CH\(_2\)) are relatively independent of oxidation and they are located at \( \sim 1375 \text{ cm}^{-1} \) and \( \sim 1460 \text{ cm}^{-1} \) respectively [248]. In the investigated samples, these modes cannot be observed.

Two bands, which overlap with modes of calcite are located at \( \sim 2852 \text{ cm}^{-1} \) and \( \sim 2924 \text{ cm}^{-1} \), which correspond to the symmetric and asymmetric stretching mode of –CH\(_2\)– and C–H from the aldehyde group respectively [249, 252]. These two modes can be observed in any investigated bituminous sample.

With this background, the following assignment of the further observed modes can be made for the OPA 8 40/100-65 sample:

- \( \sim 470 \text{ cm}^{-1} \): A mode of S–S in diphenyl disulfide located at \( \sim 472 \text{ cm}^{-1} \), or in mercaptoethanol or benzio[B]thiophene located at \( \sim 474 \text{ cm}^{-1} \) might be the origin of this feature [252].
• \( \sim 796 \text{ cm}^{-1} \): This feature probably results from a C–S mode in dibutyl disulfide, which is typically found at \( \sim 791 \text{ cm}^{-1} \) [252].

• \( \sim 904 \text{ cm}^{-1} \): The \(-\text{CH}–\text{CH}_2\) wagging vibration located at \( \sim 910 \text{ cm}^{-1} \) probably leads to the observed feature [251].

• \( \sim 1005 \text{ cm}^{-1} \): Might relate to a stretching mode of C–O in ester, which is typically located between \( \sim 1000 \text{ cm}^{-1} \) and \( \sim 1300 \text{ cm}^{-1} \) [251].

• \( \sim 1037 \text{ cm}^{-1} \): This mode comes from sulfoxide stretching \(-\text{S}–\text{O}\) and is located at \( \sim 1030 \text{ cm}^{-1} \) [201, 241, 243, 247–249, 251, 252, 254].

• \( \sim 1092 \text{ cm}^{-1} \): Probably related to a stretching mode of C–O in ester, which is typically located between \( \sim 1000 \text{ cm}^{-1} \) and \( \sim 1300 \text{ cm}^{-1} \) [251]. However, it cannot be excluded that there are traces of other minerals present which contribute to this feature, for instance SiO\(_2\). The presence of SiO\(_2\) is supported by the following mode.

• \( \sim 1164 \text{ cm}^{-1} \): This mode somehow indicates that there is again SiO\(_2\) involved, which would correspond to an Si–O stretching mode located at \( \sim 1160 \text{ cm}^{-1} \) [218].

• \( \sim 2856 \text{ cm}^{-1} \): This mode can be assigned to the symmetric stretching mode of \(-\text{CH}_2–\), which is located at \( \sim 2852 \text{ cm}^{-1} \) [249].

• \( \sim 2927 \text{ cm}^{-1} \): The last feature can be allocated to the asymmetric C–H mode of the aldehyde group, which is located at \( \sim 2924 \text{ cm}^{-1} \) [249].

In Fig. 6.5, optical spectra are illustrated for AC 11 DS 50/70, AC 14 surf 35/50, and the mix of raw material pellet (compare Fig. 6.3 b)). There is a very good agreement between the mix of different stone types and the actual AC 11 DS 50/70 sample. Mainly in the NIR and VIS region, small deviations appear. While the mix
Figure 6.5: Comparison between the mixture of stones and the AC 11 DS 50/70 asphalt. Additionally, MIR to VIS data for the AC 14 surf 35/50 are illustrated. The high granite content has a direct impact at the SiO$_2$ mode at $\sim$ 1040 cm$^{-1}$. In the inset, Fabry-Pérot oscillations can be identified for the AC 14 surf 35/50 sample.

sample displays a rather constant reflectivity dependent on frequency, the reflectivity of the AC 11 DS 50/70 sample decreases with increasing frequency. This decrease originates from the bitumen content of the sample, which absorbs more light than the bare stone material. The AC 14 surf 35/50 exhibits the same behavior even though its main material is white granite, which confirms the conclusion about the effect of the bitumen. Granite consists mainly of quartz (SiO$_2$), which has a direct impact on the strength of the mode at $\sim$ 1000 cm$^{-1}$. Additionally, the high quartz content leads to Fabry-Pérot oscillations in the MIR range, which can be better seen in the inset of Fig. 6.5. In the FIR region, besides the mode located at $\sim$ 310 cm$^{-1}$, following modes are observed for the AC 11 DS 50/70 pellet (see Fig. A.3) and at least partly identified:
• $\sim 100\,\text{cm}^{-1}$: This mode—like most of the following modes—corresponds to a TO mode of CaCO$_3$, which is typically located at $\sim 102\,\text{cm}^{-1}$ [226].

• $\sim 156\,\text{cm}^{-1}$: LO mode of calcite (CaCO$_3$) located at $\sim 159\,\text{cm}^{-1}$ [226].

• $\sim 224\,\text{cm}^{-1}$: TO mode of calcite at $\sim 222\,\text{cm}^{-1}$ [226].

• $\sim 262\,\text{cm}^{-1}$: This feature might be assigned to a TO mode of aragonite (CaCO$_3$), which is normally located at $\sim 259\,\text{cm}^{-1}$ [255].

• $\sim 372\,\text{cm}^{-1}$: LO mode of calcite at $\sim 376\,\text{cm}^{-1}$ [226].

• $\sim 395\,\text{cm}^{-1}$: LO mode of calcite located at $\sim 396\,\text{cm}^{-1}$ [226].

• $\sim 460\,\text{cm}^{-1}$: This feature corresponds to the Si–O–Si asymmetric bending mode in biotite at $\sim 461\,\text{cm}^{-1}$ [213], while in pure quartz it is rather located at $\sim 450\,\text{cm}^{-1}$ [210].

• $\sim 513\,\text{cm}^{-1}$: An optical feature allocated to the Si–O bending mode in $\alpha$-cristobalite, which is located at $\sim 513\,\text{cm}^{-1}$ [218], while in quartz the symmetric bend is located at $\sim 520\,\text{cm}^{-1}$ [210]. Additionally, an LO mode of Al$_2$O$_3$ located at $\sim 512\,\text{cm}^{-1}$ [227, 228] might broaden the feature.

The relatively broad features show that a single affiliation to one specific mode is rather unlikely. Since heavy atoms like Ca, Ti, Fe, Ni, Cu, and others are contributing to the chemical composition, the already mentioned inorganic, diatomic molecules (see Tab. 6.3) might contribute and broaden the features. Also the mode at $\sim 310\,\text{cm}^{-1}$ probably originates from such a vibration.

In total, the AC types show similar optical features, with the one from Portugal (AC 14 surf 35/50) possessing a higher contribution of quartz. The chemical composition of the OPA asphalt and its raw material EloMinit varies a lot. While our raw material sample clearly indicates a Drude like behavior at low frequencies, the
OPA sample does not. In all samples, the NIR and VIS region only exhibit weak optical features, which can be mainly assigned to overtone and combinations bands of OH and CaCO$_3$. These features are located on a broad electronically driven transition.

**Kramers Kronig analysis**

For modeling or simulating a layered system consisting of any aggregate state of H$_2$O and asphalt in the NIR region, it is desirable to use the complex refractive index from H$_2$O in its liquid or solid state and from the asphalt layer. Broadband spectroscopy combined with a Kramers Kronig relation is one method to obtain refractive index data of any material. By measuring the reflectivity over a broad frequency range, the real and imaginary part of the refractive index can be extracted via the Kramers Kronig analysis.

![Reflectivity vs Frequency and Wavelength](image)

Figure 6.6: Broadband reflectivity dependent on frequency a) and wavelength b). Data and fit are illustrated for the AC 11 DS 50/70 pellet. The green line represents the fit for version 3 of the extrapolation.

In the following sections, the discussions are mainly restricted to the NIR range. For this, the unit of choice is wavelength instead of frequency. To provide a smoother transition and overview between frequency and wavelength, Fig. 6.6 to 6.8 show the same data twice, once for each unit.

In Fig. 6.6, the frequency-dependent reflectivity for the AC 11 DS 50/70 pellet is illustrated from the FIR to VIS region. The green line represents a qualitative fit of the data, which is obtained in several iterations in WAsf. Here, only main features are modeled, while every feature is described by a Lorentzian oscillator. In
total, 20 oscillators are necessary to model the data, while one of them is located at 30724 cm$^{-1}$ and hence, beyond the measured frequency range. This last oscillator is necessary in order to describe the decreasing tail with increasing frequency.

For the Kramers Kronig analysis to work properly, the data have to be extrapolated to low and high frequencies. In Fig. 6.7, the effect of three different extrapolation methods is compared to each other. For version 1, the low frequency region is extrapolated with a frequency-independent constant value, which is at the same level as the lowest measured data points. For the high frequency extrapolation, an $\omega^{-4}$ decay is applied up to a frequency of $10^6$ cm$^{-1}$, which normally models the response of a free electron gas [41]. For version 2, the low frequency extrapolation is done by the fit consisting of Lorentzian oscillators, while the high frequency extrapolation consists of two elements, namely, a frequency-independent constant followed by the already mentioned $\omega^{-4}$ decay. The constant value extrapolation is a common procedure for organic materials in the high frequency region [256]. In version 3, both extrapolations are realized via the obtained fit. The impact of each extrapolation method on the data points within the measured range is illustrated in Fig. 6.7 and 6.8. For $\sigma_1$, $n$, and $\kappa$, there is only a small difference between a constant and a Lorentzian extrapolation at frequencies below 100 cm$^{-1}$. For the high frequency extrapolation, the different versions stronger affect the results within the measured range down to roughly 4000 cm$^{-1}$. Version 1 exhibits only slight deviations compared to version 3, while version 2 clearly deviates from the others.
Figure 6.8: Real part $n$ a) to b) and imaginary part $\kappa$ c) to d) of the complex refractive index $N$ as a function of frequency a), b) and wavelength c), d). The green line represents the fit of version 3 extrapolation.

Since the main focus of this thesis is on the NIR region, the measured range would have to be extended into the UV region to avoid any influence of the high frequency extrapolation on the NIR region. Thus, from IR spectroscopy, the resulting complex refractive index has to be handled with special care. In order to classify the results for the complex refractive index from the Kramers Kronig relation, the same pellet is studied with an ellipsometer. This technique does not need a Kramers Kronig relation in order to obtain the complex refractive index. However, is not more exact for samples with a large surface roughness (see Sec. 6.1.2)

**$N$ from ellipsometry**

A broadband ellipsometer was utilized in order to determine the complex refractive index $N$ of the AC 11 DS 50/70 pellet. As model, the Cauchy-Urbach dielectric
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Figure 6.9: Ellipsometric result $\Psi$ and $\Delta$ at a wavelength of 1300 nm for the AC 11 DS 50/70 pellet. In a), the fit with a surface roughness fixed to zero. In b), the imaginary part $\kappa$ of the refractive index fixed to zero. For both approaches, good agreement is achieved between fit and data.

function was applied, which is the typical model for insulating materials. The resulting complex refractive index from ellipsometry depends a lot on the utilized model, which is applied to the actual measurement variables $\Psi$ and $\Delta$. For the actual modeling of the data, an effective media approximation is additionally applied to the Cauchy-Urbach model, since—even though the surface is quite flat—a micro surface roughness remains at the pellets, which influences the measurement results. An effective media approximation takes this roughness into account by an additional fitting parameter. In Fig. 6.9, $\Psi$ and $\Delta$ is illustrated for the AC 11 DS 50/70 pellet at 1300 nm. At the first view, the fits in Fig. 6.9 a) and b) are identical. However, in Fig. 6.9 a), the imaginary part $\kappa$ of the complex refractive index stays constant at zero with a surface roughness of 19.5 nm, while in Fig. 6.9 b), the roughness parameter stays at zero with $\kappa \approx 0.1$. Even though two different approaches are used for fitting, both lead to similar results with only slight deviations in the real part $n$ of the complex refractive index with a value around 1.5. As a consequence, obtaining a reliable value for $\kappa$ is challenging, since both parameters, surface roughness and $\kappa$ lead to a similar behavior of $\Psi$ and $\Delta$.

By increasing the surface roughness parameter even further into the $\mu$m range, the resulting real part $n$ decreases to a value of around 1.3. However, even though a $\mu$m-roughness is in general a very smooth surface for a pellet, the roughness exceeds the $\frac{1}{100} \lambda$-limit [45]. Thus, it is too high for applying the effective medium approximation, since surface scattering effects cannot be neglected in this case.
Indeed, in his master thesis, Christoph Müller performed some atomic force microscopy (AFM) measurements and observed a surface roughness in the low µm regime [160].

In summary, ellipsometry in combination with our pellets is not more exact for the determination of an effective complex refractive index \( N \) of asphalt.

### 6.1.3 Scattering properties

From polarization-dependent measurements, the cross polarization\(^6\) is an indicator for the contribution of volume and multiple surface scattering \( (I_{sp} \approx I_{ps}) \). Since the pellets have a rather flat surface, the latter effect should have only a minor contribution. Depending on the pellet, \( I_{sp} \approx I_{ps} \) is observed up to a certain incident angle. In the following, we will provide a short summary of these measurements, for more details, see Ref. 160.

For the AC 14 surf 35/50 and OPA 8 40/100-65 pellets, those angles are relatively large with \( \sim 55^\circ \). For larger incident angles, the two cross polarizations split up with \( I_{sp} > I_{ps} \), indicating less volume scattering. For the EloMinit pellet, the splitting already begins at \( \sim 30^\circ \). The high metal content, and thus the short penetration depth, might be the reason for the reduced contribution of volume scattering compared to the other pellets.

### 6.2 Asphalt samples

For water and ice-covered samples, the asphalt acts as a substrate. During its lifetime, an asphalt surface changes its structure as well as its appearance and thus, also its optical properties. Therefore, it is important to know the optical properties of asphalt very well and how they develop over time in order to utilize it for further measurements on H\(_2\)O-covered systems.

#### 6.2.1 Spot size dependence

As already mentioned in Sec. 3.3, asphalt is an inhomogeneous mixture of several types of rocks and binder material. In addition, its surface has a macroscopic roughness with grain sizes in the order of mm to cm. All together, it is a rather untypical

\(^6\)Cross polarization: Incident channel in one polarization for example s-polarization and detector channel with the perpendicular polarization respectively (here p-polarization) [160].
material for optical spectroscopy.

Thus, it is necessary to first determine an appropriate illumination and detection spot size. Here, a minimal spot size is favored, where negligible sensitivity to surface features like single pores or grains occur. In general, the larger the spot size, the more average over the surface, however, the less signal and therefore, a worse signal-to-noise ratio (SNR). Several combinations of illumination and observation spot sizes were tested, indicated by following notation: $L_xM_y$, where the illumination (light L) spot has a diameter of $x$ mm and the detection (measurement M) spot a diameter of $y$ mm. For determining a proper optical spot size, several asphalt samples were investigated with three different spot sizes (L20M10, L20M20, and L40M40). The setup depicted in Fig. 4.7 b) was utilized for the measurements, which will be simply called standard setup from now. The samples were moved in 5 mm steps, resulting in a scanned line versus the asphalt samples. In Fig. 6.10, an image of the AC 11 DS 50/70 sample is shown as example, where the green scale highlights the different measurement positions. The image provides also an impression about the utilized optical spot sizes with respect to the asphalt sample (diameter: 150 mm).

In the following, only results from the AC 11 DS 50/70 sample are presented, since
all the measurements provide similar results with the same conclusions. Nevertheless, the interested reader can compare the presented results to results from some other samples in the Appendix (see Fig. A.4 to Fig. A.6). The measurements are performed with a zenith angle of $\theta_i = \theta_r = 0^\circ$ and $\theta_i = \theta_r = -20^\circ$. The resulting wavelength-dependent reflectance factors can be found in Fig. 6.11. Between the two utilized zenith angles, there is barely any difference within the presented spot sizes. This behavior is quite interesting and will be discussed in more detail in Sec. 6.2.3. The spread in absolute values of the reflectance factor between the different measurement positions on the sample surface decreases with increasing spot size. Fig. 6.12 illustrates the reflectance factor dependent on the measurement position for $\sim 1000\text{ nm}$, $\sim 1300\text{ nm}$, and $\sim 1600\text{ nm}$. These wavelengths are located close to the beginning, the middle, and the end of the observable range of the spectrometer. For L20M10, not only the absolute values scatter strongly dependent on the measurement position, there is also a wavelength-dependence identified. The spread in absolute values as well as in the wavelength-dependence (relative values) decreases significantly with the L20M20 geometry. By extending the spot size further to L40M40, only a little improvement can be identified with respect to the position-dependence. However, at low wavelengths ($\lambda < 950\text{ nm}$), the SNR gets worse for L40M40 (see Fig. 6.11).

From the presented results, together with the knowledge about the main grain size

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7For $\theta_i = \theta_r = 0^\circ$, a version as 3D plot can be found in the Appendix (Fig. A.7 to Fig. A.9).
of 11 mm for this asphalt sample, one can conclude that a proper light spot size has to be at least two times bigger than the main grain size of the sample. A further enlargement of the light spot will for sure lead to a better average and less position dependence, however, on cost of SNR. Therefore, all results presented in the next sections are measured with L20M20, if not stated otherwise.

**Simulation results**

As a first capability test of the simulations, a flat Lambertian surface is simulated for different light and measurement spot sizes: $L < M$, $L = M$, and $L > M$. The resulting angle-dependent reflectance factors are compared in Fig. 6.13 for an incident angle of $0^\circ$. From the measurements, only L7M20 follows the cosine curve, which is expected for a Lambertian surface (see Sec. 2.5.5). The bigger the light spot compared to the measurement spot, the bigger the deviation to the cosine

![Graph](image-url)
curve. This deviation is explained by the overlap between light spot (circular for an incident angle of 0°) and measurement spot. For angles\(^8\) up to \(\sim 50°\), the most

![Figure 6.13: Comparison of the reflectance factor from measurement a) and simulation results b) of a Lambertian surface. Three different combinations of light and measurement spot sizes are compared with an incident angle of 0°. The simulation is performed with \(10^7\) rays. The data in a) was measured by Simon Amann during his master thesis.](image)

intensity reaches the detector. For larger angles, the elongation of the measurement spot (FOV) gets bigger. However, since the center of the ellipse is moving out of the center of the illumination spot, the light spot gets cut by the FOV. Thus, the intensity decreases faster with increasing observing angle. The simulations show the same trend as the measurement with only slight deviations. The origin of this deviation is most probably the light source within the simulation. While the lens in front of the detector uses the same parameters as in the real measurements, in the simulations—for terms of simplicity—the lighting of the sample does not use any lens at all. Hence, at the spot boundary, the light (ray) density deviates, which virtually changes the effective spot size.

Since the investigated samples possess a notable surface roughness (see Tab. 3.2), we also need to simulate rough surfaces. In order to get a feeling about all the different roughness parameters (introduced in Sec. 2.9), a statistical evaluation is performed and presented in Fig. 6.14. For generating the rough surfaces, a grid is set in \(x\)-direction. This grid consists of equidistant steps \(x_s\). The \(y\)-values are

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\(^8\)The exact angle depends on the spot sizes \(L_xM_y\).
Figure 6.14: Statistical distribution of the six roughness parameters $R_t$ a), $R_a$ b), $R_q$ c), $R_z$ d), $R_p$ e), and $R_v$ f) for three different spacing values $x_s$ in $x$-direction. The results are shown for a spacing of 0.1 mm in black, 0.5 mm in red, and 1 mm in blue. The aimed value for $R_t$ is 1 mm for all three spacings. For each spacing, 10000 samples are computed.

determined by a random value between a certain boundary.

In the here presented case, the boundary is between 0 mm and 1 mm. Independent
of the exact value, this range is comparable to the maximum height \( R_t \) of the profile, which is actually measured by the sand-patch method (see Sec. 4.6) and provided for the different asphalts in Tab. 3.2. The values 0 mm and 1 mm are chosen, because it represents roughly the mean value from Tab. 3.2.

For the evaluation in Fig. 6.14, three different \( x_s \) are used, where 10000 samples are computed for each step size. The sample itself has a size of 60 mm in \( x \)-direction, which is three times larger than the light spot diameter. The mean line \( L_m \) is directly connected to the randomly generated \( y \)-values. For the three different step sizes, \( L_m \) reveals a Gaussian distribution around 0.5 mm, which broadens for increasing \( x_s \) (see Appendix, Fig. A.10).

As expected, \( R_t \) delivers values \( \leq 1 \) mm with the maximum between 0.98 mm and 1 mm. The slight broadening for increasing \( x_s \) is probably related to the limited size of 60 mm in \( x \)-direction, because there is less probability that two random values are located close to the boundaries of 0 mm and 1 mm. The arithmetical mean roughness \( R_a \) as well as the quadratic arithmetical mean roughness \( R_q \) exhibit a Gaussian distribution around 0.25 mm and 0.29 mm, respectively. Both distributions are quite narrow since all peaks an valleys have the same probability of appearance. When there would be some single peaks or valleys which differ significantly from the others, \( R_q \) would be more affected than \( R_a \). For example, the insets of Fig. 6.14 exhibit only one strong valley. In this case \( R_q \) would be more affected. The averaged surface roughness \( R_s \) shows a similar result as \( R_t \) for \( x_s = 0.1 \) mm, while for increasing \( x_s \), the center of distribution is shifted towards lower roughness and the distribution itself broadens. Since the total length of the ground stays constant, each of the five segments (compare Sec. 2.9) contains less peaks and valleys, thus it is less likely that within one segment \( y \)-values appear close to the boundaries (0 mm and 1 mm).

Therefore, the center of distribution shifts to lower roughness values for increasing step size \( x_s \). In terms of absolute values, the average peak height \( R_p \) and average valley depth \( R_v \) exhibit the same results. For \( x_s = 0.1 \) mm, a very narrow Gaussian distribution is located around \( | \pm 0.5 | \) mm. With increasing \( x_s \), the distribution broadens and is shifted to smaller values due to the same reason as mentioned for \( R_z \).
6.2.2 Measurements at small incident angles

In this subsection, the results for small incident angles are summarized and discussed. From the obtained observations, conclusions about the optical properties can be made dependent on the asphalt’s aging state.

Aging effects

![Figure 6.15: Averaged curvature $a$ of the reflectance factor from all investigated dry asphalt samples. The curvature is calculated by a polynomial fitting function of 2$^{nd}$ degree ($a\lambda^2 + b\lambda + c$). As sampling points, only the reflectance factors at 1000 nm, 1300 nm, and 1600 nm are utilized. Black symbols highlight untreated, red ones sandblasted, and blue ones (drilling cores) actual used asphalt samples.](image)

A road has to endure all kind of weather, humidity, heat, salt, load from vehicles, and more over many years, up to decades. The surface is directly affected by those parameters, which causes structural and chemical changes$^{9}$. Therefore, also the op-

$^{9}$For instance, over time, UV radiation from the sun causes oxidation of several types of molecules inside the bitumen as well as breaks chains from polymers.
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Figure 6.16: Averaged slope $m$ of the reflectance factor from all investigated dry asphalt samples. The reflectance factors at 1000 nm and 1600 nm are utilized for the fit of a straight line ($m\lambda + b$). Black symbols highlight untreated, red ones sandblasted, and blue ones (drilling cores) actual used asphalt samples.

...tical properties of asphalt change over time. For a sensor, where an asphalt surface represents the substrate, it is essential to know how its optical properties change over time by wear and environmental influences.

A freshly deposited road surface is coated with a layer of bitumen, which is the reason why it appears so dark. This coating is also the reason why there is an additional speed limit for new wearing courses, because its effective friction value is relatively low, especially in combination with water. By time, the vehicle tires ablate this sticky upper bitumen layer. It depends on the traffic density, temperature, as well as the type of bitumen itself, how long this erosion needs to completely remove the top bitumen coating. In general, the higher the temperature, the softer the bitumen and the faster the erosion; the first effect of aging. Additionally, loosely

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The actual friction value for dry bitumen is not really bad, but the soft material acts as a viscous layer between tire and sturdy stone material.
and weakly bound stone grains are removed from the surface layer, which can be identified as the second aging state. The missing material leaves behind vacancies in the surface structure. The load caused by vehicles squeezes surrounding material into those vacancies. During this process, some of the grains also break apart since the stabilizing surrounding material is missing. In total, the surface first gains a higher coarse roughness (due to missing large particles: high amplitude), which is later reduced by a filling of the vacancies. Nevertheless, the roughness due to missing small particles (small amplitude) increases over its lifetime with a likely trend towards saturation.

Fig. 6.15 - 6.17 illustrate the aging effects on the optical spectra in the NIR region. Additionally, they help to compare the different investigated asphalt samples with each other.
For the curvature in Fig. 6.15, a polynomial function of 2nd degree is utilized to fit the wavelength-dependent reflectance factor. For the fit, values at only three wavelengths are considered, namely at 1000 nm, 1300 nm, and 1600 nm. The resulting points are the results from averaging several measurements of different spots on the particular asphalt samples. The error bars show the resulting standard deviation. For the slope in Fig. 6.16, the same principle is utilized, using only the reflectance factor at 1000 nm and 1600 nm. The integral in Fig. 6.17 represents the area below the spectra between 840 nm and 1650 nm, in order to compare the reflectance factor absolute values between the different asphalt samples.

From Fig. 6.15, it seems that already used and thus aged asphalt from the AC type rather exhibit a negative curvature with two exceptions: AC 8 DN 50/70 (core) and AC 14 surf 35/50. For the latter one, the high granite contribution might explain the different behavior. The first one, like the SMA 8 N 50/70, SMA 8 S 25/55-55 A, and SMA 11 S 25/55-55 A, all include granodiorite, which probably causes the positive curvature. However, in total, nearly all asphalt types exhibit a rather linear behavior with slightly more likely positive curvature, especially for the SMA types.

Among the investigated samples, there are four specimen (AC 8 DN 50/70 (new), AC 11 DN 50/70, AC 14 surf 35/50, and SMA 8 S) which are untreated and explicitly produced for our measurements; thus, they still possess their bitumen coating on top. They clearly distinguish from the others by comparing their absolute values of the reflectance factor, illustrated in Fig. 6.17. They exhibit the lowest values and there exists only little spot dependence, indicated by their small standard deviation. Additionally, their curvature is close to zero. The bitumen coating reflects the incident light more specularly. Thus, their diffuse reflecting contribution is very weak, and the overall reflectance dominated by surface scattering. In terms of absolute values, there are two exceptions: The first one is AC 14 surf 35/50 (new), which exhibits a larger integrated reflectance factor. This is caused by sand residuals on the surface. They are bright in the VIS region and clearly enhance the reflectance factor in the NIR region as well. The irregularly distributed sand leads to the higher standard deviation, too. The sand also causes the stronger curvature and higher slope (see Fig. 6.15 and 6.16 respectively). The second exception is OPA 8 40/100-65, which exhibits similar absolute values as the untreated samples, even though it is sandblasted. Additionally, it is the only asphalt which possesses a negative slope for

\[11\] AC 11 DS 25/55-55 A II also includes granodiorite and additional lysi (natural brightener), which causes still a positive curvature, however, close to zero.
nearly all single measurements, by simultaneous negligible curvature. Therefore, a more detailed discussion about this asphalt takes place in Sec. 6.3.3.

The sandblasted asphalts—which are explicitly produced for our measurements—did not face any load from vehicles, only the bitumen coating is removed without any significant structural change of their surface. Thus, they represent the already mentioned first aging state. The integrated reflectance factor exhibit enhanced values compared to untreated samples and their curvature is mostly positive.

The investigated drilling cores actually faced load from vehicles. They represent the most advanced aging state, where structural changes of the surface already appeared. From all asphalts, they exhibit the largest values for the integrated reflectance factor. At a closer look, this enhancement is wavelength-dependent. For example in Fig. 6.18, a sandblasted and a drilling core of the same type of asphalt (AC 11 DS 50/70) is shown for a direct comparison. The reflectance factor at lower wavelengths exhibits a stronger enhancement than at higher wavelengths. As a result, the slightly curved wavelength-dependent reflectance factor of the sandblasted sample changes to a rather linear one for the drilling core. These changes are probably caused by different surface scattering events for the changed surface structure. Most of the asphalts exhibit a very similar slope between 1000 nm and 1600 nm, which is illustrated in Fig. 6.16. In total, only three asphalts yield a larger devi-

Figure 6.18: Direct comparison of the reflectance factor between a rectangular sample (sandblasted) a) and an actual used sample (drilling core) b). Both are from the same type: AC 11 DS 50/70. For each asphalt, several spots on the surface are measured. While the curvature at higher wavelengths are less affected, between 840 nm and 1200 nm it changes significantly.
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ation. For the AC 14 surf 35/50 (new) asphalt, the residual sand particles on top of the surface are already identified to enhance not only the slope, but also the curvature and integrated reflectance factor values. The AC 8 DS 50/70 sample exhibits a positive slope for the mean value, however, few single measurements exhibit a negative slope. Since it is the only asphalt which includes greywacke, it seems logical, that grains of this material causes the deviating behavior. The only asphalt where even the mean value exhibits a negative slope is the OPA 8 40/100-65 sample. Thus, it clearly differs from all other investigated asphalts. As already mentioned, the optical behavior of this asphalt is investigated in more detail in Sec. 6.3.3.

6.2.3 Scattering properties

As already shown in Fig. 6.11, the direct comparison of the wavelength-dependent reflectance factor between the 0° and −20° geometry reveals only minor differences in their absolute values. This result already indicates that asphalt scatters light diffusely following a Lambertian behavior, at least for small angles. In order to analyze the scattering properties in more detail, for four different asphalt types, BRF measurements enabled the extraction of BRDF data. In Fig. 6.19, the results are illustrated for chosen incident angles at two wavelengths. For all the results, the azimuth angle stays at 0°, only the zenith angle is varied.

The investigated asphalts reveal similar behavior in scattering. For small incident angles up to ±40°, the BRDF function—thus, also the angle-dependent reflectance factor—is rather flat for observing angles between approximately −50° to 50°, corresponding to Lambertian behavior. For the development of a sensor, which utilizes asphalt as a reference material, an angular range with Lambertian behavior is a useful property, since it allows angular tolerances in its alignment. Within these tolerances, the results from measurements barely deviate from a perfect alignment. For larger incident as well as observing angles, the BRDF function increases with a slight tendency towards forward scattering. This is in good agreement to previous work from Puttonen et al. [91].

In his master thesis, Christoph Müller investigated some of the listed asphalt samples in Tab. 3.2 via polarization-dependent measurements. It was found that the s-polarized light exhibits stronger forward scattering compared to p-polarized light. Therefore, the enhanced forward scattering can be attributed to surface scattering effects and single scattering events, where s-polarization is the dominating polarization [257].
In Fig. 6.18, there is already a hint that volume scattering also contributes to the overall scattering behavior. A small dip located at approximately 1410 nm corresponds to an OH vibration (see Sec. 6.1.2). This kind of feature is only observed in transmission measurements. Therefore, the scattered light contributing to this feature originates from volume scattering; only a certain penetration depth can lead to this transmission-like feature.

In Sec. 6.1.3, it was already discussed that the pellets also exhibit a contribution of volume scattering. Polarization-dependent measurements on asphalt samples show a similar result for small incident angles [160]. For an incident angle of $-20^\circ$, there is barely any splitting observable for the cross polarization measurements [160]. However,
ever, since the surface roughness cannot be neglected for these samples, multiple surface scattering might contribute to the observed depolarization.

**Opposition effect**

In Fig. 6.19, all the BRDF curves exhibit enhanced values around their incident angles. For the AC 5 DL 70/100 and OPA 8 40/100-65 samples, this effect is more distinct than for the other two asphalts, especially for high incident angles. The enhanced backscattering for small phase angles\(^{12}\) is the opposition effect also known on vegetated land\(^{13}\) [259] and even Spektralon [257]. The opposition effect is caused either from coherent backscattering or shadow hiding (see Sec. 2.5.4), while the latter one is caused by structures much larger than the wavelength. Both effects could be present in the observed asphalt samples. For coherent backscattering, it is known that absorption leads to a broadening of the—in general—narrow backscattering cone from phase angles of 1° up to 10° [68]. Additionally, polarization-dependent measurements by Christoph Müller revealed negative polarization for phase angles up to 20° for AC 11 DS 50/70 and OPA 8 40/100-65 [160]. This effect is called the polarization opposition effect (POE) and is in good agreement with observations on other materials [86].

**Simulation results**

In Fig. 6.20, BRDF simulation results are illustrated for two different surface roughnesses (\(R_t = 0.4\) mm in Fig. 6.20 a) and \(R_t = 1.2\) mm in Fig. 6.20 b)). These roughnesses correspond to the AC 5 DL 70/100 and LOA 5 DS 25/25-55 samples, respectively. The L20M20 spot size configuration and \(10^6\) rays per wavelength are used for the simulations. In order to enable a better comparison with the measurement results—which are depicted in Fig. 6.19 a) and b)—each facet of the ground is given a reflectance value, which corresponds to the asphalt samples. For this purpose, the reflectance factor at given wavelengths is extracted from a real measurement at \(-20°\) incident and observing angle. The reflectance value of the facets is adjusted in a way that for the same geometry (\(-20°\) angle), the reflectance factor of the simulation and measurement are identical. Since each facet behaves like a Lambertian surface in the simulation, for small roughnesses, the reflectance value is

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\(^{12}\)Phase angle: Angle between incident and reflected beam.

\(^{13}\)Peltoniemi et al. showed that more dense materials exhibit more brightening in backward direction [258].
the same as the reflectance factor at $-20^\circ$ angle. The larger the surface roughness, the higher reflectance is necessary compared to the reflectance factor.

From the direct comparison to Fig. 6.19, the simulation delivers reasonable results for small incident angles and intermediate observing angles. At the real measurement, the BRDF delivers increasing values with increasing absolute observing angles. From the simulations, this behavior appears only at very larger observing angles and $0^\circ$ incident angle. Furthermore, it is much weaker than in the measurements. At larger incident angles there is even an enhanced backscattering compared to forward scattering, especially for the larger surface roughness. The reason for the enhanced scattering into the back direction is a similar effect as the shadow hiding. Facets with a normal vector pointing in forward direction are less illuminated than facets oriented into back direction. Since each facet behaves like a Lambertian surface, in total, backscattering is enhanced for large incident angles.

For the same reason and related to the Lambertian-based simulation model, the signal decreases for large observing angles in forward direction when the incident angle is large. In this case, the surface roughness leads to areas which are not covered by the Lambertian hemisphere (see Fig. 6.21). Only via multiple reflection processes on the surface (green line in Fig. 6.21), these blind areas get illuminated, however, the intensity in these angular regions is much weaker since they need at least two involved reflection processes. For the actual measurement results shown in Sec. 6.2.3,
this behavior is not observed because specular reflection is present. Especially for large angles, the specular reflection leads to very strong signals (see Fig. 2.4) which compensates the loss of signal, which is not considered in the simulation\textsuperscript{14}.

![BRDF graph](image)

Figure 6.21: Sketch of reflection processes at a rough surface. The red rays represent the Lambertian case, while the blue one represents the specular case. The green ray is the Lambertian case resulting from multiple reflection.

As expected, the simulation based on randomly oriented facets with Lambertian optical behavior is not capable to model the opposition effect (enhanced intensity into direct backscattering direction), which is normally caused by coherent backscattering and shadow hiding. Nevertheless, the overall results for small incident angles are in good agreement with results from real measurements.

### 6.3 Comparison: Pellets – asphalts

In this section, the results from measurements on pellets and macroscopic asphalt samples are compared to each other. Similarities and differences are pointed out. Additionally, the negative slope in reflectance factor measurements of OPA 8 40/100-65 is discussed in more detail.

#### 6.3.1 NIR at small incident angles

For small incident angles, broadband spectroscopy on pellets, as well as reflectance factor measurements on macroscopic asphalt samples are able to resolve the OH overtone at 1410 nm. Depending on the type of asphalt and its stone components, this feature is more or less developed. The slope of the reflectance factor for the asphalt samples and reflectivity for the pellets show the same tendency, except for the OPA 8 40/100-65 and EloMinit pellet. While both of them exhibit a negative slope in the reflectance factor at an incident and observing angle of $-20^\circ$ (see also

\textsuperscript{14}The consideration of this effect within the simulation model requires an effective complex refractive index for the ground, whose determination was shown to be challenging.
CHAPTER 6. DRY ASPHALT

Fig. 6.26 j)), the reflectivity at $0^\circ$ incident and observing angle exhibit a positive slope for the same wavelength range. This interesting discrepancy is discussed further in Sec. 6.3.3.

While for the macroscopic asphalt samples, conclusions about their aging state can be taken by investigating the curvature, slope, and integrated reflectance factor, it is not possible to do the same for the pellets. Most of the changes in the optical properties of the asphalt samples are caused by structural changes of their surfaces. The pellets are produced in a hydraulic press, therefore, bitumen as well as stone material is located at their surfaces, meaning that their surface corresponds roughly to a mixture between the untreated and the first aging state of the macroscopic samples. Thus, only oxidation of the containing bitumen might lead to any aging influence on the pellets.

6.3.2 Scattering properties

BRF measurements on asphalt samples could not resolve a specular peak, only for very large incident angles, some kind of specular broad lobe can be resolved (see Fig. 6.19). In contrast, the larger macroscopic surface roughness of the asphalt samples suppress the specular peak at small incident angles. Measurements on the pellets, performed by Christoph Müller [160], clearly resolved a distinct specular feature, even for small incident angles. This feature should be still rather called a lobe instead of a peak, since it is quite broad. There are at least two reasons for the broad width: A small surface roughness in the $\mu$m range is present at the pellets and inhomogeneous materials (small grains) directly below the surface reflect the penetrated light depending on the orientation of the grains.

Moreover, the degree of linear polarization (DLP) of the pellets is two to five times larger\textsuperscript{15} than for the asphalt samples [160]. This can be easily explained by their surface roughness. For the high macroscopic roughness of the asphalt samples, light is scattered multiple times on the surface, which acts depolarizing when it scatters out of the incident plane.

Nevertheless, cross polarization results from ellipsometric measurements on the pellets deliver strong indications for volume scattering, which results in a diffuse background signal [160]. Similar cross polarization measurements on macroscopic asphalt samples, however, exhibit a stronger deviation from the Lambertian behavior

\textsuperscript{15}At $-20^\circ$ incident angle [160].
at larger observing angles. The effect of the macroscopic roughness comes together with the volume scattering contribution; thus, a stronger deviation is observed compared to the pellets.

While the BRDF results (see Fig. 6.19) clearly indicate the opposition effect for macroscopic asphalt samples, for the pellets, there is barely any enhanced signal around the incident angle detected, even for measurements with the same homemade setup (see Fig. 4.7a) [160]. The geometry of the setup causes a blind spot in the observing angle of roughly 8° to 10° around the incident angle16. Thus, the pellet might exhibit some less pronounced opposition effect, however, due to the blind area it is not possible to resolve it with the utilized setup.

Results from ellipsometric as well as NIR scatterometry on the pellets exhibit a more pronounced Lambertian like behavior for small incident and high observing angles [160] than on the macroscopic asphalt samples. Only the broad specular lobe—which is missing at the macroscopic asphalt samples—prevents a nearly perfect Lambertian response.

6.3.3 Negative slope of reflectance factor

In this section, a closer look into the negative slope of the reflectance factor of the OPA 8 40/100-65 sample is given. It was already mentioned that measurements on the macroscopic asphalt sample of −20° incident and observing angle result in a negative slope for the NIR region, while measurements on the pellets with the FTIR spectrometer for 0° geometry exhibit a positive slope for the same wavelength range. This is a first indication that the negative slope only appears for diffuse off-specular reflection. Further investigations in the following will systematically rule out possible mechanisms, leading to a conclusion which property causes the negative slope.

BRF with high incident angle: negative slope

An excerpt of a BRF for two large incident angles (−70° and −74°) is provided for the OPA 8 40/100-65 asphalt sample in Fig. 6.22. Here, only 1000 nm and 1600 nm are presented, the same wavelengths as already used earlier to determine the slope (see Sec. 6.2.2).

For the spot with an incident angle of −74°, a maximum at positive observing an-

16Depending whether polarizers are attached or not.
Figure 6.22: BRF excerpt from the OPA 8 40/100-65 asphalt sample. Results are shown from two different spots (red and blue) on the sample surface for two different incident angles. The red and blue arrow at 63° mark the position where the slope of reflectance factor changes its sign. The inset provides an overview about the angle-dependent reflectance factor.

Angles appear, indicating a specular lobe\(^\text{17}\). In this region of large incident angles, the specular reflection dominates the overall signal; depending on the surface structure, such peaks can appear or the signal just increases further with increasing the angle (like for the incident angle of \(-70°\)). From our simulations, we were able to show that a strict Lambertian reflection behavior from facets of a rough surface is not able to develop such an increasing signal at large incident angles, confirming that the specular contribution is dominating this angular region for the macroscopic asphalt sample.

Interestingly, the slope of the reflectance factor also changes its sign at high observing angles, indicated by the arrows. In Fig. 6.23, three observing angles for the

\(^{17}\)An off-specular maximum at large incident angles was also observed in simulations for rough surfaces from Kalantari et al., where specular reflection processes are not neglected within the simulation [93].
Figure 6.23: Wavelength-dependent reflectance factor from the BRF of Fig. 6.22 at three observing angles. In a) results from spot A ($\theta_1 = -70^\circ$) and in b) from spot B ($\theta_1 = -74^\circ$) are presented. The dashed lines are guides to the eye.

wavelength-dependent reflectance factor show the different slope types: negative, zero, and positive\textsuperscript{18}. The change of sign is not observed for small incident angles. The transition from negative to positive sign appears at an angular region where the specular peak/lobe is expected. In this region, single scattering events are the dominant scattering mechanism. This supports the hypothesis, that specular reflection results in a positive and diffuse reflection in a negative sign of the reflectance factor’s slope for the OPA 8 40/100-65 sample.

For the macroscopic asphalt samples at small incident angles, volume scattering and surface scattering posses a higher contribution than single scattering events. Additionally, at small incident angles, a single reflection event is rather weak (when considering Fresnel’s equations). Therefore, no positive slope is observed.

**Raw material investigations: metallic character and negative slope**

Another possible mechanism for the negative slope in the reflectance factor is a property of one or more raw materials. Pure bitumen reveals a positive slope for specular as well as for diffuse reflection (see Fig. A.11). In order to investigate the impact of the single scattering events on the grains of the asphalt, raw material of this asphalt type—which is simply electric furnace slag (EloMinit)—is investigated separately.

\textsuperscript{18}For the other asphalts, the slope gets slightly flatter with increasing observing angle. Thus, a trend which is vice versa than for OPA 8 40/100-65.
A stack of EloMinit grains acts as a replacement for the actual asphalt sample. Since the grains are only stacked without any bitumen content, its contribution to the optical spectrum can be excluded. The results for three different spots (L20M20) on the stack with $-20^\circ$ incident and observing angle are shown in Fig. 6.26 j). The inset illustrates the measured stack. Similar to the OPA 8 40/100-65 sample (Fig. 6.26 g)), the slope of the reflectance factor is negative for all spots. As comparison, results for the AC 11 DS 50/70 and AC 14 surf 35/50 (new) are shown in Fig. 6.26 a) and d) respectively. Both exhibit a positive slope for all spots.

These investigations already confine the origin of the negative slope to the raw material EloMinit.

EloMinit is sturdy enough to withstand the high load even for very porous asphalt types. Its chemical composition varies a lot, depending on which material is molten and how close the slag is located to the liquid metal. For instance, in Sec. 6.1.2, it was already shown that the EloMinit pellet exhibits a Drude like behavior in the low frequency range; indeed, some grains of the available raw material are magnetic. For the available OPA 8 40/100-65 sample, no magnetic forces can be observed but the broadband spectroscopy indicates a metallic contribution as well, for instance modes assigned to Al-compounds. It is likely that a small fraction of metal atoms is not bound to other molecules. In Fig. 6.24 a), a small metal sphere is illustrated,
which was actually extracted from a grain of EloMinit. Fig. 6.24 b) and c) also show metal traces on some grains, where some in Fig. 6.24 c) actually look like traces of gold.

Related to the structures observed in Fig. 6.24, another effect which might contribute to the observed slopes from the OPA 8 40/100-65 and EloMinit sample is Mie scattering. By looking at Fig. 6.24 e) and f), small particles in the size of the wavelength and above can be identified on the grains’ surfaces, leading to Mie scattering. This type of scattering exhibits stronger scattering in forward direction. However, for the observed small range of wavelengths, the effect should be rather wavelength-independent and weaker than the effects discussed earlier.

In order to find out whether Mie scattering effects from the fine surface structures lead to the observed negative slope, we put grains of EloMinit into a home-built ball mill. Several iterations were performed and after each iteration, a stack of the grains was measured with our grating spectrometer. Fig. 6.25 displays the resulting reflectance factor. The absolute values of the reflectance factor decreases after each iteration\(^\text{19}\) (Fig. 6.25 a)). From the normalized curves in Fig. 6.25 b), it is shown that the slope stays rather constant, even after several polishing iterations. Thus, we exclude that Mie scattering as mechanism for the negative slope of the reflectance factor.

![Graph showing reflectance factor vs wavelength for EloMinit after different iterations of polishing.](image)  

**Figure 6.25:** Reflectance factor of an EloMinit stack after several iterations of polishing. The absolute signal decreases after each iteration, however, the slope stays rather constant.

\(^{19}\)After each iteration, the grains were cleaned with water in order to remove the dust from the grains.
Pellet investigations: negative slope only for diffuse OPA 8 40/100-65 and EloMinit

Figure 6.26: Comparison of the mainly diffuse, wavelength-dependent reflectance factor between the samples with macroscopic surface roughness (asphalts and raw material) a), d), g), and j) (−20° geometry) and the pellets b), e), h), and k) for different incident θi and observing angles θe (θi = θe, diffuse for |θi| > 0°). In the third column, the results for the pellets are normalized to the lowest observed wavelength. The first row are results for the AC 11 DS 50/70, the second row for AC 14 surf 35/50 (new), the third row for the OPA 8 40/100-65, and the last row for the EloMinit sample.
Figure 6.27: The same illustration as Fig. 6.26 but with angle-dependent results from the macroscopic samples instead of the pellets. Results in a), d), g), and j) are measured with the −20° geometry at different spots on the surface and the results in b), e), h), and k) one spot for different incident θ_i and observing angles θ_r (θ_i = θ_r). In the third column, the angle-dependent results are normalized to the lowest observed wavelength. The first row are results for the AC 11 DS 50/70, the second row for AC 14 surf 35/50 (new), the third row for the OPA 8 40/100-65, and the last row for the EloMinit sample.

The EloMinit, as well as the OPA 8 40/100-65 pellet exhibit a positive slope in the NIR region of the FTIR measurements (specular direction). Even though
bitumen leads to a positive slope, independent of the measurement geometry, it is not the mechanism for the positive slope in broadband measurements with the FTIR spectrometer. Otherwise, EloMinit would not exhibit a similar behavior as OPA 8 40/100-65. The FTIR spectrometer analyzes the specular reflection at 0°. Since the surface of the pellets is quite flat, the contribution of multiple surface scattering to the overall diffuse signal is small. Thus, the signal into the specular direction is dominated by specular reflection, with a “background” signal caused by volume scattering. From this consideration, we can study the hypothesis whether the negative slope might be a feature from volume scattering.

The AC 11 DS 50/70 and AC 14 surf 35/50\textsuperscript{20} pellets exhibit a positive slope for all diffuse measurements between 0° and −20° (see Fig. 6.26 b) and e) respectively). By multiplying the spectra with a constant factor, it gets obvious that both show an increasing slope with increasing angle (see Fig. 6.26 c) and f)). For the OPA 8 40/100-65 and EloMinit pellet, the results for the wavelength-dependent reflectance factor exhibit a positive slope at 0° and a rather flat curve at −5° (see Fig. 6.26 h) and k) respectively). For a further increasing of the angle with respect to the surface normal, the slope finally gets negative. The flat spectra at −5° must be the result of a mixture between diffuse and specular signal caused by the relatively large spot dimensions of L7M7. By multiplying the spectra from the OPA 8 40/100-65 and EloMinit pellet with a constant factor, the slope clearly gets more negative with increasing the angle, illustrated in Fig. 6.26 i) and l) respectively. This is the opposite trend compared to the AC 11 DS 50/70 and AC 14 surf 35/50 pellet.

As a comparison, Fig. 6.27 shows the same plot as Fig. 6.26 but with angle-dependent results from the asphalt samples instead of pellets. Interestingly, the normalized curves do not exhibit any change in the slope at all. Only the absolute values are slightly affected by the different angles ($\theta_i = \theta_t$). The macroscopic surface roughness leads to a broadening of the specular part, thus to a very weak contribution into a specific direction. This result supports the hypothesis that the negative slope is caused by the volume scattering of the sample.

Depending on whether the absorption of the material (imaginary part of the effective refractive index N) is stronger at lower or higher wavelengths, would explain why two different trends can be observed, for the different asphalt materials. This would mean that the furnace slag-based material has stronger absorptions at high wave-

\textsuperscript{20}Even though it is made from the AC 14 surf 35/50 (new) asphalt, it is simply called AC 14 surf 35/50 because after pressing, the surface does not consist of a closed bitumen coating.
lengths, while for moraine-based materials, stronger absorptions appear at lower wavelengths.

The spectra in specular direction are dominated by single scattering events (pellets), where the wavelength-dependent reflectance factor is mainly determined by the change of the complex refractive index \( N \) at the air-to-asphalt interface. Assuming a signal solely from multiple surface scattering, the absolute signal varies, but the relative shape stays positive, because it is a product of multiple reflection events due to a rough surface. Therefore, multiple surface scattering alone would result in an even more positive slope and volume scattering (determined by the change of \( N \) at different material-to-material interfaces) is needed to explain the negative slope. For validation of this theoretical view, the next part provides results from asphalts with larger void and surface roughness; thus from samples with more surface scattering.

**Void content and overall surface structure: slope trend**

Asphalts with larger surface roughness possess stronger multiple surface scattering. If an enhanced surface scattering leads to a negative slope, the slope should change by increasing the surface roughness.

In Fig. 6.28, results of wavelength-dependent reflectance factor measurements are presented for different spots on specifically produced asphalt samples. These samples are not utilized in roads in the available composition. They represent three different types of asphalt in terms of void content (related to the surface roughness \( R_t \)). For each type, one sample was made mainly of furnace slag and one completely of moraine material. Interestingly, spectra from the bare furnace slag asphalts do not show any negative slope; they are quite flat but possess still a positive slope. This is clearly different from the OPA 8 40/100-65 sample (see Fig. 6.26 g)), even though the grains in the samples have the same size (8 mm) with comparable void content (OPA 8 40/100-65: \( R_t = 3.4 \text{ mm} \)). If the absorption of the bulk material alone causes the negative slope, then the only explanation for the positive slope is that the chemical composition of the used furnace slag varies a lot, compared to the OPA 8 40/100-65 and EloMinit samples.

Compared to their moraine counterpart, the absolute reflectance factor is much smaller, especially for the ones with larger void contents (see Fig. 6.28 c) and e)). The AC 8 DS (FS/KsESP) 50/70 sample has still quite high reflectance factor values, because furnace slag is only one part of the composition, beside the typically
Figure 6.28: Wavelength-dependent reflectance factor from specially produced asphalt samples, which are not utilized in roads. They represent three different types. Each one made once out from furnace slag (FS) and once from double-crushed chips (KsESP) from moraine material, with the exception of the AC 8 DS (FS/KsESP) 50/70 which consists of a mixture from both. The AC 8 DS 50/70 samples possess the lowest void content (corresponding to the smallest surface roughness $R_t$).

moraine part. That is also the reason why it is the only furnace slag-based asphalt exhibiting the OH absorption at $\sim 1410$ nm, which originates from moraine grains.
In total, a higher void content is not leading to the negative slope in the reflectance factor; it only varies the absolute values slightly with a trend to less signal for increasing void content.

Conclusion: mechanism for the negative slope

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Experiment</th>
<th>Result (slope)</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen</td>
<td>Investigating the raw material</td>
<td>positive</td>
<td>No</td>
</tr>
<tr>
<td>Mie scattering</td>
<td>Polishing EloMinit grains</td>
<td>stays negative</td>
<td>No</td>
</tr>
<tr>
<td>Specular reflection</td>
<td>Asphalt at large incident angles, and pellet at small incident angles: specular observing direction</td>
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<td>No</td>
</tr>
<tr>
<td>Surface scattering</td>
<td>Increase void content</td>
<td>positive</td>
<td>No</td>
</tr>
<tr>
<td>Volume scattering</td>
<td>Asphalt at large incident angles, and pellet at small incident angles: off-specular observing direction</td>
<td>negative</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 6.4: Overview about the experiments regarding the negative slope in the reflectance factor.

Tab. 6.4 summarizes our tests in order to find the mechanism which causes the negative slope in the reflectance factor for the OPA 8 40/100-65 asphalt. Compared to other asphalts, it has a very high void content with a surface roughness of $R_t = 3.4$ mm. Experiments on specifically produced EloMinit-based asphalts with different void contents and surface roughnesses did not show any negative slope. Due to their roughness, they possess a strong surface scattering, thus, surface scattering as mechanism for the negative slope can be excluded.

A closer look into the involved raw materials showed that bitumen provides a positive slope in specular as well as in diffuse direction, leaving the material EloMinit itself as possible origin. Even though the surface of the EloMinit grains possess surface structures where Mie scattering can appear, it was excluded as mechanism for the negative slope by polishing the surfaces of EloMinit grains.

OPA 8 40/100-65 exhibits only a positive slope for large incident angles and in specular direction. Its pellet, with its smooth surface even shows a positive slope at small incident angles and in specular direction. All off-specular observing angles revealed a negative slope.
In total, only volume scattering can explain the negative slope, where in the NIR the material absorbs stronger at larger wavelengths than at shorter ones, which seems to be vice versa compared to the moraine based asphalts\textsuperscript{21}.

### 6.4 Chapter summary

In this chapter, we investigated dry “microscopic” (pellets) and “macroscopic” (asphalts) samples.

**“Microscopic” pellet measurements:** From optical broadband investigations, it was shown that the optical features of asphalt are mainly determined by CaCO\textsubscript{3}, SiO\textsubscript{2}, and bound –OH molecules. The low frequency regime is probably dominated by inorganic, diatomic molecules, consisting of one metal and one halogen atom. In addition, the investigated EloMinit pellet exhibits a Drude-like behavior in its low frequency regime, indicating a higher metal content. The NIR region exhibits nearly no optical feature, which enables this frequency range to be a perfect choice for measurements where the asphalt acts as a substrate.

From the Kramers Kronig analysis of the pellets’ broadband reflectivity we get an effective refractive index for asphalt of $n \approx 1.5 \pm 0.3$. For a better Kramers Kronig analysis of the data, we extended the range to higher frequencies via ellipsometric measurements. However, the diffuse reflecting properties and remaining surface roughness of the pellets could not increase the accuracy of the determined complex refractive index of our pellets.

From scatterometry measurements on the pellets, we were able to show that volume scattering contributes to the overall signal; for the EloMinit pellet, internal absorptions caused by the high metal content suppress this type of scattering.

**“Macroscopic” asphalt measurements:** For measurements on the macroscopic asphalt samples, we determined a minimal spot size and FOV (at least twice the diameter of the main grain size) which should be used in order to average over the surface roughness and different grain materials, otherwise the measurement results are to specific too some of the grains within the sample. Optical simulations and

\textsuperscript{21}Since the chemical composition of EloMinit varies strongly, no negative slope appeared from the specifically produced samples (see also the FIR region between OPA 8 40/100-65 and EloMinit pellet).
measurements showed that the combination of illumination spot and FOV size affects the angle-dependent intensity of a Lambertian scatterer. Therefore, only for $L < M$, the non-normalized angle-dependent signal is well described by Lambert’s cosine behavior.

From a systematic study of the reflectance factor for various types of asphalt samples, a correlation was shown between the age of the asphalt and the absolute values of the reflectance factor. From the untreated to the actual used samples, the absolute values increase. The NIR slope in the reflectance factor is very similar for almost all investigated asphalt types. This property is very important for a type-independent analysis of the data. Only the OPA 8 40/100-65 asphalt sample displays a negative NIR slope in the reflectance factor. The curvature in the reflectance factor for the AC types (made of moraine) decreases with increasing age of the sample.

While NIR scatterometry measurements on the pellets lead to a broad specular peak, the same measurements on the macroscopic asphalt samples cannot detect such a peak, which is caused by their surface roughness. For the macroscopic samples, their optical behavior is well described by Lambert’s law for incident angles between $\pm 40^\circ$ and observing angles between $\pm 50^\circ$. Only for larger incident angles, a tendency towards forward scattering develops. For some of the asphalts, even the polarization opposition effect [160] as well as the opposition effect [69] could be resolved. The simulated BRDF of rough grounds exhibit good results for small incident and intermediate observing angles. However, since each facet contains only the property of a perfect Lambertian scatterer and no refractive index, the simulation is not capable to mimic the enhanced forward scattering for larger angles as well as the enhanced backscattering at small phase angles.

**Comparison between microscopic and macroscopic results:** From the direct comparison of results between pellets and macroscopic asphalt samples we conclude that the optical properties of the material itself are well described by Lambert’s law for small incident angles, indicating volume scattering. For larger incident and observing angles, single scattering events get more prominent, leading to a stronger deviation from Lambert’s law at the macroscopic asphalt samples.

By this comparison, we also concluded that the origin of the negative slope in the reflectance factor from the OPA-8 40/100-65 asphalt is most probably related to volume scattering, thus from its material property of EloMinit.


7 Water-covered asphalt

In this chapter, results from liquid water measurements are presented and discussed. It starts with an explanation why the measurements are not performed with the $0^\circ$ geometry and continues with the discussion about the optical features of liquid water. It will be shown that the presented measurement technique is feasible to determine the imaginary part of the complex refractive index $N$ from water. Measurements are compared to simulations and at the end, a short section provides an overview about the optical features of leaves in the NIR. Some of the results are already published in Ref. 194.

7.1 Characteristics

7.1.1 Measurements with $0^\circ$ geometry

The most simple way to measure with a sensor is at $0^\circ$ incident and observing angle. At this geometry, p- as well as s-polarized light is transmitted and reflected the same way. Additionally, in the previous chapter, it was already shown that asphalt behaves close to a Lambertian scatterer for small incident angles.

In Fig. 7.1 a), a simplified sketch of the light path is provided for this kind of geometry and a water-asphalt system. Light which passes the lens diverges depending on the fiber diameter, distance between fiber and lens, as well as the lens parameters. It reaches the liquid water surface, where the minor part is reflected and the major one transmitted according to Fresnel’s equations and Snell’s law. The lens of the detector is located close to the one for illumination, at roughly the same zenith angle\(^1\). One part of the reflected light on the water surface is collected by the lens of the detector, containing information about the complex refractive index $N$ of water. The transmitted part is attenuated by the imaginary part $\kappa$ of the

\(^1\)Only a small angle of $\sim 4^\circ$ zenith at $90^\circ$ azimuth separates them, see Sec. 4.3.3.
Figure 7.1: Sketch of the light paths for a water layer on top of asphalt a) and the resulting optical spectra b) and c) for the 0° geometry. In a), light (red arrow) reaches the water layer surface, it gets reflected (dark red arrow) and transmitted (red arrow). At the ground, the light gets reflected back to the water surface and back to the detector (green arrows). Measurements for a water layer of 400 µm ± 100 µm are shown for L20M20 b) and L40M40 c) at different spots on the AC 11 DS 50/70 sample.

Figure 7.2: Water layers on top of an aluminum plate for the 0° geometry. For thick water layers, the offset caused by the surface reflection on water is clearly visible and indicated by the double arrow.
complex refractive index $N$ of water. At the ground, the light is reflected back\textsuperscript{2} to the water surface and gets attenuated further. At the interface water to air, most of the light is transmitted, while the rest is reflected back to the ground, contributing to multiple reflections between asphalt and water surface.

In Fig. 7.1 b) and c), the resulting wavelength-dependent reflectance factor from different spots with L20M20 and L40M40 geometry, respectively, are provided for a water asphalt system. In both cases, the water layer thickness is around $400 \mu m \pm 100 \mu m$, depending on the measured spot on the surface. Most of the spectra in Fig. 7.1 b) are located around unity and rather wavelength-independent\textsuperscript{3}. The latter property is also valid for the spectra in Fig. 7.1 c), however, most of the spectra are between a reflectance factor of 1.25 and 1.5 (more to this later on page 142). In both cases, around 1400 nm the reflectance factor exhibits a slight kink and lower values. Additionally, the spectra are quite noisy in this wavelength range.

In the previous section, it was already shown that an OH absorption leads to a dip around 1410 nm. For liquid water, this absorption is expected at 1450 nm. However, even though the water layer thickness is $400 \mu m \pm 100 \mu m$, the absorption in the spectra is developed much weaker than expected on first view. The chosen illumination and observing geometry (0°) can be identified as root cause for this: The signal gained from the water surface is the incident intensity times the reflectivity. For a water surface the reflectivity is 1.98\% at 840 nm and 1.84\% at 1600 nm [25]. This signal from the surface reflection does not possess the characteristic absorption features, which are only seen in transmission measurements. Still, roughly 98\% of the incident intensity is transmitted into the water, which contains the absorption features after leaving the water sample.

However, asphalt absorbs and diffusely scatters light, thus, its reflected intensity into a small solid angle is much lower than the fraction reflected directly at the water surface. Let us quantify this in more detail:

The dry spectra are all normalized to the optical response of a Zenith Polymer standard. At the given illumination and observing geometry, such a standard exhibits a reflectivity (normalized to a gold mirror) of only $\sim 0.3\%$ (see Fig. A.12)\textsuperscript{4}. I. e. for an asphalt sample, the reflectivity is only $\sim 0.03\%$ or even lower. In a simplified

\textsuperscript{2}This is simplified. In reality, the light gets diffusely reflected by surface and volume scattering effects.

\textsuperscript{3}The specular reflection of a mirror (for instance gold) is higher than for the reference white standard (WS): $R_s(\text{mirror}) > R_s(\text{WS})$, while the (diffuse) reflectance of the WS is roughly equal to the specular reflection of the mirror: $R_d(\text{mirror}) \approx R_d(\text{WS})$.

\textsuperscript{4}This value further depends on the spot sizes and alignment.

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consideration for a single ray, the intensity which contains directly the absorption feature is only

\[ I_{\text{absorption}} \approx 0.98 \cdot 0.0003 \cdot e^{\frac{4\pi n}{\lambda} \cdot 2d} = 2.49 \cdot 10^{-4} \cdot e^{\frac{4\pi n}{\lambda} \cdot 2d}. \]  

(7.1)

Thus, the intensity from the water surface is between one and two orders of magnitude larger than the part which contains the absorption features. Therefore, the absorptions are barely visible in the spectra. The strong intensity variations of the spectra are most probably caused by a wavy pattern of the water surface. In order to measure the different spots, the box containing the asphalt sample and water has to be moved. Depending on the delay between moving the box and the moment of measurement, these wave patterns have a stronger or lower amplitude and orientation, causing different incident angles as well as focusing or defocusing patterns with respect to the detector. Depending on the orientation, more or less specular reflected light from the water surface is collected by the detector. From optical simulations of a perfect flat water surface, the collected intensity should decrease with an increasing spot size at one single observing angle (see Fig. 7.8), as the larger the spot, the higher the fraction of specular light which is not collected by the detector. However, the water surface is never perfectly flat due to weak vibrations of the ground and setup. The resulting wavy water surface causes a somehow time-dependent specular reflection at angles ≠ 0°. Additionally, there is a small angle of 4° zenith at 90° azimuth. Both leads to a slightly higher signal for the L40M40 geometry, due to the larger detection spot.

In order to prove that the diffusely scattering asphalt causes the weakly developed absorption features, the same measurement—with 0° geometry—is repeated, with an unpolished aluminum plate as substrate (instead of asphalt). The aluminum plate has a strong reflection, thus, the signal containing the absorption information should contribute stronger to the total signal. In Fig. 7.2, the wavelength-dependent reflectance factor is illustrated for this measurement. Already the dry signal exhibits values five to twelve times (depending on the wavelength) larger than the reference standard itself. For all water layer thicknesses, the water absorptions are clearly visible. Between the thicknesses 1100 µm and 1850 µm, the reflectance factor does not change anymore at wavelengths around 1450 nm. Here, the signal is already very close to zero due to the absorption and only the offset, which results from specular reflection of the water surface is left. Thus, the experiment with the aluminum plate
verifies our explanation why the $0^\circ$ geometry is not suitable to measure water layer thicknesses on asphalt.

### 7.1.2 Measurements with $-20^\circ$ geometry

![Figure 7.3: Simplified sketch of the light paths in case of a water layer on top of asphalt and the resulting optical spectra b) and c) for the $\theta_i = -20^\circ$ geometry. In a), light (red arrow) reaches the water layer surface, gets reflected (thin red arrow) and transmitted (red arrow). At the ground, the light gets diffusely reflected. It reaches again the water surface where some part is transmitted (green arrow) and another reflected (dashed arrow). Results for a water layer of $400 \mu m \pm 100 \mu m$ are shown for L20M20 b) and L40M40 c) at different spots on the AC 11 DS 50/70 sample. No specular reflection from the water surface is collected by the detector.](image)

In order to bypass the signal from specular reflection on the water surface, a small zenith angle of $-20^\circ$ is chosen\(^5\). At this angle of incidence, the reflectivity of the water surface is still very low and the difference between both polarization directions is quite small\(^6\). Fig. 7.3 a) illustrates a simplified sketch of the light paths for the $-20^\circ$ geometry. Like before, light which reaches the interface air to water is

---

\(^5\)In more detail: The whole lens holder is tilted in zenith direction by $-20^\circ$. The illumination lens has an additional angle of $\sim 4^\circ$ perpendicular to the tilting.

\(^6\)At 840 nm: $R_s = 2.38\%$, $R_p = 1.61\%$ and at 1600 nm: $R_s = 2.22\%$, $R_p = 1.5\%$ [25].
reflected specularly and refracted. This time, no fraction of the reflected part is collected by the detector, even for large spot sizes. The refracted part is diffusely reflected at the ground and follows the same description as for the 0° geometry. It is worth mentioning that especially for thin\(^7\) water layers on top of substrates with high reflectance, multiple scattering has a non-negligible impact and can enhance the signal. For typical asphalt samples, multiple scattering provides only a minor contribution.

Fig. 7.3 b) and c) displays the results for spot size geometries of L20M20 and L40M40 respectively. The presented spectra are for the same spots on the asphalt surface as the ones previously in Fig. 7.1 at the 0° geometry. The water layer thickness is also the same with 400 µm ± 100 µm. Now, the absorption due to the bulk water is clearly visible. There is no contribution of specular reflection from the water surface; thus, the wavy pattern of the water surface does not disturb the measurements. Another evidence for the absence of specular reflection can be seen from the spectra with higher layer thickness (see Fig. 7.4): The signal reaches almost 0 at wavelengths around 1450 nm, thus, no offset signal occurs. Additionally, the resulting reflectance factor from both spot size configurations exhibit the same values within the measurement accuracy. The spectra from the L40M40 configuration are a little bit more noisy compared to the L20M20 configuration, because the SNR gets worse for bigger light spots.

Summing up, for reliable measurements on a diffuse reflecting multilayer system with the goal to investigate the absorptions of the upper medium, a geometry of 20° is advisable, while a geometry of 0° should be avoided. Depending on the polarization state, larger angles might be advantageous for incident p-polarization, because the transmission of the upper layer increases in this case. However, at a certain angle, the light will be trapped inside the medium due to the total reflection angle at the water-to-air interface; thus, no or barely any signal will be received. This also means, theoretically and depending on the polarization state, there exists an optimum incident angle with respect to maximum signal.

\(^7\)If the water layer is thin and the light spot relatively large, light which is totally reflected at the water to air interface reaches the ground again within the FOV of the detector.
7.2 Theoretical and observed absorption modes

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<th>$v_1$</th>
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<th>$v_3$</th>
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<th>Solid (nm)</th>
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<td>0</td>
<td>871</td>
<td>868</td>
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Table 7.1: On the basis of a harmonic oscillator, theoretically possible overtones and combination bands located in the NIR region. Calculations are based on the values presented in Tab. 2.1. In general, the higher the order of overtone, the weaker its influence on the spectra. Many overtones and combination bands are closely located to each other, which probably leads to an enhancement of the respective optical feature. Values to the left of the | are calculated from fundamental modes of Ref. 118 and to the right from Ref. 7.

Before the observed absorption features from the spectra are discussed, the theoretically possible modes within the NIR are calculated and noted in Tab. 7.1, with the upper three being the most prominent ones. For the calculations, we used the harmonic oscillator model, which is known to be accurate for the lower orders of overtones and combinations bands, while for higher ones it slightly deviates from the more accurate anharmonic oscillator model. Since we are more interested in
the lower orders, the model is sufficient for our needs and provides a good overview where higher orders are likely to be located. One can see that many of the overtones

Figure 7.4: Wavelength-dependent reflectance factor for several water layer thicknesses on top of the AC 5 DL 70/100 a) and LOA 5 DS 25/55-55 b) sample. In b), the spectra with the gray background represent the layer thicknesses where the asphalt is fully covered by water, without the appearance of water islands caused by the surface tension.

Table 7.2: Observed locations of the minima in the reflectance factor measurements for water. The minima \( \nu_{2m} \) and \( \nu_{3m} \) are located very close together and sometimes it is hard to distinguish them. Values are provided in frequency (cm\(^{-1}\)) and wavelength (nm).

<table>
<thead>
<tr>
<th>State</th>
<th>( \lambda_{1m} ) (nm)</th>
<th>( \nu_{1m} ) (cm(^{-1}))</th>
<th>( \lambda_{2m} ) (nm)</th>
<th>( \nu_{2m} ) (cm(^{-1}))</th>
<th>( \lambda_{3m} ) (nm)</th>
<th>( \nu_{3m} ) (cm(^{-1}))</th>
<th>( \lambda_{4m} ) (nm)</th>
<th>( \nu_{4m} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
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<td>1155</td>
<td>8658</td>
<td>1199</td>
<td>8340</td>
<td>1450</td>
<td>6897</td>
</tr>
</tbody>
</table>

and combination bands possess similar energies (located at the same wavelengths), which might be the reason why the absorption features are particularly pronounced in the NIR region.

The optical spectra for dry asphalts and several water layer thicknesses are illustrated in Fig. 7.4. For a first overview, the results for the AC 5 DL 70/100 sample in Fig. 7.4 a) focus on selected layer thicknesses, while a larger number of layer thicknesses for the LOA 5 DS 25/55-55 sample in Fig. 7.4 b) provide a better overview about the development of optical features. The largest surprise is the big jump between the wavelength-dependent reflectance factor of a dry spectrum and the spectrum resulting from a water layer thickness of 100 \( \mu m \). This jump cannot be explained by the absorption process. During his master thesis, Simon Amann showed...
that most of this jump is caused as the solid angle $\Omega_r$ of the scattered light on the ground, which contributes to the detected signal, gets reduced by the refraction at the water-to-air interface [21]. This process is illustrated in Fig. 7.5. For example, from an infinitesimal point on a surface, light is illuminated diffusely into the upper hemisphere ($\Omega_h = 2\pi$ sr). Only a small fraction of the diffuse light is collected by the detector. This fraction is represented by $\Omega_c$, i.e. the solid angle which is completely collected by the detector. In case of an additional water (or any other lucent layer) on top with $n_{\text{layer}} > n_{\text{air}}$, the cone gets bigger at the water-to-air interface, because light is refracted away from the surface normal. In order to keep a cone, which only illuminates the detector, the solid angle of the scattered light on the ground has to decrease to $\Omega_r < \Omega_c$. This corresponds to a reduction of the signal by $\sim 42\%$ [21].

![Figure 7.5: Sketch of the reduced solid angle $\Omega_r$ in a 3D and 2D representation (zoom). The refraction at the water-to-air interface leads to a distortion of $\Omega_r$ in a way that at the detector, the cone overlaps with $\Omega_c$, which is the solid angle for the dry case. The zoom shows the opening angle $\omega$ where this effect is better visible. The orange dashed lines are the normal vectors of the water surface.](image)

This calculation explains most of the jump between dry and wet, however, by comparing the values in Fig. 7.4 a), the jump is roughly about 60% at 850 nm, i.e., there must be a second effect. Most probably, the BRDF of the asphalt samples changes...
CHAPTER 7. WATER-COVERED ASPHALT

with respect to its angular dependency, because water penetrates inside the grains of asphalt, effectively changes its optical properties and affects the volume scattering. Additionally, the water-to-asphalt interface provides different results from Fresnel’s equations than for an air-to-asphalt interface (see also Sec. 7.4). However, measuring the BRF takes too much time for a wet sample. During this time, evaporation would continuously change the optical properties, especially when the water layer is very thin or completely soaked into the grains. Such a measurement might work in a room with very high humidity, where the evaporation process is suppressed. However, whether the measurement devices would work under these circumstances is questionable.

In Fig. 7.4 b), three layer thicknesses (two moist and the 100µm) are located within the jump described earlier. Due to the surface roughness, for such low layer thicknesses, the water layer is not fully closed. Some grains stick out and reduce the effective flat water surface, which is responsible for the reduced solid angle. Additionally, the surface tension of water leads to island formation. This means, even if all grains are wet, as long as they stick out of the closed water layer, there is some fraction within the spot size where the solid angle reduction is not fully developed. For all the water layer thicknesses within the gray area, the layer is closed; thus, the large changes at low water layers result not from absorptions, but from the change of the interfaces and their refraction properties.

As can be seen in Fig. 7.6, the reflectance factor for a single wavelength follows the exponential behavior of the Lambert-Beer’s law from Equ. 2.21 for closed layers, i.e. thicknesses ≥ 100µm. Due to the limited resolution of the utilized spectrometer, the values for the reflectance factor exhibit a kink at high thicknesses, when the signal gets too weak.

In the spectra of Fig. 7.4, the impact of some overtones and combination bands of the vibrational modes are clearly visible, which are noted in Tab. 7.1. The overtones and combination bands manifest themselves as minima in the reflectance factor spectra, which are actually caused by transmission through the bulk water (see Sec. 7.1.2). In Tab. 7.2, the positions of the minima λim (i = 1...4) are given. One of the most prominent features is located at λ1m, corresponding to the ν1 + 2ν3 overtone and combination band. The strongest feature λ4m is attributed to the ν1 + ν3 combination band. For layer thicknesses above approximately 700µm (depending on the reflectance of the substrate), no intensity is resolved anymore at the detector; this implies that water does not provide any detectable diffuse signal. Other overtones
and combination bands noted in Tab. 7.1 lead to a broadening of the absorption features. In the middle of the spectra, around 1200 nm, two features $\lambda_{2m}$ and $\lambda_{3m}$ are located very close together. Especially for thinner water layer thicknesses, the two features can be hardly distinguished from each other. From Tab. 7.1, they can be attributed to the combination bands $\nu_1 + \nu_2 + \nu_3$, $2\nu_1 + \nu_2$, and $\nu_2 + 2\nu_3$. Other overtones and combination bands of higher order might broaden the features slightly.

### 7.3 Absorption coefficient

In Sec. 2.10, some measurement techniques for obtaining the complex refractive index $N$ were already described. These techniques are relatively time consuming and extensive; thus, they are not suited to build up a big database in a short amount of time.

It was already mentioned that the measurements for gaining the reflectance factor basically correspond to transmission measurements of water. Therefore, from the results it is possible to calculate the imaginary part $\kappa$ of the complex refractive index and the absorption coefficient $\alpha$ of water. For this, only the intensities from
two different water layer thicknesses are needed\textsuperscript{8}. The layer thicknesses which are combined should be chosen that for the relevant wavelength range, the absorption bands are clearly visible, but not strong enough to suppress the signal below the spectrometer’s resolution. Their ratio via Lambert-Beers law (see Equ. 2.21)

\[
\frac{I(d_2)}{I(d_1)} = \frac{I_0 e^{-\alpha \cdot 2d_2}}{I_0 e^{-\alpha \cdot 2d_1}} \approx \frac{I_0}{I_0} e^{-\alpha \cdot 2d_2} I_0 e^{-\alpha \cdot 2d_1}
\]

(7.2)

combines the two layer thicknesses with their intensities. Here, \(d_m\) with \(m = 1, 2\) corresponds to the beam path distance through the water, with \(d_2 > d_1\). The pre-factor of 2 is necessary since the light passes the layer thickness twice, once from the air-to-water interface to the ground and once from the ground to the water-to-air interface. The approximation \(\cos(\theta_t) \approx 1\) is valid due to two reasons: On the one hand, for small angles like in the \(-20^\circ\) geometry, the cosine term from refraction is anyway \(\cos(\theta) \approx 1\). On the other hand, the uncertainty in the physical determination of the water layer thickness yields a stronger effect on the result than this approximation. From Equ. 7.2, the absorption coefficient is calculated via:

\[
\alpha = -\ln\left(\frac{I(d_2)}{I(d_1)}\right) \frac{2(d_2 - d_1)}{2(d_2 - d_1)}
\]

(7.3)

The results from measurements on the AC 5 DL 70/100 asphalt sample are provided in Fig. 7.7. Here, the calculated wavelength-dependent absorption coefficient from three different combinations of layer thicknesses are compared to the literature data from Kedenburg et al. [25]. The overall agreement is very good. Deviations from the reference data are only noticeable in the logarithmic scale in Fig. 7.7 b). For wavelengths between \(\sim 1300\) nm and \(\sim 1650\) nm, the absorption coefficient can be calculated with high accuracy at rather small layer thicknesses. The absorption of the \(\nu_1 + \nu_3\) combination band at 1450 nm is very strong. Therefore, already at intermediate layer thicknesses the reflected intensity can barely be resolved with the spectrometer, leading to a bad SNR and thus to a slightly deviating result of the absorption coefficient. For the same reason, small layer thicknesses exhibit deviating results for the absorption coefficient between 800 nm and 1300 nm. Here, the \(\nu_1 + 2\nu_3\)

\textsuperscript{8}\text{The actual water layer thickness is measured with a measurement comb for layers between 50 \(\mu\)m to 1 cm and a caliper for thicknesses > 1 cm. The less surface roughness, the more accurate the measured layer thickness.}
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Figure 7.7: Wavelength-dependent absorption coefficient $\alpha$ extracted from the reflectance factor for two different water layer thicknesses. For a better SNR, 2 s of integration time is used for the measurement. Same data once in linear a) and logarithmic scale b). The dashed line is the reference data from Kedenburg et al. [25].

(around 970 nm) and $\nu_1 + \nu_2 + \nu_3$ (around 1190 nm) combination bands affect the spectra weakly. Therefore, higher layer thicknesses lead to better results within this range.

In summary, with the utilized setup and analyzing method, very good results are achieved for the absorption coefficient of water. The measurements are done fast and do not need a precise alignment. Therefore, it is suited to build up a database in a short amount of time. The only important factor is a non-zero angle with respect to the surface normal in order to avoid any signal from specular reflection of the water surface. Small deviations from literature and different noise levels in the results originate from the limited resolution and SNR of the used spectrometer. Depending on the strength of the absorption features in the reflectance factor, the layer thickness of interest has to be chosen accordingly.

7.4 Simulation results

7.4.1 Simulations with 0° geometry

Results from simulations for the reflectance factor of water on asphalt are illustrated in Fig. 7.8. The figure corresponds to the measurement result displayed in Fig. 7.1 b) and c) for near-normal incident. While Fig. 7.8 a) and c) are results for L20M20, b)
Figure 7.8: Simulation results for the reflectance factor of 700 µm water layer thickness on asphalt for two different spot sizes and a $-4^\circ$ incident angle. In a) and b) the wavelength-dependent reflectance factor for L20M20 and L40M40, respectively. The observing angle-dependent reflectance factor for L20M20 and L40M40 is illustrated in c) and d), respectively. Surface roughness and reflectance factor values of the dry ground correspond to the AC 5 DL 70/100 asphalt sample. Dotted and solid lines are guides to the eye.

and d) illustrate results for L40M40. Each wavelength at the L20M20 configuration is simulated with $10^6$ rays$^9$, while $3 \cdot 10^6$ rays are used for the L40M40 configuration in order to increase the SNR. For both configurations, the incident angle is $-4^\circ$ and 700 µm of water are placed on top of a ground with 300 µm effective surface roughness$^{10}$, corresponding to 400 µm water level determined by our experimental

$^9$Each simulation is done twice: Once with perpendicular (s) and once with parallel (p) polarized light. From these results, the unpolarized result is determined via $R = 1/2(R_p + R_s)$.

$^{10}$Compared to the measurement, there is an offset in the water layer thickness. This offset yields from the way how the water layer thickness is measured in reality compared to the computed thickness. With the measurement comb and caliper, the zero level is close to the upper boundary
measuring method which refers to the asphalt surface. Every time when comparing results from simulations to measurements, such an offset has to be determined for each surface roughness.

The wavelength-dependent reflectance factor in Fig. 7.8 a) and b) is presented for observing angles between $-6^\circ$ and $6^\circ$. The results for an observing angle around $4^\circ$ ($\pm 6^\circ$) are affected by the specular lobe. The values are clearly enhanced, although not as enhanced as for the real measurements presented in Fig. 7.1. The reason for the lower values of the reflectance factor compared to the measurements is probably a wavy pattern of the water surface, as already discussed in Sec. 7.1.1. The observing angle-dependent reflectance factor in Fig. 7.8 c) and d) visualize the broadness of the specular lobes for both configurations. Interestingly, the L20M20 configuration exhibits lower values for $4^\circ$ than for $2^\circ$ and $6^\circ$. This is caused by the distance between lens and detector, causing a ring-like intensity shape and a less-intense center. Comparing the results for the L40M40 spot size, the simulation reveals that the bigger the illumination spot, the broader the specular lobe from the water surface. The total intensity of the area of the lobe stays always the same. This is also the case for a small spot size—for instance 1 $\mu$m—resulting in a sharp specular peak (see Fig. A.14).

### 7.4.2 Simulations with $-20^\circ$ geometry

In Fig. 7.9 a), raw results of the wavelength-dependent reflectance factor are presented from a simulation of several water layer thicknesses. For the simulation, each wavelength is computed with $10^6$ rays in the L20M20 and $-20^\circ$ (incident and observing angle) configuration. The ground possesses the surface roughness and reflectance parameters which correspond to the AC 5 DL 70/100 asphalt sample. Therefore, the results should match the ones presented in Fig. 7.4 a); two of the measured spectra shown there are also displayed in Fig. 7.9 b) (solid lines)\(^\text{11}\). The results for the dry case perfectly fit together. There is a clear mismatch between the wet measurements and simulations.

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\(^\text{11}\)The layer thicknesses from the measurements are adapted to the ones from the simulations because the latter ones consider the effective surface roughness (see Sec. 7.4.1).
**Influence of simulation dimensionality**

There are two possible reasons for the observed deviations: The first is the two-dimensional framework of the simulation. While in reality, it is the solid angle $\Omega$, which leads to a reduction of the detected intensity, in our simulations the reduction corresponds only to the opening angle $\omega_{\text{sa}}$ in two dimensions. Since their relation is not linear (see Eq. 2.55), the effect is not directly projected from the two-dimensional simulation to the real three-dimensional world. In Fig. 7.10 a), the solid angle is illustrated in dependence of the opening angle. As can be seen in the inset, the zoom into the interesting region for the performed simulation shows that even for a small angular range the relation is not linear.

In Sec. 7.2, it was already mentioned that the solid angle reduction leads to a signal which is only $\sim 58\%$ of the dry value. Fig. 7.10 b) displays the real wavelength-dependent behavior\textsuperscript{12} [21] which shows a variance of $\sim 1.3\%$. In general, the solid angle reduction is also dependent on the incident and observing angle, however, for a Lambertian ground, the cosine dependence cancels this effect, leading to an angular-independent influence.

The raw results from the 2D simulations for low water layer thicknesses are only

\textsuperscript{12}It is not possible to calculate this effect analytically. The shown results are from numerical calculations, which are compared to 3D-simulations, performed in Zemax by Simon Amann during his master thesis [21].
Figure 7.10: Solid angle as a function of the opening angle a) and its influence on the optical spectra determined for a closed water layer b). Data in b) are numerically calculated by Simon Amann [21].

Figure 7.11: a) Simulated 550 µm water spectrum (dots) after adapting the solid angle correction (open triangle) and the second influence factor (crossed triangle) compared to the measurement (solid line). b) The second influence and its linear fit ($y = m\lambda + b$). In a), the simulation results are shown before and after adaption of the second influence factor. After the adaption, the result is in very good agreement with the measurement. In b), the result for 550 µm of water from the measurement is divided by the one from the simulation (solid triangle) where only values between 850 nm and 1310 nm (gray area) are considered for the fit. The red line is the ratio between the measurement results for 400 µm and dry divided by the solid angle factor of 0.58. For low wavelengths, it is described by the same fit as the ratio of a water layer between measurement and simulation.
CHAPTER 7. WATER-COVERED ASPHALT

reduced by $\sim 25\%$ compared to the dry curve. The factor in $0.75 \cdot RF_{\text{dry}}$ is exactly the ratio of the opening angle between a dry condition and a water layer ($\omega_{\text{ratio}} = \omega_{\text{wet}}/\omega_{\text{dry}}$). In order to test the influence of the opening angle, all simulation results are multiplied by $\Omega_{\text{ratio}}/\omega_{\text{ratio}}$. This correction is illustrated for a layer thickness of 550 $\mu$m in Fig. 7.11 a).

**Second influence factor: BRDF change by surrounding water**

However, there is still a wavelength-dependent deviation between measurement and simulation, indicating a second influence factor. By dividing the reflectance factor from the measurement by the corresponding solid angle-corrected one from the simulation, a linear dependence is revealed. Such a ratio is shown exemplary for a layer thickness of 550 $\mu$m in Fig. 7.11 b). In order to perform this analysis, thin water layers should be utilized to avoid a strong influence of the absorption features on the spectra. For the same reason, the linear fit $y = m\lambda+b$ is only applied for wavelengths between 850 nm and 1310 nm. The resulting fit parameters are $m = 5.74 \cdot 10^{-4}$ nm$^{-1}$ and $b = 0.16$.

The origin of this factor is that penetrating and surrounding water changes the scattering and reflectance behavior of the asphalt, as already discussed in Sec. 7.2. The real part of the refractive index $n$ of water at 20 $^\circ$C varies between 1.3272 and 1.3142 [25] within the wavelength range between 850 nm to 1650 nm. These $n$ are closer to the value of asphalt$^{13}$ than air ($n = 1$), thus the resulting reflectivity from Fresnel’s equation is lower than expected for surrounding air.

It is also interesting to note that this second influence factor can be also derived from fitting the ratio between the wavelength-dependent reflectance factor from a thin water layer and the dry asphalt in a range which is barely affected by absorption lines. If one additionally considers the reduction of the solid angle via

$$\Xi = \frac{RF(400 \text{ nm})}{RF_{\text{dry}}} \cdot \frac{1}{0.58},$$

then the resulting curve is well described by the fit, illustrated in Fig. 7.11 b). Only the absorptions—which are not considered—lead to a deviation from the fit.

Unfortunately, this second influence is not ground-independent, since the composition of the asphalt strongly determines how water is able to penetrate inside the grains, thus, it determines how the scattering characteristic changes. Therefore, the

$^{13}$Depending on the fit between 1.3 and 1.55 (see Sec. 6.1.2 on page 104-106 f.).
fit should be adapted to the specific measurement in order to have a better agreement between simulation and measurement.

In order to validate the assumption of the reduced reflectance by surrounding water, a dense, black plastic board (Polyamide (PA) 66) with a flat surface was measured with the $-20^\circ$ geometry like the asphalt. The results for three different water layers and the dry curve are shown in Fig. 7.12. The spectrum for 150 nm is normalized to the spectrum of the dry board, indicating a decrease of the reflectance factor by $\sim 78.5\%$ at 850 nm compared to the dry board.

![Figure 7.12: Reflectance factor of a water-covered PA 66 board a) and the normalized 150 µm water layer to the signal of the dry board. The reflectance factor of a thin water layer decreases by $\sim 78.5\%$ at 850 nm compared to the dry board.](image)

The reduction of the solid angle has the same impact, independent of the ground material. Thus, the second influence factor has to be the one which causes the difference between PA 66 and asphalt. Considering the reduction of the solid angle, the second influence factor at 850 nm has to be $x = RF(150\, \text{nm})/(RF_{\text{dry}} \cdot 0.58) \approx 0.37$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\text{PA 66}$</th>
<th>$R_1$ air-to-PA 66 (%)</th>
<th>$R_2$ water-to-PA 66 (%)</th>
<th>$R_2/R_1$ (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>4.00</td>
<td>0.37</td>
<td>0.0925</td>
<td></td>
</tr>
<tr>
<td>1.55</td>
<td>4.65</td>
<td>0.60</td>
<td>0.1290</td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>5.33</td>
<td>0.87</td>
<td>0.1632</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.3: Resulting reflectivity for an incident angle of $0^\circ$ at 850 nm. For the calculations, the refractive index of air was set to $n = 1$ and for water literature data are used from Kedenburg et al. [25] with $n = 1.3272$ and $\kappa = 2.8003 \cdot 10^{-7}$. 
The refractive index in the visible for PA 66 is roughly between 1.5 and 1.6 [260, 261]. Since we did not find any literature data for the NIR region, we assume that the refractive index is similar at 850 nm. For checking how the reflectivity is affected as soon as the board is covered by water, we used Fresnel’s equations. In Tab. 7.3, the resulting reflectivity for the air-to-PA 66, water-to-PA 66 interface at 850 nm, and the ratio of the water-covered and the dry result are given. Even for $n = 1.6$, the calculated reflectivity is only half of the necessary second influence factor of 0.37. This is an interesting result, because it means that the effect from the interface alone would result in an even lower signal than observed. For the interface, the conservation of energy is $R + T = 1$, therefore, the transmission increases when the reflectivity decreases. This means that the intensity which is transmitted into the ground material is higher when the reflectivity decreases. One can speculate that this transmitted intensity could lead to an enhanced contribution of volume scattering, causing a higher reflectance. However, the anisotropic material could absorb a small amount of water, as every plastic does over time, leading to a different volume scattering behavior.

![Figure 7.13: Reflectance factor for the AC 5 DL 70/100 asphalt sample from the measurement (solid lines) and adapted simulation. After the adaption of the simulation results (solid angle and second influence factor), a good agreement is achieved between simulation and measurement.](image)

In order to achieve a comparison of the absolute values between measurement and
simulation, the resulting fit for the second influence factor (see Fig. 7.11) can be applied as a correction for all water layer thicknesses, as exemplarily shown for 550 µm in Fig. 7.11 a). Here, both, solid angle correction and the resulting fit were applied (which is the same for all layer thicknesses), leading to a perfect match between measurement and simulation. The corrections are performed after the simulations, however, since all of them are multiplicative factors, they could be already taken into account within the simulation for each single ray. For non-closed layer thicknesses, it is also possible to consider these corrections factors only for the rays, which come from the wet areas.

In total, with considering two additional factors, namely the reduced solid angle and changed BRDF of wet asphalt (the second influence factor), the simulation provides an excellent agreement with real measurements, as can be shown in Fig. 7.13, where results for the measured layer thicknesses from Fig. 7.4 a) are compared to the adapted results from the simulation.

Water layer-dependent reflectance factor

Interestingly, the relative behavior (jump and exponential behavior) for the reflectance factor—dependent on the layer thickness at a single wavelength—(see Fig. 7.14 a)) is in very good agreement to the results presented in Fig. 7.14 b)\textsuperscript{14}, even without applying any adaption of the simulation data. The results shown in Fig. 7.14 are fitted with following equation:

\[
RF(d, \lambda, \theta_i) = \begin{cases} 
\beta(\lambda, \theta_i) \cdot RF_{\text{dry}}(\lambda, \theta_i) \cdot e^{-\frac{2\pi n(\lambda)}{\lambda} \frac{d - (R_t - dR_t(\lambda))}{\cos(\theta_i(\lambda))}}, & d \geq R_t \\
\frac{(1 - \beta(\lambda, \theta_i))RF_{\text{dry}}(\lambda, \theta_i) + (\beta(\lambda, \theta_i) - 1)RF_{\text{dry}}(\lambda, \theta_i) \cdot d}{R_t}, & \text{else ,}
\end{cases}
\]

(7.5)

with the reflectance factor of the dry asphalt \(RF_{\text{dry}}\), the reduction factor \(\beta\) of the jump\textsuperscript{15} from dry to wet (see Sec. 7.2), the wavelength \(\lambda\), the water depth\textsuperscript{16} \(d\), the

\textsuperscript{14}The simulation is not limited by any instrument resolution, therefore, it is able to reach lower values than in the actual measurements.

\textsuperscript{15}Including the solid angle reduction and the second influence factor.

\textsuperscript{16}Measured from the lowest point of the deepest valley.
effective layer thickness $d_{R_t}(\lambda)$, the imaginary part of the water’s refractive index $\kappa$, and the angle of refraction $\theta_t$ which results from the incident angle $\theta_i$ in combination with Snell’s law (see Equ. 2.25). The cosine contribution considers the difference between the optical path length through the water and its vertical layer thickness $d$. The derivation of Equ. 7.5 can be found in Sec. A.3 on page 210.

From the logarithmic plots in Fig. 7.14, one can identify two different regions: For layer thicknesses up to $\sim 400$ nm ($R_t$), the reflectance factor decreases rapidly. Afterwards, it follows an exponential behavior. The latter part is determined by Lambert-Beer’s law and sets in as soon as the water surface builds a closed layer, meaning that the water height $d$ is larger than the surface roughness $R_t$. For these thick layers, the reflectance factor is simply described by the upper case of Equ. 7.5. The rough surface makes it necessary to modify the exponent of Lambert-Beer’s law with a negative offset of $R_t - d_{R_t}(\lambda)$, which results in the effective layer thickness $d_{R_t}$ when for $d = R_t$ all the water within the valley would be spread on a flat surface, leading to the equivalent signal as for the rough surface (see also Sec. A.3). For small absorption coefficients and surface roughnesses (up to several 100 µm) like in our case, one can set $d_{R_t}(\lambda) \approx R_t/2$ which simplifies Equ. 7.5 (see Equ. A.13).
The first case of Equ. 7.5 is only applicable for the areas which are completely covered with water.

For water levels below the surface roughness $R_t$, the detector collects a fraction of the dry and another fraction of the wet asphalt. The relation between dry surface and wet surface depends linearly on the water height $d$, which is described by the second case of Equ. 7.5. While, the second row of Equ. 7.5 describes this linear relationship, the bottom row is again Lambert-Beer’s law; the derivation of the exponent can be found in the Appendix in Sec. A.3.

In Fig. 7.14, the raw simulation results as well as results from measurements are shown to be well described by Equ. 7.5. Unfortunately, this equation is not continuously differentiable and has to be split up into two cases. A more empirical approach is Equ. 7.6:

$$RF(d, \lambda, \theta_i) = a(\lambda, \theta_i)e^{-\left(\frac{d}{b \cos(\theta_i(\lambda))}\right)^2} + c(\lambda, \theta_i)e^{-\frac{4\pi c(\lambda)}{\lambda \cos(\theta_i(\lambda))} \cdot d}.$$  \hspace{1cm} (7.6)

In this equation, the parameters $a$, $b$, and $c$ can be also assigned to specific properties of the samples as will be seen in the following:

As before, the second term of Equ. 7.6 is determined by Lambert-Beer’s law (see Equ. 2.21). The parameter $c(\lambda, \theta_i)$ is the reflectance factor of the wet asphalt sample for a layer thickness $\rightarrow 0 \mu m$, including the solid angle reduction and the second influence factor for all areas which are covered by water, i.e. when no absorption of the bulk water would influence the reflectance factor.
The first term of Equ. 7.6 corresponds to the fraction of signal which is detected from dry areas. It resembles a Gaussian distribution where the parameter $b$ is in the range of the surface roughness $R_t$. A flaw of this model is that the exponential part of the first term does not reach zero, meaning that even for $d > R_t$, a tiny fraction of the dry signal contributes to the overall signal. However, since the exponential term decreases fast with increasing layer thickness, the contribution is negligible for $d > R_t$. The advantage of this equation, it is continuously differentiable and does not need a division into two cases. Additionally, the parameters can be attributed to the physical properties of the sample.

The parameters $a$ and $c$ are independent from the water layer thickness and for $d \to 0$ the parameter $a$ results from $c$ and $RF_{dry}(\lambda, \theta_i)$ via $RF_{dry}(\lambda, \theta_i) - c(\lambda, \theta_i) = a(\lambda, \theta_i)$. In Fig. 7.15, the same data as in Fig. 7.14 are fitted with Equ. 7.6. Like Equ. 7.5, this empirical fitting function is able to describe the simulation as well as the measurement results with very good agreement.

### 7.5 Leaf-covered asphalt

![Figure 7.16: Wavelength-dependent reflectance factor for dry and wet leaves. The soaked leaves were put into water for several hours. The dashed lines are the observed positions of the minima from pure water given in Tab. 7.2.](image)

Figure 7.16: Wavelength-dependent reflectance factor for dry and wet leaves. The soaked leaves were put into water for several hours. The dashed lines are the observed positions of the minima from pure water given in Tab. 7.2.
CHAPTER 7. WATER-COVERED ASPHALT

Leaves are also a material which is often found on roads and causes accidents. Therefore, their optical response is also of interest. In Fig. 7.16, selected results for the wavelength-dependent reflectance factor are illustrated from dry, wet, and soaked leaves on top of the AC 8 DN 50/70 sample. Compared to Fig. 7.4, the same absorption features are observed within the leaf spectra. For the dry and wet leaves, the mode at 970 nm ($\nu_1 + 2\nu_3$) is not resolved. The reflectance factor of the soaked leaves—which were put into water for several hours—exhibits all water absorption features as the pure water spectra in Fig. 7.4. Thus, all three spectra resemble the water spectra significantly.

Since leaves consist mainly of water [262–264], this result is not astonishing. However, the overall absolute reflectance factor exhibits quite large values, which are even larger than for the dry asphalt samples. These high values can be attributed to two properties of the leaves. First, due to their internal structure, leaves are very good volume scatterer [265, 266]. Furthermore, the absorptions are rather weak in the low-NIR region [265], leading to a strong contribution of volume scattering. Second, the surface structure of some leaves—like the appearance of hairs [267]—increase the reflectance even further.

7.6 Chapter summary

In order to resolve the bulk absorption features of water, we showed that a non-zero incident angle (most of the time we used $-20^{\circ}$) is necessary, since results from an incident angle of $0^{\circ}$ are influenced too much by the specular reflection of the water surface.

In total, we resolved four absorption features for H$_2$O within the covered NIR range of our grating spectrometer: $\nu_{1m} \equiv \nu_1 + 2\nu_3$, $\nu_{2m} \equiv \nu_1 + \nu_2 + \nu_3 \wedge 2\nu_1 + \nu_2$, $\nu_{3m} \equiv \nu_2 + 2\nu_3$, and $\nu_{4m} \equiv \nu_1 + \nu_3$ (from lower to higher wavelengths). The prominent drop of signal for even very thin water layers is caused by a solid angle reduction of the signal, which reaches the detector due to the refraction at the water-to-air interface [21] and a second influence factor, described by a linear function. This second influence factor probably originates from a change in the scattering and reflection behavior due to penetrating water into the grains and the thus different transitions at the water-to-asphalt interfaces.

The simulation results have to be adapted to these two factors since they are not automatically covered by the two-dimensional simulation. If this is done, the simu-
lation results are in good agreement with the ones from measurements.
With our utilized measurement setup and analysis method, we were able to determine the absorption coefficient $\alpha$ of liquid water with high accuracy. The layer thickness-dependent reflectance factor can be well fitted with a theoretically derived equation (Equ. 7.5), taking the roughness of the asphalt samples into account as a fitting parameter. Additionally, we also provide a more simple, empirical fitting function (see Equ. 7.6), which describes the data also very well.
The spectra of leaves are dominated by water absorptions. However, compared to water alone, leaves exhibit much larger reflectance factor values, originating from their strong diffuse scattering behavior.
8 Ice-covered asphalt

In this chapter, results from ice-covered asphalt surfaces are presented and discussed. In the first section, the observed absorption features for the solid H₂O state are introduced and discussed. In the following section, a closer look into the freezing process is provided, continued by the discussion about the influence of enclosed air bubbles on the reflectance factor. As already presented for water, also results from simulations are presented and compared to measurements. At the end, optical features from icy leaves are shortly introduced and compared to water-ice spectra. Some of the results are already published in Ref. 194.

8.1 Observed absorption modes

![Graph showing reflectance factor comparison between water and ice-covered AC 11 DS 50/70 sample. Absorption features are marked with dashed lines and listed in Tab. 8.1.]

Figure 8.1: Comparison of the wavelength-dependent reflectance factor between a water and ice-covered AC 11 DS 50/70 sample. Absorption features are marked with dashed lines and listed in Tab. 8.1.
### Table 8.1: Observed locations of the minima in the reflectance factor measurements of ice. The values for water from Tab. 7.2 are given down for a direct comparison. Like for water, the minima $\nu_2m$ and $\nu_3m$ are located close together. $\Delta$ provides the difference between the states. Values are provided in frequency (cm$^{-1}$) and wavelength (nm).

<table>
<thead>
<tr>
<th>State</th>
<th>Water</th>
<th>Ice / Snow</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_1m$ (nm)</td>
<td>974</td>
<td>1030</td>
<td>56</td>
</tr>
<tr>
<td>$\nu_1m$ (cm$^{-1}$)</td>
<td>10267</td>
<td>9709</td>
<td>-558</td>
</tr>
<tr>
<td>$\lambda_2m$ (nm)</td>
<td>1155</td>
<td>1225</td>
<td>70</td>
</tr>
<tr>
<td>$\nu_2m$ (cm$^{-1}$)</td>
<td>8658</td>
<td>8163</td>
<td>-495</td>
</tr>
<tr>
<td>$\lambda_3m$ (nm)</td>
<td>1199</td>
<td>1256</td>
<td>57</td>
</tr>
<tr>
<td>$\nu_3m$ (cm$^{-1}$)</td>
<td>8340</td>
<td>7962</td>
<td>-378</td>
</tr>
<tr>
<td>$\lambda_4m$ (nm)</td>
<td>1450</td>
<td>1490</td>
<td>40</td>
</tr>
<tr>
<td>$\nu_4m$ (cm$^{-1}$)</td>
<td>6897</td>
<td>6711</td>
<td>-186</td>
</tr>
</tbody>
</table>

Temperature-dependent measurements on asphalt samples are performed with the modified freezer (introduced in Sec. 4.4). The setup enables insight into the optical response of the freezing process of water. Additionally, ice-covered (icy) as well as snow-covered (snowy) (see Ch. 9) samples can be investigated without worrying about the melting process.

In Fig. 8.1, a direct comparison between a water and ice spectrum illustrates the optical differences among these states. Compared to water, for ice, all absorption features $\lambda_{im}$—developed as minima in the spectra—shift to higher wavelengths. Tab. 8.1 provides the corresponding locations of absorption features.

For ice, a stronger contribution of hydrogen-bonding causes this shift to higher wavelengths. In the “frozen” structure of the molecules in their solid state, the hydrogen-bonding weakens the covalent OH-bonding, thus, mainly affecting the two fundamental stretching vibrations $\nu_1$ and $\nu_3$ (compare Tab. 2.1). In contrast, the fundamental mode $\nu_2$ is only weakly affected and stays nearly constant at the same frequency (see Tab. 2.1). The higher the energy location of the mode, the less shift occurs, causing that the features $\nu_2m$ and $\nu_3m$ nearly overlap for the ice spectra. Basically, they can only be distinguished for very thin ice layers.

In the ice spectrum at 1361 nm and 1380 nm, small peaks can be identified. These peaks are artifacts caused by less humidity within the freezer compared to the starting condition:. The reference (WS) is measured at room temperature at a certain humidity level. When the freezer gets cold, most of the humidity freezes out at
its inner walls, resulting in these two absorption peaks when building the ratio (reflectance factor).

Besides the horizontal shift of the absorption features, the whole curve is shifted upwards to larger reflectance factor values. This latter shift is caused by the inclusion of air bubbles and is discussed in more detail in Sec. 8.3. At this point, it should be mentioned that the investigated water was neither degassed nor demineralised, in order to mimic outside conditions.

8.2 Freezing process

![Graph](image)

Figure 8.2: Wavelength-dependent reflectance factor during a freezing process of a roughly 3 mm thick water layer on top of AC 11 DS 50/70 (core) a) and the corresponding temperature dependent on time b). In a), the two dashed lines highlight spectra which are within the freezing process, where the state is a mixture of liquid water and ice. The water is supercooled to $-4.5\, ^\circ\text{C}$, before the freezing process starts.

Exemplary results of the wavelength-dependent reflectance factor during a freezing process are presented for selected temperatures in Fig. 8.2 a). The initial layer thickness is $\sim 3.3$ mm at 20°C.

The first changes in the spectra can be assigned to evaporation (see also Fig. 8.3), as can be proven by directly comparing the time-dependent reflectance factor for room temperature with that of a cooling run (see Appendix in Fig. A.18). Thus, the spectra gain higher reflectance factor values, because with increasing time less water is on the sample. The rate of evaporation is estimated from Fig. A.18 with roughly 2 $\mu$m/min; thus, right before the phase transition, about 3 mm of water re-
Figure 8.3: Time-dependent reflectance factor of three selected wavelengths for the cooling process shown in Fig. 8.2. The dashed lines represent the start and end of the freezing process. These two particular points are characterized by the same temperature $T_1 = T_2$. The continuously growing reflectance factor for times $> 250$ min originates from an increasing amount of cracks within the ice, caused by increasing tension with lowering the temperature. These cracks lead to an offset at all wavelengths due to specular reflection.

...
In general, no explicit temperature dependence of the reflectance factor can be resolved\(^1\) from Fig. 8.2 and 8.3. Most of the changes are dominated by evaporation for temperatures \(> 0 \, ^\circ\text{C}\) and cracks for \(< 0 \, ^\circ\text{C}\). For a larger temperature range, one would observe a temperature-dependent shift and narrowing of the absorption features [271]. For example, Grundy \emph{et al.} showed that the peak in the absorption coefficient (corresponding to \(\lambda_{4\text{m}}\)) shifts from \(\sim 1490 \, \text{nm}\) to \(\sim 1510 \, \text{nm}\), when cooling the ice from 270 K to 20 K [271]. This corresponds to a horizontal shift of \(\sim 0.08 \, \text{nm/K}\), which is only 1.2 nm for a temperature range of 15 K and thus, below the resolution of our grating spectrometer (see Sec. 4.3.1).

### 8.3 Influence of air bubbles on the optical spectra

![Sketches for two different configurations of air bubble formation](image)

Figure 8.4: Sketches for two different configurations of air bubble formation with \(\theta_i = -20^\circ\). In a), the air bubbles are distributed homogeneously between the ground and the ice surface. In b), air bubbles occur only close to the ground.

In this section, the previously mentioned effect of embedded air bubbles within the ice layer is discussed in more detail. Fig. 8.4 provides two sketches with different

\(^1\)With an FTIR spectrometer and better resolution, one should be able to resolve a temperature effect even for the observed temperatures. Here it should be also possible to investigate the quasi-liquid layer which is—depending on the temperature—very thin and normally between several nm up to roughly 100 nm [268–270].
Figure 8.5: Wavelength-dependent reflectance factor for two different configurations of air bubble formation. In a), results from the AC 11 DS 50/70 sample are illustrated for a 3 mm thick ice layer. In this case, air bubbles are distributed rather homogeneously. In b), results from the SMA 8 LA 40/100-65 A sample for a 2.3 mm thick ice layer provide an example for a formation of air bubbles only close to the ground. The dashed arrow highlights the trend of the reflectance factor for cooling down.

ice configurations for the utilized −20° and L20M20 measurement geometry. While in Fig. 8.4 a), the air bubbles are randomly distributed over the whole ice layer thickness, in Fig. 8.4 b) they are only located close to the asphalt sample. Corresponding spectra for the first case are shown in Fig. 8.5 a). Here, the ice layer is roughly 3 mm thick and the sample is the AC 11 DS 50/70 asphalt. A clear offset in the spectra appears for the ice layers, generated by the air bubbles. Similar results were observed from Sun *et al.* who measured clear and bubbly ice samples, where the ones containing air bubbles exhibit higher reflectance values [177]. Each air bubble provides at least two surface orientations perpendicular to the incident ray, leading to a contribution of specular reflection from the ice sample. These contributions are composed as follows:

- Reflection at the interface ice to air (bubble).
- Reflection at the interface air (bubble) to ice, followed by the transmission at the interface air (bubble) to ice.
- Total reflection within the ice bubble, followed by a transmission signal into the upper hemisphere. This process is not really determined by a specular
reflection, however, it leads to the same effect. The single event is supposed to yield the strongest signal of all the mentioned contributions, but also arises rather rarely compared to the others.

- Multiple reflections of a ray between the air bubbles, which then leaves the sample into the upper hemisphere. This contribution is rather weak compared to the three previous ones.

Interestingly, the offset does not appear immediately after freezing. It develops with time and temperature. One possible reason for this behavior is the inhomogeneous freezing process from outside to inside. At the boundary between water and ice phase, bubbles appear, somehow reminding of boiling water. Additionally, within the ice, small thin channels\(^2\) appear, where air leaves the ice sample. Moreover, the freezing process seems to take longer than expected on first view: For example, at \(-5^\circ\text{C}\), the measured spot is not yet fully frozen; the plateau between 1300 nm and 1400 nm is not fully developed in Fig. 8.5 a), indicating a residual liquid water content\(^3\). Moreover, the temperature-dependent expansion of ice is quite strong\(^4\), which affects the air bubble density, too. For instance, the ice freezes from its surface down to the asphalt. At the beginning, the ice is quite clear, because it can expand. However, when the trapped water between asphalt and ice freezes, its tension due to expansion breaks the ice layer, causing cracks in the ice and resulting in a very diffuse ice manifestation due to many transitions between air and ice.

In order to prove these assumptions, it is necessary to produce clear ice. Therefore, a computer fan with an unbalanced fan wheel is mounted to the box, which contains the sample and the water. The fan shakes the box and disturbs the water, causing a slower freezing process without the appearance of supercooling. The result is illustrated in Fig. 8.5 b). Here, a roughly 2.3 mm thick ice layer was produced on top of the SMA 8 LA 40/100-65 A sample\(^5\). The ice was visually quite clear, air bubbles occurred only close to the asphalt sample, at its interface. The freezing causes again the shift of the absorption features to higher wavelengths. This time, however, an offset of the wavelength-dependent reflectance factor only appears at

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\(^2\)They are probably caused in order to reduce internal stress.

\(^3\)The temperature sensor is close, but not directly located at the measured spot to avoid any artifacts in the spectra of the sensor itself. Therefore, especially during the freezing process, deviating temperatures can occur between sensor and measurement position.

\(^4\)Its volume increases by roughly 9% upon freezing [272].

\(^5\)Another example, where this effect is nicely illustrated can be found in the Appendix in Fig. A.17. Here, the layer thickness is roughly 6.3 mm and the offset at small wavelengths is even more pronounced.
low wavelengths. This observation can be explained as follows: Within the covered spectral range, the absorption coefficient of ice is stronger at higher wavelengths. Since the bubbles are only located near the ground, the light intensity at wavelengths with strong absorption (for example around $\sim 1500$ nm) is already very low when it reaches the air bubbles. Thus, intensities at these wavelengths barely contribute to the overall signal. In contrast, for regions with weaker absorption coefficients, enough signal is left after propagating through the bulk water (for example around 1000 nm), leading to the observed offset in the reflectance factor.

8.4 Simulation results

Reflectance factor simulations from ice layers on top of a rough surface follow the same principle as for liquid water\textsuperscript{6}. Only the complex refractive index of the upper layer is exchanged to the one of ice\textsuperscript{7}. By following this approach, the simulation takes a perfect ice layer into account, without any contribution of air bubbles. However, this approach makes it challenging to compare the results with real world measurements. The problem is not really the simulation itself, it is rather the preparation of a defined very clear ice layer, which is challenging, especially when the water is not degassed. Even with the preparation of the box via an unbalanced fan—which disturbs the water in order to achieve a slower freezing process—there are most of the time some enclosed air bubbles present within the ice layer. Anyway, Fig. 8.6 compares a measurement of clear ice with only little amount of air bubbles with simulations. In this case, a roughly 1.3 mm to 1.5 mm thick water layer\textsuperscript{8} was investigated. In the following, a quick and simple\textsuperscript{9} wavelength-independent method as well as a more precise wavelength-dependent method for a comparison between simulation and measurement are introduced.

For the simple comparison, the ground of the AC 5 DL 70/100 sample is given the same parameters (roughness and reflectance) for the simulation as previously in Sec. 7.4 for the simulation of water. The optical response is again computed via $10^6$ rays at each wavelength.

In general, one should note that the measurement is performed on a different spot.

\textsuperscript{6}This includes that each simulation is done twice, once for perpendicular (s) and once for parallel (p) polarized light.

\textsuperscript{7}Data from Warren \textit{et al.} [192].

\textsuperscript{8}Like in Sec. 7.4.1, the values are adapted to the ones from the simulations due to the surface roughness of the ground ($R_t \approx 200$ nm).

\textsuperscript{9}As the ice layer thickness measurement accuracy is rather low.
on the asphalt surface than for the utilized ground parameters; thus, it exhibits a slightly different asphalt spectrum and surface roughness. Both aspects influence the absolute value of the reflectance factor. By multiplying the simulation results by a factor of 1.28 the simulation results are in very good agreement with the results from the actual measurement. Thereby it is important to note, that this factor of 1.28 does not originate from the different spots alone which only explains a difference of $\sim 4\%$, revealed by dividing the dry spectra through each other (see Fig. A.19). Therefore, most of this factor is attributed to a different second influence factor.

Like for the simulation of water (see Sec. 7.4.2), the two-dimensionality of the simulation makes it necessary to adapt the effect of the solid angle reduction to the signal\textsuperscript{10}. Moreover, also the second influence factor has to be taken into account by using the same fit as in Sec. 7.4.2. The already fully adapted results are illustrated in Fig. 8.6. In Fig. 8.6 a), the simulation result corresponds to a water layer thickness of 1250 µm, while Fig. 8.6 b) shows the result for ice\textsuperscript{11} resulting from a freezing

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\textsuperscript{10}While for water and in three dimensions, the solid angle causes a reduction of $\sim 42\%$, for ice it results in a reduction of $\sim 39\%$. In two dimensions, the opening angle is only reduced by $\sim 22\%$ for an ice layer. Therefore, an additional factor of $\sim 0.78$ is multiplied to the signal in order to get the properties of three-dimensionality (compare to Sec. 7.4.2).

\textsuperscript{11}The water layer thickness was actually measured with the measurement comb, which yields an accuracy of $\sim \pm 100$ µm. The ice layer thickness was not measured.
of the before shown water with a thickness of 1500 µm. It is known that the water expansion upon freezing is roughly 9% [272], however, a thickness of ∼1360 µm slightly underestimates the measurement result; 1500 µm are more suitable. As the water was stirred by hand with a plastic rod to guarantee a slow freezing process of the water from the asphalt to surface direction, this could lead to an enhanced layer thickness within the FOV of the detector during the ice measurement.

Figure 8.7: Adaptation of the simulation data b) by using a new second influence factor resulting from the water and ice data a). In a), the results from the actual measurements of water and ice are divided by the simulation data. The resulting data between 850 nm and 1310 nm are fitted via \( y = m\lambda + b \). Since \( n \) of ice differs only ∼1.8% from water in the NIR, the second influence factor is very similar between the two states. In b), the simulation data for a water and ice layer is multiplied by the corresponding linear fit from a).

In the more precise comparison, the simulated reflectance of the dry ground is adapted to the spot of the water “reference”, while the total roughness is kept constant. Layer thicknesses between 900 µm and 1600 µm are simulated in steps of 100 µm. The adaptation from the opening angle to the solid angle is done as previously for both, water and ice. Differently to the first comparison, the fit of the second influence factor is calculated directly from the simulation and measurement results. This is realized by dividing the measured wavelength-dependent reflectance factor by the simulation results for water and ice. The resulting ratio is fitted with a linear function \( y = m\lambda + b \), the wavelength-dependent second influence factor. The
presented data in Fig. 8.7 a) are based on the simulation results for water with a 1300 µm thick layer and for ice with a 1600 µm thick layer. The fit parameters for the water case are: \( m = 5.97 \cdot 10^{-4} \text{ nm}^{-1} \) and \( b = 0.33 \) (which is roughly 1.28 times the fit from Sec. 7.4.2 in the NIR) and for the ice case: \( m = 5.45 \cdot 10^{-4} \text{ nm}^{-1} \) and \( b = 0.37 \). Since in the NIR, the real part \( n \) of the complex refractive index differs only \( \sim 1.8\% \) between water and ice (see Fig. A.21), the second influence factor barely differs between the two states. A very good indicator for the quality of the water and ice layer thickness simulation is that the ratio of simulation and measurement data does not possess minima or maxima at the absorption wavelengths\(^\text{12}\). An ice layer with a thickness of 1600 µm delivers a very good agreement with the measurement result (see Fig. 8.7 b)). The 1600 µm are again more than the roughly 9% expansion for water upon freezing [272], confirming the consistency of our argumentation.

For wavelengths above 1400 nm, the simulation delivers lower results for the reflectance factor than expected. This observation is further discussed in the next chapter, where similar behavior is observed for the simulation of snow layers.

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Figure 8.8: Raw results from simulations for the wavelength-dependent a) and thickness-dependent b) reflectance factor of ice-covered asphalt. The asphalt’s parameters correspond to the AC 5 DL 70/100 sample. The reflectance factor displays—like water—an exponential behavior for layers thicker than the surface’s roughness and is fitted with Equ. 7.5 (solid lines). The fitting parameters can be found in Tab. A.7. The inset illustrates a zoom into the region which is affected by the surface roughness. Dashed lines are guides to the eye.

\(^{12}\)Around 1400 nm, the presented ratio still exhibits some scattered points. These originate from the already very low signal (same order as measurement noise) at these wavelengths.
Since both methods of comparison deliver good results, the first method which utilizes the same fit for the second influence factor as the previous simulation for water in Sec. 7.4.2 is chosen for a direct comparison between a water and ice simulation. For that reason, the same layer thicknesses are simulated as previously for water in Sec. 7.4.2, using the same parameters. In Fig. 8.8 a), the raw simulation results of the wavelength-dependent reflectance factor are illustrated for the dry sample and selected ice layers. Fig. 8.8 b) reveals the same exponential dependence of the reflectance factor as for water and is fitted with Equ. 7.5.

After adaptation of the opening angle to the solid angle reduction and the second influence factor, the wavelength-dependent reflectance factor results, which is illustrated in Fig. 8.9. The factor of 1.28 is not considered in this case, since it was only needed for the different spot compared to the measurement from Sec. 7.4.2. The direct comparison with Fig. 7.13 shows that the absorption $\lambda_{1m}$ develops slower for ice than for water.

As presented above, the simulation of clear ice delivers results which are in good agreement with actual measurements. However, since most of our measured ice layers include air bubbles, another approach/model is necessary to describe these layers. It is possible to construct a simulation, which considers randomly placed
air bubbles. A similar approach is used for simulating snow, as will be discussed in more detail in the next chapter.

8.5 Icy leaves

![Graph showing wavelength-dependent reflectance factor from frozen leaves on top of the AC 11 DS 45/80-50 sample. A green (watery) and brown (arid) leaf sheet is investigated. A spectrum for just the frozen asphalt provides a comparison in terms of absolute values. The dashed lines are exemplary observed positions of the minima ($\lambda_{4m}$) from pure water (blue) and ice (cyan) (see Tab. 8.1).]

During autumn and winter time, frozen leaves represent another layer, which cause traffic accidents. In Fig. 8.10, the wavelength-dependent reflectance factor is shown for a watery (green) and arid (brown) leaf sheet, both separately frozen. Additionally, the spectrum of a cold asphalt surface is shown for the AC 11 DS 45/80-50 sample. The measurement is performed outside the freezer. At the cold asphalt sample, humidity condenses and freezes directly. Therefore, the spectrum exhibits the absorption feature of ice around 1490 nm. The absorption strength for the arid leaf sheet is clearly weaker than for the watery leaf sheet. Both leaf types show a shift of absorption bands to higher wavelengths when cooled down. The absorption features in total match very well with the ones of pure ice, verifying
the results from Sec. 7.5. Compared to the pure ice spectra in Fig. 8.5, the absolute values are multiple times higher. The reflectance factor of the lower wavelengths exhibits absolute values in a range typical for snow, however, in contrast to snow it stays rather constant between 850 nm and 1350 nm. In the region around $\lambda_{\text{min}} = 1490$ nm, the frozen leaves even possess a larger reflectance factor than the snowy samples. The large values do not originate from the frozen water inside the sample and can be rather explained by the diffuse reflectance of the organic leaf compound (compare to Sec. 7.5). For a spot where the frozen leaves are already partly melted, the minima in the spectra clearly shift to lower wavelengths, while the absolute values barely change.

From these results, the utilized measurement technique is also capable to roughly determine a relative water content for leaves. A finding which might be interesting for different tasks in nowadays agriculture.

8.6 Chapter summary

The modified freezer enabled a detailed insight into the optical behavior of ice-covered asphalt samples. It also enabled measurements during the freezing process, clearly showing how the spectra change from water to the ice phase. The spectrum of a very clear ice layer on top of asphalt is very similar to the water-covered one. The only clear difference is the shifted absorption features to larger wavelengths for the ice-covered sample, caused by a stronger contribution of hydrogen-bonding, which actually weakens the covalent OH-bonding. In contrast, trapped air bubbles or cracks within the ice lead to a diffuse appearance of the ice layer and a wavelength-dependent offset in the reflectance factor, due to the additional contribution of specular reflection from the ice-to-air and air-to-ice interface. The influence of this offset is strongly affected by the locations of the air bubbles within the ice layer. For example, air bubbles which are located close to the ground in a thick ice layer barely influence the reflectance factor at wavelengths with strong absorption coefficients of ice, because the intensity is already suppressed significantly within the ice.

The influence of trapped air bubbles and cracks make a general comparison between simulations and measurements rather challenging due to the wavelength-dependent influence on the spectra and the exact location of the air bubbles. For a rather clear ice layer, we presented a good match between simulation and measurement.

The spectra of frozen leaves are dominated by ice absorptions, while the absolute
values are similar to ones from wet leaves (see Sec. 7.5), indicating that its volume scattering is barely affected in the frozen phase. For the frozen as well as partly melted leaves, the reflectance factor above 1400 nm strongly differs between a watery and arid leaf sheet. This indicates that analyzing this region might be promising to determine the water content of leaves, which might be interesting for applications in agriculture.
9 Snow-covered asphalt

This chapter provides an overview about the optical response of snow-covered asphalt samples in the NIR region, focused on the comparison of two-dimensional simulations with own measurements and results from literature. Some of the results are already published in Ref. 194.

9.1 Snowy asphalt

Figure 9.1: Wavelength-dependent reflectance factor from various snow configurations. Own measurement results (solid lines) are compared to data from Sun et al. [130] (dashed lines). Snow residues—within the surface roughness—already exhibit the absorption feature around 1490 nm. The asphalt curve is the dry result from the AC 11 DS 50/70 sample. Data from Sun et al. provide values for the reflectance from different snow grain sizes. While they used an incident angle of 45° and a measurement angle of 0°, the own data is measured with the −20° geometry.
As the third remaining configuration of water, snowy samples are investigated. The wavelength-dependent reflectance factor for various snow configurations is illustrated in Fig. 9.1. The black spectrum represents the dry response from the AC 11 DS 50/70 asphalt sample. Even small traces of snow—only present in the pores of the asphalt—(snow residues) already affect the optical spectrum. For closed layers, the strongest absorption feature \( \lambda_{4m} \) \((\nu_1 + \nu_3 \text{ combination band})\) suppresses the reflectance factor down to the resolution limit of the spectrometer. In contrast, for wavelengths below 1440 nm, the whole spectrum is shifted to higher values.

In the experiment, also a thicker snow layer with a rough, wavy surface (uneven surface) was compressed to a flat surface by hand with the help of a squared plastic board (pressed snow). The board has to be placed inside the freezer as well, otherwise the snow surface would partly melt and some of the snow be stuck to the board. The reflectance factor of both configurations (uneven and pressed) are very similar with minor differences. This observation already indicates that the optical properties of snow resembles that of a Lambertian scatterer.

The minima in all the presented spectra are located at the identical wavelengths as the ones of pure ice (see Tab. 8.1). This result is expected, because snow is nothing else than ice mixed up with a lot of air. Since all the absorption features are well developed and the reflectance factor is rather independent of the surface structure, snow can be expected to be a good volume scatterer. This is also the reason why snow appears white in the visible range even though ice is transparent\(^1\).

In Fig. 9.1, the results for the wavelength-dependent reflectance factor of closed snow layers can be also compared to data from Sun et al. (dashed lines) [130] who measured snow samples with different grain sizes. They showed that the larger the grains, the lower the reflectance factor of the sample. Unfortunately, for the measurements performed during this thesis we had no equipment to experimentally determine the grain size of our samples. Typically, the older the snow\(^2\), the larger grains are present, which manifests in a more icy snow for older samples. Indeed, for a fresh sample of snow, the reflectance factor exhibits larger values, which correspond to samples with smaller grain sizes. The overall agreement between the measurement results in this work to data from Sun et al. is very good. While we measure in the \(-20^\circ\) geometry, Sun et al. measure with an incident angle of 45\(^\circ\) and an observing angle of 0\(^\circ\). This again indicates that the scattering behavior of

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\(^1\)The absorption bands in the VIS range are very weak for ice.
\(^2\)The utilized snow for the uneven and pressed configuration was already a rather “old” snow, i.e. conserved in the freezer.
snow is close to the one of a Lambertian scatterer.

Figure 9.2: Wavelength-dependent reflectance factor from various snow configurations on the AC 8 DN 50/70 sample a) and the ratio of the reflectance factor at two wavelengths as an indication for ground-independence b). In a), results are shown from different spots for several snow configurations, where the thin snow configuration is \(<\ 1\ \text{cm}\) thick. In b), a ratio of the reflectance factor at 1301 nm and 1599 nm provides a hint at which snow layer thickness the asphalt itself does not contribute to the signal anymore.

Results for the wavelength-dependent reflectance factor of more snow configurations are illustrated in Fig. 9.2 a). The snow for these measurements was quite fresh, only a few days old. For each configuration, several spots were measured with the \(-20^\circ\) geometry. As already shown in Fig. 9.1, snow residues lead to a slightly enhanced reflectance factor up to 1440 nm, while for higher wavelengths the \(\lambda_{4m}\) absorption feature leads to decreased values. For a thin snow layer (below 1 cm), the absorption feature \(\lambda_{4m}\) stronger affects the spectra. Below 1440 nm, the whole spectra exhibit values between 0.2 and 0.4, while \(\lambda_{1m}\) to \(\lambda_{3m}\) manifest themselves in the spectra. Between a fluffy snow layer, uneven surface structure of snow, compressed snow, and grooves through the snow layer, the reflectance factors overlap with each other, depending on the measured spot. The main differences are probably be deviating distances from snow surface to detector.

Interestingly, for all the mentioned snow configurations and wavelengths above 1440 nm, the reflectance factors are equal, while below 1440 nm, there are still some variations. This behavior results from the low penetration depth\(^3\) \(\lambda_p\) of solid ice (see

\(^3\)Calculated via Eq. 2.23 and data from Warren et al. for \(\kappa\) of ice [192].
Fig. A.20), which is less than 1 mm for wavelengths between 1440 nm and 1730 nm. As the snow layer consists of several ice grains, the light gets scattered multiple times and gets completely absorbed by the snow after 1 mm of ice. Therefore, the measurement is not sensitive to grains located deeper in the sample or the ground itself. For lower wavelengths, the penetration depth is larger; thus, it is also sensitive to the underlaying ground.

Indeed, by calculating the ratio of the reflectance factor at \(~1300\,\text{nm}\) and \(~1600\,\text{nm}\), one can clearly identify a dependence of the layer thickness (see Fig. 9.2 b)). The thicker the layer, the larger the values from the ratio, while at a certain layer thickness, the ratio does not change anymore. With the help of such a ratio one can determine the lowest needed snow layer thickness in order to be independent of the underneath asphalt sample to \(~10\,\text{mm}\).

**9.2 Simulation results**

In this section, the impact of different parameters on the optical spectra is investigated and compared to real measurements as well as literature data. With the introduced setup for measurements below 0°C, it is yet not possible to perform angle-dependent BRF measurements. Nevertheless, in the simulations also the BRF is investigated and compared to literature data as well as to some measurements performed with the ellipsometer on pellets.

**9.2.1 Principle parameters and their influence**

The geometric shape of ice crystals is the Ih group, which is under normal conditions a hexagonal pattern (see Sec. 2.10.2). Therefore, the simulations of the snow reflectance factor as well as albedo\(^4\) are based on hexagonal shaped particles with a diameter of 300 \(\mu\text{m}\). By considering these diameters for the size factor \(a = 2\pi r/\lambda\) (with the particle radius \(r\)) together with the given NIR range, size parameters result between 571.2 at 1650 nm and 1122 at 840 nm. Such large values easily fulfill the given limitation of at least \(a \geq 20\) in order to utilize geometric optics in the simulations [191].

The typical simulated sample size is 90 mm in length and 6 mm in thickness. Un-

\(^4\)The term albedo used in this thesis refers to the spherical albedo, which is basically the reflectance integrated over the whole upper hemisphere [273]. The geometric albedo can be compared to the reflectance factor [274].
less otherwise stated, the geometry is again at $-20^\circ$ incident and observing angle, with the L20M20 configuration for the spot diameters. From simulations where the random distribution of the hexagonal shaped particle orientations stays constant, the minimal necessary amount of rays can be determined, which leads to a convergence of the detected signal. In Fig. 9.3, the results for a total number between $50 \cdot 10^3$ rays per wavelength and $800 \cdot 10^3$ rays per wavelength are compared. For the wavelength-dependent albedo, the signal converges already for $50 \cdot 10^3$ rays per wavelength. However, the reflectance factor needs a lot more rays in order to minimize the noise. The result in Fig. 9.3 b) reveals that even for $800 \cdot 10^3$ rays per wavelength, the reflectance factor is still slightly affected by noise. Nevertheless, the changes in the reflectance factor from $300 \cdot 10^3$ rays upwards are not too significant, therefore, in order to have a compromise between computation time and convergence of the reflectance factor, further simulations are performed with $300 \cdot 10^3$ rays per wavelength, unless otherwise stated. For the results presented in Fig. 9.3 and all following results, each simulation is performed twice, once for perpendicular (s) and once for parallel (p) polarization. The unpolarized results for the albedo and reflectance factor is then achieved via

$$ R = \frac{1}{2} (R_p + R_s) \quad . $$

(9.1)

As will be shown later, for small angles of incidence, the angle-dependent reflectance factor can be well described by Lambert’s law. Therefore, for such angles, the wavelength-dependent albedo from simulations—which exhibits a better SNR—can be directly compared with the measured wavelength-dependent reflectance factor. This is done in Fig. 9.4 a), where the gray spectra represent several results from measurements and the scatters the results for different particle shapes from simulations. The overall agreement between simulation and measurement is very good. Only at wavelengths above 1500 nm, there are some visible deviations. Interestingly, a similar behavior is already observed from simulations of closed ice layers in Sec. 8.4. The utilized complex refractive index $N$ for ice from Warren et al. [192] provides data from 400 nm to 1690 nm. Thus, the wavelength range, which exhibits slightly stronger deviations between simulation and measurement is closely located to the border of the available data. Since the deviations appear for both, ice and snow in the same wavelength range, it indicates that the utilized
Figure 9.3: Wavelength-dependent albedo a) and reflectance factor b) at the $-20^\circ$ geometry for different amount of rays. The particle diameter is 300 µm and hexagonal shaped. Their orientation is not changed between the different runs. While in a) for the albedo, already with 50 thousand rays convergence is reached with barely any noise, for the reflectance factor in b) it seems that even for 800 thousand rays the signal is still slightly affected by noise.

\(N\) might deviate from reality. Therefore, we have searched for alternative literature data. Indeed, the determination of \(\kappa\) in this wavelength range seems to be challenging. When comparing the utilized data from Warren et al. [192] to more recent data [275], the imaginary part \(\kappa\) exhibits some deviations for wavelengths $>1400\,\text{nm}$, while the real part \(n\) yields nearly identical values. The comparison is illustrated in Fig. A.22. The utilized data have stronger absorptions compared to more recent data for $\lambda > 1400\,\text{nm}$; thus, from the simulations, the reflectance factor as well as albedo might be lower compared to real measurements in this wavelength range. In Fig. A.23, we show the simulation results for 4-sided particles utilizing the more recent data for \(\kappa\) from Warren et al. and compare them with the previous result. The albedo for $\lambda > 1400\,\text{nm}$ certainly increased, however, not as much as necessary to be within the range of the measurements. We also repeated the ice simulation already presented in Fig. 8.7 b). Also here, the effect of the new data on the reflectance factor for $\lambda > 1400\,\text{nm}$ is smaller than the discrepancy. Therefore, it is not yet clear what causes the deviations at these wavelengths.

With less sides of the polygons higher reflectance values result. As expected, the values converge towards a round shape of the particles. Larger reflectance values for less polygon sides originate from the average propagation path inside the snow/ice
Figure 9.4: Wavelength-dependent albedo from the simulation of a snow layer made of different grain shapes a) and normalized simulation results b). In a), the shapes consist of polygons with different number of sides, but constant particle diameter of 300 µm. The albedo decreases, the more sides a polygon has. Towards the shape of a sphere, the less impact a higher amount of polygon sides has on the optical spectrum. For comparison, several results of the reflectance factor from snow measurements (−20° geometry) are displayed as gray spectra. In b), the simulation results are normalized to the result with 11 sides. From that plot, it gets clear that the relative reflectance factor is stronger affected at larger wavelengths by the particle shape.

particle. For a constant circumradius of the particles, the ones with less sides exhibit a smaller area and thus, less absorption. For a real sample, there are all kinds of shapes present, because some merge together or partly melt. Therefore, we expect the measurement to be an average of the simulation, while in the measurement, shapes with even smaller area/volume are present.

When the results for the different shapes are normalized to the one with eleven sides (see Fig. 9.4 b)), it is revealed that the relative reflectance factor at larger wavelengths (≈ 1200 nm) is more affected by the shape, which can be attributed to the stronger extinction coefficients in this wavelength range.

The similar results for six and eleven sides is in good agreement with results obtained from Leroux et al. [181]. They performed more complex simulations in three dimensions for columned and sphere-like snow flakes. Leroux et al. could show that the scattering and extinction cross section as well as the single scattering albedo of

\footnote{Single scattering albedo: scattering cross section divided by the extinction cross section [181]. A value of 0 means that all attenuation is due to absorption, while a value of 1 means that all attenuation is due to scattering.}
hexagonal shaped columns and plates deliver the same results as spheres do, when their diameter of the hexagonal base and the thickness of the plates or columns are similar [181].

Figure 9.5: Albedo dependent on the particle diameter from simulations of snow in linear a) and logarithmic scale b). The incident angle is $-20^\circ$, and particle diameters from 200 $\mu$m up to 900 $\mu$m are investigated, while the layer thickness stays at $\sim 6$ mm. The albedo decreases with increasing particle diameter. The logarithmic scale in b) indicates that the albedo has a logarithmic dependence with respect to the particle diameter. Dashed lines are guides to the eye.

Besides the particle shape, their size has an impact on the optical properties of snow, too. Fig. 9.5 illustrates the simulated albedo in dependence of the hexagonal shaped particle size for several wavelengths. The layer thickness is—depending on the particle diameter—approximately 5.7 mm. The albedo decreases with increasing particle diameter, which is in good agreement to similar simulations from Kaempfer et al. [186] or Xiong et al. [182] and measurements from Sun et al. [130] as well as Painter et al. [175]. The logarithmic scale of the albedo in Fig. 9.5 b) indicates an exponential dependency between albedo and particle diameter. It strongly resembles the simple relation of Lambert-Beer’s law (see Equ. 2.21). For wavelengths above 1400 nm, where the absorption of ice is stronger, the behavior deviates from the exponential behavior. This deviation is probably related to the amount of utilized rays, thus, to the SNR.

Compared to the results from Kaempfer et al. [186], Xiong et al. [182], and Sun et al. [130], the obtained absolute values for the albedo are slightly smaller and the degree of reduction with increasing particle diameter faster. There are two major differences between the presented simulations and the mentioned results from litera-
Figure 9.6: Wavelength-dependent albedo from simulations for different layer thicknesses. Up to \( \sim 10 \) mm snow layer thickness, the albedo increases with increasing layer thickness, especially below 1440 nm. Dashed lines are guides to the eye.

In order to validate this assumption, the wavelength-dependent albedo is simulated for several layer thicknesses. Fig. 9.6 illustrates the results for four different layer thicknesses, while the particle diameter is kept constant at 300 µm. Indeed, for increasing the layer thickness, the albedo increases as well; especially at smaller wavelengths, the layer thickness has a strong impact. For a change in layer thickness from 6 mm to 12 mm, the albedo at low wavelengths is increased by \( \sim 20\% \). This result correlates with the penetration depth (see Fig. A.20), which was already mentioned earlier. In the Appendix for Fig. A.24, we revised the same simulation as performed for Fig. 9.5, however, with a layer thickness of 12 mm. As expected, the absolute values at low wavelengths increased for all particle diameters.
Another parameter which can influence the optical properties of the snow layer is its porosity. The porosity can be defined as the void content. Up to now, it is 35% for the presented simulations, which is quite small compared to simulations from Kaempfer et al., where they assumed porosities between 45% and 80% [186]. Their results show that albedo as well as transmittance are independent of the snow density (void content). Only for their highest achieved density, the albedo was slightly decreased (< 5% compared to the second highest simulated density).

Fig. 9.7 compares the simulated albedo for different void contents to one typical measurement result of the reflectance factor (solid line). For the simulations, the snow particles have a diameter of 300 µm, the incident angle is $-20^\circ$, and the snow layer has a thickness of 6 mm. The larger void content is realized by a bigger spacing in $x$-direction between the particles. There is basically no dependence of the albedo to the void content and thus, the result is in very good agreement to the ones from Kaempfer et al. [186].

In our simulations, only for the highest void content, the albedo decreases slightly. This can be explained by the two-dimensional snow pattern. Since the grains are not randomly placed but in a lattice structure, a large void content leads to a bigger
spacing between the particles; thus it creates free paths to the ground without any ice particle in between. Rays which take these paths do not contain any information about the snow layer, which is the reason for the slightly decreased albedo. These free paths are very unlikely in real three-dimensional samples, thus, Kaempfer et al. do not observe this behavior.

### 9.2.2 Scattering behavior

Figure 9.8: Angle-dependent BRF from snow simulations at several wavelengths. In a) an incident angle of $\theta_i = -20^\circ$, while in b) an incident angle of $\theta_i = -65^\circ$ is utilized. For a larger incident angle, enhanced forward scattering can be identified.

Unfortunately, the freezer setup is not capable to perform angle-dependent measurements yet; only a fixed angle can be adjusted and utilized for the measurements. However, the simulation enables some insight into the scattering behavior of snow. The results are compared and validated to literature and to measurement results taken with the ellipsometer by Christoph Müller [160].

Simulation results for an incident angle of $-20^\circ$ and $-65^\circ$ are illustrated in Fig. 9.8. It is important to note that the presented BRF is the result of averaging ten simulations. Each simulation has different random—hexagonal shaped—particle orientations. The necessity of an average is based on the two-dimensionality of the simulation. While the albedo is relatively independent of the particle orientation, the reflectance factor is affected directly. In three dimensions, much more particles, thus more orientations contribute to the reflectance factor. Therefore, in the three-dimensional case, there is already some kind of average due to the larger amount
of involved particles. In order to overcome this issue, the approach with averaging independent simulations is chosen.

The results for a small incident angle (see Fig. 9.8 a)) indicate a rather observing angle-independent behavior of the BRF, which is best described by Lambert’s law. For a larger incident angle of $-65^\circ$, like in Ref. 113 (see Fig. 9.8 b)), a clear tendency towards forward scattering in form of a broad peak appears.

Fig. 9.9 provides a direct comparison of the BRF for both incident angles and two exemplary wavelengths. One can identify an angular region between $\sim -40^\circ$ and $\sim 20^\circ$, where the BRFs possess the same values. For these angles, snow can be best described by Lambert’s law, consistent with various measurements in Ref. 160, where it was attributed to volume scattering. The observed forward scattering for large incident angles is also in very good agreement to literature, which mostly concentrate on large incident angles [113, 182, 185, 276].

Ellipsometer measurements on snow-like ice particles on pellets delivered similar results. For incident angles of $-40^\circ$ and $-53^\circ$, enhanced forward scattering is observed, which is more distinct for the larger incident angle [160].

We did not find any literature data for the angular-dependent BRF at small incident angles. This is probably the case as in terms of the solar angle with respect to cold
areas on our earth, larger incident angles are of more interest. However, the incident angle seem to be an important parameter for angular-dependent BRF measurements of snow.

Peltoniemi et al. also report some results for wet snow, where the wetness exhibits spectral as well as directional signatures [277]. They were able to show that the BRF of wet melting snow exhibits a maximum close to the specular direction, which is followed by a minimum, before it further increases for increasing phase angles. For dry snow samples, they only observed a monotonic increase of the BRF in forward direction. Since the morphology—especially for wet snow—changes quite fast, such field measurements have to be performed very fast [277]. Therefore, it will be very interesting to expand the here presented simulation also to water-snow mixed states.

**Adapting the simulation principle to air bubble-containing ice layers**

The presented simulated snow samples are constructed from randomly orientated grains, which possess the complex refractive index $N$ of ice and the surrounding medium that of air. This approach could be also utilized for simulating air bubbles within a ice layer, where these properties could be easily exchanged, which would lead to air grains within an ice layer. However, an additional closed layer with the properties of ice would be needed on top of these grains, which should also be variable in its thickness. Moreover, in the simulation of a snow layer, the grains are made of polygons, a replacement by spheres would be favorable in order to guarantee their specular contribution in backscattering direction. Another challenging part of such a simulation is the inhomogeneity of the air bubble distribution, which provides a huge amount of possibilities of ice configurations.

### 9.3 Chapter summary

Since snow consists of ice and air, the location of the absorption features are identical to the ones from ice. However, its porous structure leads to strong scattering, thus to large absolute values in the reflectance factor. With our measurements, we showed that the ratio of the reflectance factor at specifically chosen wavelengths can be used to determine the snow layer thickness at which the ground below does not contribute to the overall reflectance factor anymore. Moreover, our measurements focused on
small incident angles which are barely represented in literature. The applied two-dimensional snow simulations delivered very good results in terms of dependence on the particle size, snow density, and layer thickness. Only the absolute values are slightly smaller than reported already for instance for the dependence on the particle size [130]. Our simulations are capable to show the well-known enhanced forward scattering at large incident angles [113, 182, 185, 276]. Additional ellipsometric measurements on snow-like frost-covered pellets [160] are also in good agreement to this enhanced forward scattering at large incident angles. For small angles like we used it in our measurements, the simulation results of snow are well described by Lambert’s law.
10 Summary and Outlook

This work revealed the optical properties of typical asphalt types, as well as of their layered systems with an aggregate state of $H_2O$. From this we conclude that the near-infrared (NIR) region is perfectly suited for a working range of an optical sensor for state detection.

Broadband infrared measurements on pellets—made of raw stone materials of typical AC and SMA asphalt types—reveal that their optical features are mainly dominated by CaCO$_3$ and SiO$_2$ (see Ch. 6). In the mid-infrared (MIR) region, also bound –OH as well as trapped H$_2$O within the stone materials lead to broad absorption features. In contrast, the low frequency regime is probably dominated by inorganic, diatomic molecules, consisting of one metal and one halogen atom. However, also CaCO$_3$ exhibits some transverse optical (TO) and longitudinal optical (LO) modes in this region and might have a strong contribution. Interestingly, the investigated EloMinit pellet—the raw material of the OPA 8 40/100-65 sample—exhibits a Drude-like behavior in its low frequency regime (due to a significant metal content), while the pellet made from the available OPA 8 40/100-65 asphalt does not. Since EloMinit is a waste material from electric blast furnaces, the chemical composition can vary significantly, which directly affects the optical spectrum. In total, the NIR region exhibits nearly no optical feature for all investigated samples. Thus, this region is a perfect choice for measurements where the asphalt surface acts as a substrate.

The Kramers Kronig analysis shows that the results for the complex refractive index $N$ in the NIR depends significantly on the high frequency extrapolation. To avoid that, the measurement was extended to higher frequencies. However, ellipsometric measurements on the pellets are challenging due to the diffuse reflection properties of the samples. Additionally, their surface roughness is in the $\mu$m range, which is actually too much for modeling the data using the effective medium approximation (EMA) [160]. Therefore, the combination of Cauchy-Urbach model and EMA do not enhance the accuracy of the determined complex refractive
index $N$ of our pellets. Nevertheless, NIR scatterometry measurements on the pellets deliver a clear evidence for volume scattering; for the EloMinit pellet, a high metal content suppresses this type of scattering, due to an absorption-based shortened path through the material.

Measurements on the macroscopic asphalt samples—which were also discussed in Ch. 6—should be performed with a light spot size and field of view (FOV) at least twice the diameter than the main grain size, in order to average over the surface roughness and different grain materials. Simulations as well as measurements show that the detected intensity from a Lambertian scatterer depends on the combination of light $L$ and measurement (FOV) $M$ spot diameter. For $L < M$, the angle-dependent signal is well described by Lambert’s law. However, deviations from Lambert’s law already appear if $L \approx M$ and get even more pronounced if $L > M$. For the optical simulations of a rough surface, the maximum height $R_t$ of the surface roughness is taken as input parameter, which is determined from the asphalt via the sand-patch method [178, 179].

A systematic study of the reflectance factor for various types of asphalt samples reveals a correlation between the absolute values of the reflectance factor and the age of the sample. Overall, untreated new samples possess rather low values, while sandblasted ones, which represent the first aging step, already exhibit higher reflectance factors. Actual used samples from a road, which are further aged, possess the largest absolute values in the reflectance factor. The NIR slope of the reflectance factor is very similar for almost all asphalts, which is an important property for a type-independent analysis. There is one exception, the OPA 8 40/100-65 asphalt sample displays a negative slope in the reflectance factor. For the AC types made of moraine, the curvature in the reflectance factor decreases with increasing age.

NIR scatterometry measurements on the pellets reveal the presence of a broad specular peak [160], which is not observed for the macroscopic asphalt samples. For small incident angles up to $\pm 40^\circ$ and observing angles between $\pm 50^\circ$, the optical response can be well described by Lambert’s law. For larger incident angles, a tendency towards forward scattering develops, which is in good agreement with literature [91]. For some of the asphalt samples, the polarization opposition effect (POE) [160] as well as the opposition effect [69] can be resolved. The simulated bidirectional reflectance distribution function (BRDF) of a rough ground exhibits good results for small incident and intermediate observing angles. However, due to the Lambertian
model of each facet, it is not capable to mimic the enhanced forwards scattering for larger angles as well as the enhanced backscattering for small phase angles. Via the direct comparison between the results from the pellets and the macroscopic asphalt samples it can be concluded that the optical properties of the material itself are well described by Lambert’s law for small incident angles, indicating volume scattering. However, the macroscopic surface roughness leads to an increased contribution of surface scattering; thus, larger incident and observing angles deviate more from Lambert’s law at the macroscopic asphalt samples.

Angle-dependent measurements on the pellets and the OPA 8 40/100-65 asphalt indicate that the observed negative slope in the reflectance factor most probably originates from volume scattering, thus from the actual material properties. At the EloMinit and OPA 8 40/100-65 pellet, the reflectance factor in specular direction at $0^\circ$ incident as well as for large incident angles $\geq |\pm 70^\circ|$ the reflectance factor undergoes a slope change from negative to positive sign in specular direction. Single scattering events are the dominant scattering mechanism at such large angles. Thus, we conclude that the observed negative slope for small incident angles is caused by the material properties of this specific asphalt, originating from volume scattering.

In Ch. 7 we first presented that measurements with an incident angle of $0^\circ$ are influenced too much by the specular reflection of the water surface. In order to avoid that influence, a small incident angle is favorable. Therefore, most of the measurements within this thesis are performed with the $-20^\circ$ geometry (incident and observing angle). This arrangement corresponds to a transmission measurement of the water layer.

In total, we resolve four absorption features for H$_2$O within the covered NIR range of our grating spectrometer: $\nu_{1m} \equiv \nu_1 + 2\nu_3$, $\nu_{2m} \equiv \nu_1 + \nu_2 + \nu_3 + 2\nu_1 + \nu_2$, $\nu_{3m} \equiv \nu_2 + 2\nu_3$, and $\nu_{4m} \equiv \nu_1 + \nu_3$ (from lower to higher wavelengths). The very prominent drop of signal for even very thin water and ice layers cannot be explained by the absorption of H$_2$O. We conclude that this jump is caused by a solid angle reduction of the signal, which reaches the detector due to the refraction at the water-to-air interface [21] and another wavelength-dependent factor, which we call second influence factor, described by a linear function. This second influence factor probably originates from a changed scattering and reflection behavior due to penetrating water
into the grains and the thus different transitions at the water-to-asphalt interfaces. When these two factors are taken into account, the simulation results fit very well to the corresponding measurement results.

The utilized measurement setup and analysis method enable the determination of the absorption coefficient $\alpha$ of liquid water with high accuracy. This technique can be utilized to determine the absorption coefficient of nearly every liquid, as long as it does not cause too much diffuse reflection by itself.

With Equ. 7.5, we were able to derive a physical fitting function for the layer thickness-dependent reflectance factor. This equation takes the roughness of the asphalt samples into account as a fitting parameter. Additionally, we were also able to provide a more simple, empirical fitting function (see Equ. 7.6), which describes the data also very well.

Since leaves are a very common layer on top of asphalt, some measurements were also performed on such systems. As expected, their spectra are dominated by water absorptions (for frozen leaves by ice absorptions). However, compared to water alone, leaves exhibit much larger reflectance factor values, originating from their strong diffuse scattering behavior.

Ice-covered asphalt samples were investigated in Ch. 8. The modified freezer enables a detailed insight into their optical behavior during the freezing process. The spectrum of very clear ice resembles the one of liquid water with the difference of shifted absorption features to larger wavelengths. In contrast, trapped air bubbles within the ice lead to an offset in the reflectance factor by an additional contribution of specular reflection from the ice-to-air and air-to-ice interface. This offset is wavelength-dependent and its influence changes strongly with the locations of the air bubbles within the ice layer. For example, air bubbles which are located close to the ground for a thick ice layer thickness barely influence the reflectance factor at wavelengths with strong absorption coefficients of ice, because the intensity is already suppressed significantly within the ice. A comparison between simulations and measurements is challenging due to the mentioned air bubbles. Nevertheless, for rather clear ice, we presented a good match between simulation and measurement.

Ch. 9 concentrated on the simulation of snow. The two-dimensional snow simulations deliver very good relative results, only the absolute values are slightly smaller than expected [130]. Our simulations show the well-known enhanced forward scat-
CHAPTER 10. SUMMARY AND OUTLOOK

tering at large incident angles [113, 182, 185, 276]. This also fits very well to ellipsometric measurements on snow-like frost-covered pellets [160]. Moreover, we were able to present measurement data for small incident angles which are barely represented in literature. Additionally, from these measurements, we showed that by calculating the ratio of the reflectance factor between two different wavelengths provides a hint at which layer thickness the ground below does not contribute to the overall reflectance factor anymore.

In total, this thesis provides a detailed insight into the optical properties of layered H$_2$O asphalt systems. We could show that the layered system is strongly influenced by a solid angle reduction and a here called “second influence factor”. The second influence factor should be investigated in more detail because it is an important factor to understand the physical background of the asphalts’ optical response. For water and ice-covered asphalts, we provide a fitting function which is able to model the layer thickness-dependent reflectance factor even on a rough surface. In addition, we built up simulations, which can save much time when creating a big database. These simulations could be extended in future to be able to simulate mixed states, for instance a water-snow mixture. Such systems are very hard to produce experimentally in a defined manner, because they change their appearance quite fast. Thus, with the presented work, we prepared the basis for a development of an optical road condition sensor, which—based on the promising results—should be further proceeded.
A Supplementary informations

A.1 Theoretical background

Figure A.1: Simulated scattering behavior for spherical particles with three different sizes. The utilized wavelength is $\lambda = 1000\,\text{nm}$ and the particle’s refractive index is $N = 1.5 + i0$. The incident light is coming from the $0^\circ$ direction. The results are normalized to 1. From a) to c) the particles possess a diameter of 10 nm, 300 nm, and 1000 nm, respectively. A zoom of c) is shown in d). The simulation is performed with Ref. 62.
In Fig. A.1, the simulated scattering behavior is shown on spherical particles with different sizes for unpolarized, parallel, and perpendicular polarized light at $\lambda = 1000 \text{nm}$. Fig. A.1 a) represents the Rayleigh limit, where the scattered perpendicular polarized light is independent of the scattering angle, while the parallel one has the same amount in forward as in backward direction. With increasing particle size in b) and c), forward scattering is enhanced and the angle-dependent degree of polarization is affected significantly. This represents the Mie effect. The larger the particle size, the stronger the polarization effect gets shifted into the backplane.

Figure A.2: Output plot from the simulation of a dry ground. The optical results as well as roughness results are provided in this plot. The single plots are explained in the text below.
The first plot in polar coordinates in Fig. A.2 (lower left corner) shows the amount of rays for each simulated wavelength which hit the detector at a certain observing angle. The intensity can then be calculated by multiplying the amount of rays with the initial intensity of each ray (100% reflectance of the reference). The red line is the perfect Lambertian response of an infinitesimal light spot size. The plot to the right is the observing angle-dependent intensity from the sample for the simulated wavelengths. The plot in the middle is the BRF which results when the intensity of the sample is divided by the one from the reference. The plot on the left side, second row represents the integrated BRF, thus shows the albedo from the sample. The plot on the left, first row, is the reflectance factor at $-20^\circ$, where the solid line is the measurement result. The bar plot in the middle of the first row provides an overview about the different parameters for determining the surface roughness of the sample. The plot to the right shows the simulated ground profile.

### A.2 Dry asphalt

![Figure A.3: Broadband reflectivity of the AC 11 DS 50/70 pellet. The strongest contributions are located in the FIR region.](image-url)
Figure A.4: Reflectance factor for three different spot sizes on the AC 11 DS 45/80-50 A sample at $\theta_i = \theta_r = 0^\circ$ a) and $\theta_i = \theta_r = -20^\circ$ b). The signals are normalized to a 99 % reflectance standard (“WS”).

Figure A.5: Reflectance factor for three different spot sizes on the AC 11 DS 25/55-55 A sample at $\theta_i = \theta_r = 0^\circ$ a) and $\theta_i = \theta_r = -20^\circ$ b). The signals are normalized to a 99 % reflectance standard (“WS”).
Figure A.6: Reflectance factor for three different spot sizes on the SMA 8 S 40/400-65 A a) and OPA 8 40/100-65 sample b). Both with $\theta_i = \theta_r = -20^\circ$. The signals are normalized to a 99 % reflectance standard ("WS").

Figure A.7: Wavelength and position-dependent reflectance factor for L20M10 and the AC 11 DS 50/70 sample. Incident and observing angle is 0°.
Figure A.8: Wavelength and position-dependent reflectance factor for L20M20 and the AC 11 DS 50/70 sample. Incident and observing angle is 0°.

Figure A.9: Wavelength and position-dependent reflectance factor for L40M40 and the AC 11 DS 50/70 sample. Incident and observing angle is 0°.
Figure A.10: Resulting $L_m$ for the three different spacings $x_s$. For the maximum height $R_t \approx 1 \text{ mm}$, $L_m$ is normally distributed around 0.5 mm. The step size $x_s$ affects the FWHM of the Gaussian distribution.
Figure A.11: Wavelength-dependent reflectance factor of bitumen (type: 40/100-65) for different incident and observing angles a) to e). In f) the results for different spots on the sample are displayed for the −20° geometry.
A.3 Water-covered asphalt

Figure A.12: Wavelength-dependent reflectivity of a Zenith Polymer standard (WS) at $0^\circ$ incident and observing zenith angle. The standard is normalized to the measurement result of a gold mirror.

Figure A.13: Wavelength-dependent absorption coefficient $\alpha$ extracted from the reflectance factor for two different water layer thicknesses. Instead of 2 s of integration time, only 0.5 s are used during this measurement. Same data once in linear a) and once in logarithmic scale b). The dashed line is the reference data from Kedenburg et al. [25].
Figure A.14: Simulation results for the reflectance factor with a 1 µm illumination spot size. Wavelength-dependent reflectance factor in a) and observing angle-dependent reflectance factor in b). Surface roughness and dry reflectance factor values correspond to the AC 5 DL 70/100 asphalt sample.

**Derivation of Equ. 7.5**

The first case of Equ. 7.5 \((d \geq R_t)\) is simply Lambert Beer’s law with an initial signal \(a(\lambda, \theta_i)\). This initial signal is the reflectance factor of a closed water layer surface which has an infinitesimal thin thickness, meaning no effect of the water’s bulk absorption. Thus, only the solid angle reduction and the second influence factor determines this factor. The reduction factor \(\beta\) takes this difference into account. Compared to the standard Lambert-Beer’s law (Equ. 2.21), the exponent gains a negative offset of \("R_t - dR_t(\lambda)\"\) so that for \(d = R_t:\)

\[
d - (R_t - dR_t(\lambda)) \overset{d=R_t}{=} R_t - (R_t - dR_t(\lambda)) = dR_t(\lambda) .
\] (A.1)

Thus, at \(d = R_t\), the layer thickness results in \(dR_t(\lambda)\) measured from the highest point of the surface roughness, illustrated in Fig. A.15 b). This effective layer thickness corresponds to a water layer on top of a flat surface which provides the same signal as the completely filled valleys from the actual rough surface. Additionally, the incident angle \(\theta_i\) makes it necessary to exchange \(d\) by \(d/\cos(\theta_i)\). Thus, the first case can be expressed as:

\[
\beta(\lambda, \theta_i) \cdot RF_{\text{dry}}(\lambda, \theta_i) \cdot e^{-24\pi\kappa(\lambda)} \cdot \frac{d}{\cos(\theta_i(\lambda))} \cdot \frac{d - (R_t - dR_t(\lambda))}{\cos(\theta_i(\lambda))} .
\] (A.2)
Figure A.15: Water schematics to explain the fit of layer thicknesses below the surface roughness. a) Side view of the 2D simulation. In this case, the dry fraction is represented by $s$ and the water by $w$. The distance $d$ gives the water level from the lowest point of the valley. The intercept theorem can be used for calculating the area of the water cross-section, which depends quadratically on changes of $d$. For instance, four triangles with the same area result with $d_2 = 2d_1$. b) Cross section of the case $d = R_t$ with the effective layer thickness $d_{R_t}$ as an equivalent replacement of the water level on a flat surface (related to Lambert-Beer’s law). c) Top view of the 3D measurement which can be described with the same approach as a).

For layer thicknesses $d < R_t$, the signal contains a fraction of the dry asphalt and a fraction of the wet asphalt. Assuming a triangular shape of the roughness, this fraction can be derived by using the intercept theorem (compare Fig. A.15 a)):

$$\frac{s_1}{s} = \frac{w_1}{w} = \frac{d_1}{R_t} . \quad (A.3)$$

Thus, the water surface $w$ is proportional to the water-covered grain surface $s$, revealing a linear relationship. Using this background, the dry area reduces linearly with the water height $d$. Therefore, a linear equation of the form $y = b + md$ describes the decreasing amount of signal from the dry areas with increasing layer thickness $d$.

The ordinate $b$ is simply determined by

$$b = c(\lambda, \theta_i) = RF_{\text{dry}}(\lambda, \theta_i) - a(\lambda, \theta_i)$$

which can be written as:

$$b = RF_{\text{dry}}(\lambda, \theta_i) - \beta(\lambda, \theta_i) \cdot RF_{\text{dry}}(\lambda, \theta_i) . \quad (A.4)$$
The slope $m$ is calculated by the points $(0|b)$ and $(R_t|0)$ via

$$m = \frac{y_2 - y_1}{d_2 - d_1} = \frac{0 - \left( RF_{\text{dry}}(\lambda, \theta_i) - \beta(\lambda, \theta_i) \cdot RF_{\text{dry}}(\lambda, \theta_i) \right)}{R_t - 0} = \frac{(\beta(\lambda, \theta_i) - 1)RF_{\text{dry}}(\lambda, \theta_i)}{R_t}.$$  

(A.5)

Thus, the linear relation of the dry fraction results to the second row of Equ. 7.5:

$$b = c(\lambda, \theta_i) = (1 - \beta(\lambda, \theta_i))RF_{\text{dry}}(\lambda, \theta_i) + \frac{(\beta(\lambda, \theta_i) - 1)RF_{\text{dry}}(\lambda, \theta_i) \cdot d}{m}.$$  

(A.6)

For the water-covered fraction, Lambert-Beer’s law provides again the contribution which resembles the first case of Equ. 7.5. The initial signal of this term is the same $a(\lambda, \theta_i)$, while the exponent looks different. For the exponent, again the surface roughness has to be taken into account. Within a pore, when the water level increases, the factor of the increased water level is squared for the surface area as can be seen in the following (compare Fig. A.15 a) for $A_1$ and $A_2$). This leads to a replacement of the distance $d$ from Equ. 2.21 which is here called $z$ to avoid confusion.

The water area $A$ provides the amount of water within one side of the pore and is given for instance for $A_1$ by

$$A_1 = \frac{1}{2} \cdot w_1 \cdot d_1.$$  

(A.7)

This amount of water is spread on a perfectly flat surface with the length $w$ which is determined by the highest point of the pore (compare with Fig. A.15 a)). The area of this rectangle is given by

$$A_1 = w \cdot d_{\text{eff}},$$  

(A.8)

where $d_{\text{eff}}$ is the resulting effective water layer thickness. By combining Equ. A.7 with Equ. A.8 we get:

$$d_{\text{eff}} = \frac{1}{2} \cdot \frac{w_1}{w} \cdot d_1.$$  

(A.9)
If one applies again the intercept theorem with \( d_1/R_t = w_1/w \), Equ. A.9 results into
\[
d_{\text{eff}} = \frac{1}{2} \cdot \frac{d_1^2}{R_t}.
\] (A.10)

This replacement of \( z \) by \( d_{\text{eff}} \) in the exponent is valid for \( 0 < d < R_t \). However, this is only an idealized view since this approach uses the simplification
\[
\frac{1}{n} \sum_i^n A e^{-\frac{4\pi n}{\lambda} z_i} \approx A e^{-\frac{4\pi n}{\lambda} \frac{1}{2} \sum_i^n z_i},
\] (A.11)

which is true for small \( \kappa \) and small \( z_i \) like we have it. In order to make this simplification more general, we assume that the principle behavior stays quadratic with \( d_{\text{eff}} = q d^2 \). The factor \( q \) is determined by a boundary condition. At a water height \( d = R_t \) there exists an effective layer thickness \( d_{R_t} \). Thus, \( q = d_{R_t}/R_t^2 \) and \( z \) within the exponent of Lambert-Beer’s law for \( 0 < d < R_t \) is exchanged by
\[
z = \frac{d_{R_t}(\lambda) \cdot d^2}{R_t^2 \cdot \cos(\theta_i)},
\] (A.12)

where the cosine contribution is again related to the incident angle \( \theta_i \). With Equ. A.11, also the exponent of the first case is simplified by \( d_{R_t} = R_t/2 \). The complete simplified version of Equ. 7.5 is given by:
\[
RF(d, \lambda, \theta_i) = \begin{cases} 
\beta(\lambda, \theta_i) \cdot RF_{\text{dry}}(\lambda, \theta_i) \cdot e^{-\frac{4\pi n}{\lambda} \frac{d-R_t/2}{\cos(\theta_i)}} & , d \geq R_t \\
(1 - \beta(\lambda, \theta_i))RF_{\text{dry}}(\lambda, \theta_i) + (\beta(\lambda, \theta_i) - 1)RF_{\text{dry}}(\lambda, \theta_i) \cdot \frac{d}{R_t} & , \text{else} \\
+ \beta(\lambda, \theta_i) \cdot RF_{\text{dry}}(\lambda, \theta_i) \cdot e^{-\frac{4\pi n}{\lambda} \frac{d^2}{2R_t \cos(\theta_i)}} & 
\end{cases}
\] (A.13)

In Fig. A.16, the same data as in Fig. 7.14 is fitted with the simplified Equ. A.13. It can be seen that also the simplified version describes the data very well.

The same considerations as presented above are also applicable for the three-dimensional case of the measurements, where the wet area is proportional to the water-covered grain surfaces, as shown in the following.
We assume again a triangular shape of a pore, which is in three dimensions a cone. The lateral surface area is given by

\[ A_M = s \cdot w \cdot \pi \]  \hspace{1cm} (A.14)

with the surface line \( s \) and the base radius \( w \) (see Fig. A.15 a) and c)). The base area is simply the area of a circle

\[ A_B = \pi \cdot w^2 \]  \hspace{1cm} (A.15)

We take two different water levels \( d_1 \) and \( d_2 \) and calculate the ratio of their bases and lateral surface areas:

\[ \frac{A_{B,1}}{A_{B,2}} = \frac{\pi \cdot w_1^2}{\pi \cdot w_2^2} = \frac{w_1^2}{w_2^2} \]  \hspace{1cm} (A.16)

and

\[ \frac{A_{M,1}}{A_{M,2}} = \frac{s_1 \cdot w_1 \cdot \pi}{s_2 \cdot w_2 \cdot \pi} = \frac{s_1 \cdot w_1}{s_2 \cdot w_2} \]  \hspace{1cm} (A.17)

Together with the trigonometric ratio \( \sin(\varphi) = \frac{w}{s} \), Equ. A.17 results into

\[ \frac{A_{M,1}}{A_{M,2}} = \frac{w_1 \cdot w_1 \cdot \sin(\varphi)}{w_2 \cdot w_2 \cdot \sin(\varphi)} = \frac{w_1^2}{w_2^2} = \frac{A_{B,1}}{A_{B,2}} \]  \hspace{1cm} (A.18)

This means that the base area and lateral surface area behaves the same as the lengths in the two-dimensional view, described by the intercept theorem in Equ. A.3.

Figure A.16: The same data as in Fig. 7.14 but this time fitted with the simplified Equ. A.13. The fitting parameters for a) and b) can be found in Tab. A.5 and Tab. A.6, respectively.
A.4 Ice-covered asphalt

Figure A.17: Wavelength-dependent reflectance factor for a ~ 6.3 mm thick ice layer on top of the AC 11 DS 50/70 sample. The reflectance factor at larger wavelengths does not exhibit an offset, since the trapped air bubbles are only located near the ground and most of the intensity was already absorbed within the bulk ice.

Figure A.18: Comparison of the time-dependent reflectance factor between evaporation a) and cooling run b). For both measurements, the initial water layer thickness is roughly 1.5 mm. Within the measurement accuracy, the behavior—i.e. the evaporation rate—is the same. The numbers provide the slope of each curve.
Figure A.19: Comparison of the dry curves from two different spots on the AC 5 DL 70/100 asphalt sample used during the water and ice measurement. The asphalt’s spectrum between the two spots differ by only $\sim 4\%$.

Figure A.20: Penetration depth for liquid water and ice in the NIR region. The penetration depth is calculated from data (imaginary part of the complex refractive index) for liquid water from Kedenburg et al. [25] and data for ice from Warren et al. [192].
Figure A.21: Real part $n$ of the complex refractive index from water [25] and ice [275] in the NIR. The dashed line is the ice data times the factor 1.0175.

A.5 Snow-covered asphalt

Figure A.22: Comparison of data from Warren et al. for the real part a) and imaginary part b) of the complex refractive index $N$ of ice from 1984 [192] (black) and 2008 [275] (red).
Figure A.23: Comparison of simulation results utilizing older and new recent data for $\kappa$ from Warren et al. in linear scale a) and logarithmic scale b). The solid lines are results from measurements.

Figure A.24: Albedo dependent on the particle diameter from simulations of snow in linear a) and logarithmic scale b). The incident angle is $-20^\circ$, and particle diameters from 200$\mu$m up to 900$\mu$m are investigated, while the layer thickness stays at $\sim 12$ mm. The albedo decreases with increasing particle diameter. The logarithmic scale in b) indicates that the albedo has a logarithmic dependence with respect to the particle diameter. Dashed lines are guides to the eye.
### A.6 Fitting parameters

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<th>$\lambda$ (µm)</th>
<th>$\beta$ (1)</th>
<th>$d_R$ (µm)</th>
<th>$R_t$ (µm)</th>
<th>$R_{F_{dry}}$ (1)</th>
<th>$n$ (1)</th>
<th>$\kappa$ (·10$^{-6}$)</th>
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<td>1.3142</td>
<td>97.912</td>
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</tr>
</tbody>
</table>

Table A.1: Fit-parameters from Equ. 7.5 for the fits in Fig. 7.14 a).

<table>
<thead>
<tr>
<th>$\lambda$ (µm)</th>
<th>$\beta$ (1)</th>
<th>$d_R$ (µm)</th>
<th>$R_t$ (µm)</th>
<th>$R_{F_{dry}}$ (1)</th>
<th>$n$ (1)</th>
<th>$\kappa$ (·10$^{-6}$)</th>
<th>$\theta_i$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.425</td>
<td>190</td>
<td>360</td>
<td>0.073</td>
<td>1.3249</td>
<td>3.1911</td>
<td>20</td>
</tr>
<tr>
<td>1.3</td>
<td>0.51</td>
<td>190</td>
<td>360</td>
<td>0.084</td>
<td>1.3200</td>
<td>15.950</td>
<td>20</td>
</tr>
<tr>
<td>1.6</td>
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<td>190</td>
<td>360</td>
<td>0.093</td>
<td>1.3142</td>
<td>97.912</td>
<td>20</td>
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Table A.2: Fit-parameters from Equ. 7.5 for the fits in Fig. 7.14 b).

<table>
<thead>
<tr>
<th>$\lambda$ (µm)</th>
<th>$a(\lambda, \theta_i)$ (1)</th>
<th>$c(\lambda, \theta_i)$ (µm)</th>
<th>$b$ (µm)</th>
<th>$n$ (1)</th>
<th>$\kappa$ (·10$^{-6}$)</th>
<th>$\theta_i$ (°)</th>
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</tr>
<tr>
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</tr>
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</table>

Table A.3: Fit-parameters from the empirical Equ. 7.6 for the fits in Fig. 7.15 a).

<table>
<thead>
<tr>
<th>$\lambda$ (µm)</th>
<th>$a(\lambda, \theta_i)$ (1)</th>
<th>$c(\lambda, \theta_i)$ (µm)</th>
<th>$b$ (µm)</th>
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<tr>
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Table A.4: Fit-parameters from the empirical Equ. 7.6 for the fits in Fig. 7.15 b).

<table>
<thead>
<tr>
<th>$\lambda$ (µm)</th>
<th>$\beta$ (1)</th>
<th>$R_t$ (µm)</th>
<th>$R_{F_{dry}}$ (1)</th>
<th>$n$ (1)</th>
<th>$\kappa$ (·10$^{-6}$)</th>
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Table A.5: Fit-parameters from the simplified Equ. A.13 for the fits in Fig. A.16 a).
### APPENDIX A. SUPPLEMENTARY INFORMATIONS

<table>
<thead>
<tr>
<th>$\lambda$ (µm)</th>
<th>$\beta$ (1)</th>
<th>$R_t$ (µm)</th>
<th>$RF_{dry}$ (1)</th>
<th>$n$ (1)</th>
<th>$\kappa$ (-10^{-6})</th>
<th>$\theta_i$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.425</td>
<td>360</td>
<td>0.073</td>
<td>1.3249</td>
<td>3.1911</td>
<td>20</td>
</tr>
<tr>
<td>1.3</td>
<td>0.51</td>
<td>360</td>
<td>0.084</td>
<td>1.3200</td>
<td>15.950</td>
<td>20</td>
</tr>
<tr>
<td>1.6</td>
<td>0.57</td>
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<td>1.3142</td>
<td>97.912</td>
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</tbody>
</table>

Table A.6: Fit-parameters from the simplified Equ. A.13 for the fits in Fig. A.16 b).

<table>
<thead>
<tr>
<th>$\lambda$ (µm)</th>
<th>$\beta$ (1)</th>
<th>$d_{R_t}$ (µm)</th>
<th>$R_t$ (µm)</th>
<th>$RF_{dry}$ (1)</th>
<th>$n$ (1)</th>
<th>$\kappa$ (-10^{-6})</th>
<th>$\theta_i$ (°)</th>
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<tbody>
<tr>
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<tr>
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<td>337.2</td>
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</tbody>
</table>

Table A.7: Fit-parameters from Equ. 7.5 for the fits in Fig. 8.8 b).
Now, at this point, I finally want to thank all the people who supported me during this thesis and beyond. Actually, I’m not that kind of person who can put his gratitude easily into words. However, be sure, I’m really grateful to all of you, without you this thesis would have never been written:

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• Andrea Rohwer, Dr. Micha Schilling, Dominik Günther, and Fabian Pfister for fruitful discussions and support whenever I needed some. Our more or less regular pool sessions will be missed. We made up some great expressions for things we do not know how to call them like *der Dude*. We also learned that some times the billiard cue actually is bended! However, the most shocking we learned, billiard balls do not care about physics and mostly do not follow the principle of equal incident and reflecting angle! Maybe it was still the table?

• All other group members of the Pi1, for the nice and familiar atmosphere, whenever I was there to work or discuss about some topics.

• All group members of the ECS6. You kindly welcomed me, are always interested in the topic, ready to help if there is some needed, and taught me a lot what is important within this company.

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My parents, siblings and friends who supported me during my studies all the time. You enabled me a life where I could spend so much time into my education. I’m really grateful for that. Thank you so much.
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Declaration of Originality

I hereby declare that the presented thesis with the title *Identifying Street Conditions by Infrared Spectroscopy* represents my original work. Information derived from work of others are acknowledged within the text and references listed in the bibliography.

Stuttgart, den 16.01.2020:

Andreas Baumgartner