Laser Ignition of Single Particles and Particle Clouds

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Summary

Laser ignition of single particles and particle clouds

The explosion sensitivity of dust/air mixtures is characterized by two quantities, namely the minimum ignition energy (MIE) and the minimum ignition temperature (MIT). As the terms already suggest, there is a certain minimum amount of energy required to ignite a dust/air mixture for an explosion to occur. The same reasoning applies to the minimum ignition temperature. These two quantities are currently determined with equipment, built on the basis of international standards. In this work both quantities are investigated on fundamental grounds, using a laser as ignition source. With a laser, the amount of energy per laser pulse as well as the duration of the laser pulse are accurately known.

The phenomenon of ignition is explained in detail, and the definition of ignition to be used in this thesis is formulated. A distinction is made between the homogeneous and heterogeneous ignition mode of particles. In the former mode, a envelop of flammable vapors is formed when heating the particle, and these flammable vapors subsequently ignite. This contrary to the latter mode, where flammable vapors are absent or present in negligible amount, with ignition taking place on the surface are of the particle. With these definitions, a thorough analysis of the ignition equipment currently used is possible and is presented. For the minimum ignition temperature, furnaces are used, and for the minimum ignition energy, equipment is used that applies a spark as the ignition source. The most significant shortcomings of the different equipment are identified and discussed.

For the different furnaces, the residence time of the suspended particles is the most important drawback. With increasing particle size, the residence time of the particles in the furnace decreases and thus the particles have less time to heat up to their ignition point. In order to compensate for this decrease in residence time, the furnace temperature can be increased to facilitate ignition. The minimum ignition temperature, determined with the furnaces, is therefore particle size variant.

While dispersing a known quantity of powder, the energy stored in a capacitor is discharged across two electrodes to achieve ignition. With the capacitance and voltage of the capacitor known, the minimum ignition energy can be determined. The energy efficiency of the spark method, is seriously doubted, in the sense that only a fraction of energy stored in the capacitor is actually used to heat the particles to the ignition point.

With the laser ignition technique, the principle was applied of first determining the ignition characteristics of a single particle, moving to a cluster of a few particles, before
the ignition behaviour of a cloud of particles was studied.

To establish the laser ignition technique, metal particles were chosen as sample material. The studied metals ignite in the heterogeneous mode, making a full description of the gaseous atmosphere around the particle unnecessary.

With a so-called ultrasonic levitator and an optical fiber thermometer, the temperature increase of a single particle was measured. The measured temperature transient was modeled by deriving the energy balance over the single particle. The measured transient could be accurately modeled. The particles were irradiated until they ignited, i.e. time was not a variable. Consequently, the minimum ignition temperature was found to be particle size invariant. The surface area underneath the temperature-time curve was calculated to give the minimum ignition temperature. Dividing the thus found minimum ignition energy by the volume of the irradiated particle again yielded a particle size invariant relationship. More importantly, the two explosion sensitivity parameters, thus far determined independently of each other (furnace and spark), are directly linked with each other, a direct feature of the energy balance over the particle.

The results obtained from the single particle experiments can be translated to a cloud comprised of the same particles. The minimum ignition temperature of a dust cloud is hypothesized to be equal to the minimum ignition temperature of the corresponding single particles. The minimum ignition energy can be calculated, when the number of particles comprising the critical ignition kernel is known. Multiplying the volume normalized minimum ignition energy of the single particles with the sum of the volume of the particles of the critical ignition kernel yields the minimum ignition energy for the cloud. In practice the thus determined minimum ignition energy of the cloud will be lower, due to the collective effect of the laser heated particles. This collective effect can be quantified by modeling the electromagnetic equations for absorption of laser light coupled with the heat balance equations over the individual particles and the entire volume of the dust cloud.

The T-matrix method provides the most attractive method for modeling the electromagnetic equations for absorption of laser light in a cloud of particles. The presented T-matrix model was validated for the the scattering of single particles with literature data. The model was subsequently expanded to include multiple particles.

John Zevenbergen
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Chapter 1

Statement of problem

1.1 Introduction

Explosions occur on a frequent basis in today’s world. Mainly these explosions are small in nature and cause only minor disruptions. However, the impact of the few large explosions that occur each year make us aware of the destructiveness of this phenomenon, like the ammonium nitrate explosion in France in 2001 and the numerous explosions in coal mines in China predominantly. Although mankind is aware of the existence of explosions, the accumulation of valuable lessons and the improved fundamental understanding have nevertheless not led to the banishment of the phenomenon. On the contrary, as the industrialization pace and world population keep on increasing, so does, unfortunately, the frequency of explosions. Due to the fact that industries are working with increasingly larger quantities and more concentrated facilities as much as possible, the devastating effects are bound to reach new levels.

In the field of explosion science two main research areas can be distinguished, namely ignition (explosion sensitivity) and propagation (explosion severity) research. This thesis concerns the former, with special focus on the ignition of dispersions of combustible particles. With powder dispersions in an oxidizing environment the two most important ignition parameters are the minimum ignition energy and the minimum ignition temperature. Ignition is here defined [1] as the transition from a non-reactive to a reactive state in which external stimuli lead to thermochemical runaway followed by a rapid transition to self-sustained combustion. The external stimuli must be deposited in a certain minimum volume to achieve self-sustaining combustion. Here the link between the two research areas is established, in that the minimum volume must equal or exceed the product of the typical flame thickness and speed of the propagating flame [2].

In explosion science, ignition is not regarded as the most important feature of an explosion. Ignition is simply a requirement to achieve flame propagation. This is reflected by the number of articles in literature and presentations during international conferences. At most, 10 percent of the work is devoted to ignition. At least in part because of this paucity of research, the fundamental understanding of the ignition processes is less well understood than flame propagation. This is most unfortunate, since ignition deserves the
utmost attention: without ignition there is no explosion.

In practice, 13 different ignition sources [3] for dust explosions have been identified, of which a hot surface, open flame, mechanical sparks, and static electricity are the most frequently occurring sources in industry. In order to quantify the minimum energy or temperature necessary to ignite a powder dispersion in air, test methods have been developed whose roots relate to the above mentioned ignition sources. Thus, for the determination of the minimum ignition energy, a spark system and for the minimum ignition temperature, a furnace system were developed.

Both the spark system and the furnace are rather straightforward techniques. While these techniques are easy to use and resemble practical situations well, their use does not elucidate the fundamental processes occurring during ignition, which concern the interaction between the energy added to the system and the particles, such that ignition results. For instance, with the spark system, a plasma is formed between two electrodes, and with a certain minimum amount of energy, ignition is achieved. How this plasma interacts with the particles, in the sense of how the particles absorb the energy, is not well understood. A more serious problem is the lack of reproducibility of data between different scientists using the same ignition principle.

To achieve a better understanding of the principles of the ignition techniques, two possible routes can be followed. The first route is to gain a better understanding of the current measurement methodologies. The second route is to use a different technique by which a better fundamental understanding can be obtained. The latter route is chosen by using a laser as the ignition source. As the laser light is absorbed solely by the particles, the processes involved can be studied and modeled. The technique, however, is in its infancy and as such the possibilities and limitations of the technique will become clear as the technique develops.

Finally, and perhaps most importantly, right from the start of the research, it was suspected that ignition energy and ignition temperature must be related to one another in some fundamental way. Therefore an experimental technique was sought that would enable the simultaneous measurement of both ignition energy and ignition temperature [4]. The previous Delft research [4], had made a begin with such measurements, but the results were preliminary and inconclusive. Use of a laser would, in principle at least, allow such measurements to be performed. This was a key reason to choose a laser as one of the most basic experimental tools.

1.2 Aim of project

The goal of this project is to achieve a deeper, more scientific understanding of the process of particle ignition. Fundamental to achieving this goal is, firstly, linking the minimum ignition energy with the minimum ignition temperature, and, secondly, modeling these processes.

To achieve a better understanding of the principles of minimum ignition energy and minimum ignition temperature, the absorption of the required amount of energy by the particles prior to ignition needs to be elucidated and linked with the spark and hot surface
techniques. With the aid of a laser, the amount of energy absorbed will be measured and modeled. The model describing single particle heating by a beam of electromagnetic radiation has an exact solution. By studying single particles first, the possibilities and limitations of the proposed approach will be explored, determined and validated. The model will be subsequently expanded to include more particles. With more particles, taking the collective effect of the particles on each other in the cloud, into account requires special attention to solve the models.

1.3 Thesis outline

In the next chapter the (inter)national standards for the determination of the minimum ignition temperature and minimum ignition energy are discussed. The equipment used is extensively described in detail, the links with the laser ignition technique are established, the fundamental advantages of the laser technique are outlined, and a concise introduction to the possible ignition mechanisms is presented. In Chapter 3 a literature survey is presented of all appropriate work related to the ignition of single and multiple particles. From these studies important lessons are learnt and summarized in the concluding remarks. These conclusions are subsequently used to design the laser ignition facility to be used for the experiments. The working principles of some key instruments are outlined in Chapter 4. Chapter 5 can be viewed as an interlude, describing the theory required to model the interaction of electromagnetic waves with multiple particles. In the penultimate chapter, Chapter 6, the experimental methodology and the experimental results are discussed in detail and linked with appropriate models. The thesis ends with the chapter stating the conclusions and perspectives.
Chapter 2

The Phenomenon of Ignition and its Measurement

In this chapter the current international standards for the determination of the minimum ignition energy and minimum ignition temperature are evaluated. The relationship between the fundamental mechanisms of the laser ignition technique and the standard techniques is established. The expected advantages of the laser ignition technique are discussed that can help elucidate some of the shortcomings of the international standards in view of the different ignition pathways of dust clouds.

2.1 The Concept of Ignition

2.1.1 Definition of Ignition

For most people ignition is an obvious concept. However, it becomes less obvious when a definition of this concept needs to be formulated. This contrary to the field of flame propagation, where a clear distinction can be made between a flame that propagates and the moment it ceases to do so. In a dust cloud of identical particles, if one particle ignites and combusts, may one speak of dust cloud ignition? What if this single particle ignites two adjacent particles in this cloud and these particles also combust without igniting other particles in the cloud. Is this a successful ignition or did ignition fail?

In case of gas phase explosions, ignition is achieved when sufficient energy in a certain time interval is deposited in a volume larger than the so-called critical ignition kernel, beyond which ignition and subsequent flame propagation will take place. Due to the fact that the fuel and oxidiser are both gases, these two components can be mixed on a molecular level. For dust clouds this critical kernel is more difficult to define, since the oxidiser and fuel are in separate phases. It is generally considered that in case of a dust cloud, the critical kernel comprises of a volume in which one or more particles are present. These particles need to be ignited and combust in order to ignite the rest of the dust cloud. However, this depends on particle size, interparticle distance, ignition mechanism
and heat of combustion. Hence, within one cloud, ignition kernels of different size can be identified, and a critical kernel size distribution can be constructed with as theoretical extremes (considering whole particles only), a kernel with the size of the smallest particle diameter present in the cloud and a kernel with the diameter of the entire, spherically assumed, dust cloud. However, one may argue that the critical ignition kernel can also be taken as a part of the volume of one particle present in the dust cloud. Taking this all one step further, it can be stated that the possibility of this kernel, composed of one or more particles, or part of the particle volume, igniting adjacent particles and eventually the entire dust cloud can be taken as a mere statistical process, because of the nature of the two-phase system (gas-dust). The consequence of this statement is that the critical kernel size distribution is time variant and thus that the minimum temperature or minimum energy required for sustained combustion is also time variant.

The numerous ways of defining the phenomenon of ignition, leads to numerous ways of measuring ignition, each with its own value. It needs to be stressed that the methods applied have to yield results that can be translated to practical situations.

In practice there are several external sources in practice, that enable one or more particles to absorb energy. These external sources are generally classified on the basis of the possibility to quantify the relevant ignition parameter, i.e., minimum temperature or minimum energy. In case of temperature, one can consider hot surfaces, mechanical sparks and open flames. Electrostatic sparks and pyrotechnic charges are considered as quantifiable energy sources.

The minimum ignition temperature (MIT) is therefore defined as the lowest possible temperature a certain minimum surface area needs, to achieve ignition within the time interval the particle is exposed to that area. Analogously, the minimum ignition energy (MIE) is defined as the lowest possible amount of energy deposited in a certain minimum volume within a certain time interval. From these requirements, one can see that the various external ignition sources can be compared when reference is made to the energy intensities (MIT) and energy densities (MIE), respectively.

Considering the classification of the external ignition sources (temperature versus energy) one can conclude that apparently a certain minimum temperature or minimum energy is required to achieve ignition. There seems to be no correlation between the two parameters, although this is to be expected based on the heat balance over a particle (or any volume for that matter),

\[ V_s \rho_s C_p,s \frac{dT}{dt} = Q_{in} - Q_{out} \]

(2.1)

The accumulation term gives the amount of energy absorbed by the particle (volume) as function of time. This term comprises temperature. Hence, when for instance a certain hot surface is capable of heating a particle to a certain (minimum) ignition temperature, the particle will also absorb a certain (minimum) ignition energy. These two parameters, temperature and energy, are linked. As will be seen in the following paragraphs, the current international standardized techniques (furnace for temperature and spark method for energy) do not consider this obvious link.
2.1. **THE CONCEPT OF IGNITION**

From the considerations above one can see that the concept of ignition is not only dependent on the variables involved, like particle size, but also on the definition applied. In this thesis, single particle ignition is defined as the transient state in which one particle has accumulated sufficient energy, either by absorption from an external source, like a hot surface, or by an autonomous self oxidation, i.e. pyrophoric behaviour, to reach self-sustaining combustion. This definition automatically considers the fact that sufficient oxygen must be available to facilitate this transition. This can best be visualized by the so-called Semenov diagram, see Figure 2.1. Consider a certain volume. Heat production is proportional with the third power of diameter (curved lines), while the heat loss is proportional with the second power of diameter (straight lines). Thermal equilibrium is achieved at the intersection points. A small positive distortion in temperature leads to an acceleration, and hence explosion.

![Semenov diagram](image)

*Figure 2.1: The Semenov diagram, relating heat production and heat loss.*

For dust cloud ignition, one or more particles in the direct vicinity of another need to fulfill the requirement for a single particle as mentioned above, and collectively facilitate a sustained combustion in the remainder of the cloud.

2.1.2 **Advantages of using a Laser as Ignition Source**

From the previous section it is clear that the number of variables needs to be reduced and that a careful selection of the ignition criterion is required, for quantitative analysis of
ignition phenomena. The application of a laser will meet both these demands. This can be explained as follows.

The laser ignition technique assumes the particles to be heated by absorption of the laser light, increasing the temperature of the particle surface and/or the entire particle volume, depending on conductivity and particle size, to the ignition temperature. With the laser technique the correlation between ignition energy and temperature can be shown to exist and be elucidated.

At first glance, a laser used for heating seems to have no direct link with a furnace or a spark. However, absorption of energy, through any mechanism, forms the basis for ignition and the subsequent occurrence of an explosion. With the laser technique, the actual absorption of energy by particles can be studied in detail previously impossible. Hence relevant parameters are identified and their working clarified; in this way the current ignition techniques can be better understood and evaluated. For instance, with the laser technique applied in this work, residence time is irrelevant because the particle is continuously exposed to optical radiation until it reaches its ignition point.

The ignition mechanism of particles is influenced by particle volatile matter content. With the laser technique, heating rates can be varied between the relatively slow rates achieved with the furnace technique and the higher heating rates achieved with the spark plasma. Too high heating rates can force an intrinsic homogeneously igniting particle (see next section) to ignite heterogeneously, since the characteristic time for heating the particle (surface) is shorter than that of the evolution of flammable gases. Careful selection of the heating rate is therefore required, in order to ignite the particle according to its ignition mode.

In the next section the possible ignition mechanisms will be discussed in detail. This section is followed by two sections describing the experimental techniques for determining the minimum ignition temperature and minimum ignition energy respectively. This chapter concludes with a critical discussion of the present measurement methods.

2.2 Ignition Mechanism

Dust particles can undergo two ignition mechanisms. These two mechanisms are:

- **Heterogeneous ignition mechanism.** Ignition occurs via oxidation taking place exclusively at the surface of the solid particles; no or insignificant amounts of gases and vapors are formed.

- **Homogeneous ignition mechanism.** Devolatilisation of the solid particles occurs, creating a flammable envelop around the particle; it is this gaseous mixture of flammable gases and vapors that ignites and controls flame propagation until char burning becomes the rate determining propagation mechanism.

These mechanisms are depicted in Figure 2.2 [5, 6]. In case of homogeneous ignition, the evolution of the flammable envelop around the particle and the mixing of the evolved gases with the surrounding oxidising gases are the rate controlling steps. For metals and other
2.2. **IGNITION MECHANISM**

non-volatile materials (e.g. graphite), the oxidation occurs as a heterogeneous surface phenomenon, and the reactions taking place exclusively on the surface are responsible for the ignition and propagation of the flame. For volatile (organic) materials, however, like bituminous coal or polyethylene, the ignition of the particles is determined by the rate of devolatization followed by the homogeneous oxidation of the volatile products.

Despite the ease of defining the two ignition mechanisms, in literature conflicting interpretations can be found. This is mainly caused by confusing the concept of ignition with the concept of flame propagation. An intrinsic heterogeneously igniting particle will ignite heterogeneously both for the case in which it is a single particle as well as in the case that it is present amongst other particles in a cloud. An intrinsic homogeneously igniting particle, on the other hand, can ignite either heterogeneously or homogeneously. This difference can be understood as follows. While the single particle is being heated, a flammable gaseous envelop is formed around the particle. The chance of creating a flammable atmosphere is highest in the direct vicinity of the hot particle surface. Diffusion will transport the flammable gases/vapors away from the particle surface. As the particle temperature rises, the flammable envelop will ignite, and the devolatilization and pyrolysis rates will increase due to the heating effect of the flame. Eventually pyrolysis slows as the particle loses its volatile matter and the char burning regime dictates the further combustion process. This sequence, of which the build-up to ignition and ignition play only a minor role, is the same both for the case of the single particle as well as the case of a cloud of identical particles whose interparticle distance is such that flame propagation is possible. For an intrinsic homogeneously igniting particle, but with a lower volatile matter content, it can be argued that the collective effect (increased momentum, heat and mass transfer) of the particles plays a significant role compared to the single particle. In the single particle mode, the particle can ignite heterogeneously, while it can be suspected to ignite homogeneously in a cloud formation. The reasoning is that the collective effect will generate higher amounts of volatile matter.

For volatile particles in the single particle mode, the ignition mechanism is controlled by particle size and volatile matter content. As particle size decreases, the production rate of pyrolysis products decreases ($\propto d_p^{-3}$). For small particles, pyrolysis is a volumetric process, but for larger particles it is a surface process. This has to do with several linked processes. The most important processes are temperature controlled. The larger the particle, the higher the temperature gradients within the particle, and hence the less isothermal the cracking process will be. Furthermore, with increasing particle size the probability of blocking pores due to soot formation is higher, disrupting the evolution of flammable vapors.

It is generally accepted that the volumetric pyrolysis process hypothesis is valid for particle diameters up to about 200 $\mu$m [7]. Furthermore, diffusion inside the particles is inversely proportional to particle diameter. The smaller the single particle, the higher the diffusion rate, and the lower the gaseous volumetric production rate due to pyrolysis; hence a change from the homogeneous mechanism to the heterogeneous mechanism, due to a significantly reduced or even absence of a volatile gaseous envelop around the particle. This explanation is consistent with oil droplet ignition that shows that smaller
Figure 2.2: Schematic of three different ignition mechanisms from top to bottom, as function of time. On the left a cloud of volatile matter (VM) is formed around the particle that ignites. With depletion of the volatile matter, char burning is observed. In the middle the pyrolysis rate is low. Only when the particle ignites and temperature rapidly increases, the burning volatile envelop around the particle is formed. On the right a heterogeneously igniting particle. Note that for metals, the concept of “char burning” is irrelevant [5].
droplets evaporate without ignition [8]. This can be understood as follows. With increasing distance from the particle surface, the concentration of flammable volatiles decreases, the oxygen concentration increases and the temperature decreases and hence the ignition probability decreases. In other words with increasing distance from the particle surface, the oxygen concentration will increase, whereas the temperature of the gaseous atmosphere around the particle will decrease, as described by the mass and energy balance. At a certain distance from the particle surface, where a flammable mixture is present, the probability of having a sufficiently high temperature to ignite this mixture is getting smaller.

2.3 Minimum Ignition Temperature (MIT)

Several factors play a role in the assessment of the minimum ignition temperature, as will be explained in this section. Factors like the shape of the furnace, the dispersion pressure and the homogeneity of the dust cloud inside the furnace are known to influence the determination. The most important factor, however, is caused by the residence time of the particles in the furnace. A difference of a tenth of a second in residence time can, for example, change the value of the measured minimum ignition temperature by hundred degrees centigrade, as depicted in Figure 2.3.

![Figure 2.3: Influence of residence time on the minimum ignition temperature [2].](image)
2.3.1 Godbert-Greenwald Furnace

This particular furnace was developed by A.L. Godbert and H.P. Greenwald [9] in 1935 and is the most commonly and traditionally used furnace for measurements of minimum ignition temperatures in the USA and Europe. The furnace is extensively described by Dorsett et al [10] and Field et al [11]. The International Electrotechnical Commission (IEC) investigated the performance of the Godbert-Greenwald furnace through several test series, and a number of details of the apparatus itself as well as the experimental procedure were specified more closely [12]. The resulting improved Godbert-Greenwald furnace was proposed as a standard for determining minimum ignition temperatures of dust clouds. A diagram of the improved Godbert-Greenwald furnace is shown in Figure 2.4.

The furnace consists of a 3.65 cm diameter vertical aluminum tube 22.9 cm long, wound with 6.4 m of 18 gauge Nichrome V wire, used to heat the furnace. The windings are placed closer together toward the two ends than in the middle of the tube, in order to obtain relatively even temperatures throughout the entire furnace. The tube is mounted between two 1.27 cm thick Transite plates in a 15.24 cm diameter sheet metal cylinder filled with a diatomaceous earth packing. A brass dust chamber is connected to the top of the furnace and to a solenoid valve with a copper tube. Polyethylene tubing connects the valve to a 0.5 liter pressure vessel and the vessel to a pressure gauge, which in turn is connected to an air cylinder. Temperatures are measured and controlled by means of a 22 gauge, Chromel-Alumel thermocouple placed near the vertical center of the tube wall. With this set-up, furnace temperatures up to 1000 °C can be maintained. One of the modifications made by the IEC was the incorporation of a mirror under the open end of the combustion tube. This allowed observation of the flame development within the tube.

Test Procedure

Before testing a dust sample, the thermocouples are calibrated to maintain temperature measurements with an accuracy above 500 °C of ± 1% and below 300 °C up to ± 3%. In tests the dust is dispersed into the furnace and observations are made whether or not flames appear at the bottom open mouth of the furnace, i.e., if the dust cloud ignites. The starting temperature for a dust cloud is 500 °C. If ignition does not occur, the test is repeated with fresh dust, having increased the furnace temperature with 50 °C until ignition occurs, or until a temperature of 1000 °C is reached. If ignition occurs at 500 °C, the temperature is lowered in steps of 20 °C until no ignition is obtained after 10 successive attempts. Once ignition is obtained, the mass in the dust holder and the dispersion pressure are varied until the most rigorous ignition is apparent. If for example unburnt dust is found at the bottom of the furnace, the pressure in the pressure vessel is too high, and if not all the dust is blown out of the dust holder, the pressure is too low.

The criterion for ignition consists of a burst of flame that must be clearly seen at the bottom of the tube or in the mirror, mounted below the furnace exit. A delay in time of ignition is acceptable; sparks without flames do not constitute ignition. The official minimum ignition temperature for a specific dust is recorded as the lowest temperature
of the furnace at which ignition was obtained using stated procedures, minus 20 °C above 300 °C and minus 10 °C below 300 °C. This extra safety margin is added to cope with measurement deficiencies or other effects that can influence the minimum ignition temperature.
Test Method Characteristics

When examining this particular test procedure method and the apparatus used, several deficiencies or disadvantages that can result in too high ignition temperatures become clear. Because of the open end of the furnace the dispersed dust cloud is not completely confined in the furnace, hence its concentration is not accurately known [13, 14]. Furthermore, the residence times of the powders can be too low in this type of furnace. In combination with ignition delays of dust clouds, this can result in higher minimum ignition temperatures.

Another deficiency of the Godbert-Greenwald furnace test method is also related to the fact that the furnace has an open end. This can result in uncertainty as to vertical temperature uniformity. Mittal [15] determined the temperature profile along the length of the tube by means of three thermocouples placed along the whole length of the tube. Mittal showed that near the center of the furnace the temperature is more or less uniform, the variation being less than 5 °C. The difference between the center and the bottom open end of the furnace can be as high as 20 °C, whereas that of the top is about 10 °C. This difference, however, is quite small compared to the temperature range and operation. In particular, it shows that the top section, where the dust-air mixture is immediately exposed, is at a relatively uniform temperature compared to the bottom section. Therefore, errors resulting from this deficiency are not expected to be very large.

The air which introduces the powder into the Godbert-Greenwald furnace is at room temperature. According to Palmer [16], the volume of air used to disperse the dust is usually more than half of the volume of hot air initially present in the furnace. It is not known what the specific effects are of this lowering of the overall furnace temperature. This last effect, however, is common to all other test furnaces (to be described in the following sections).

2.3.2 BAM Furnace

This furnace was developed by the BundesAnstalt für Materialprüfung (BAM), as described by Leuschke [17]. The furnace is illustrated in Figure 2.5.

This furnace is electrically heated and constructed horizontally. In the middle of this furnace a circular concave metal disk of about 20 cm² is mounted, to which the cloud of dispersed dust is directed. The apparatus consists of a dust sample chamber to which a rubber bulb (i.e., a manual dust dispersion system) is attached. The furnace is closed with a simple explosion vent, which consists of a metal disc with hinges at the top. In case of an explosion, the overpressure causes the valve to swing open sideways. Temperatures up to 600 °C are maintained and controlled with three thermocouples placed throughout the apparatus. Because of the relatively low maximum working temperature of the BAM furnace, this type of furnace is particularly used for dusts with low ignition temperatures.

The horizontal geometry of the BAM furnace allows dusts that do not ignite directly in suspension, to settle on to the hot internal bottom of the furnace and develop flammable vapors through devolatilization. These vapours can subsequently ignite at lower temperatures than those required for direct ignition of the particles. Ignition of such vapors
normally occurs with a noticeable time delay with respect to the ignition of the dispersed dust cloud. Because the BAM test method considers such delayed ignition of smouldering vapours as equivalent to direct explosions of dust clouds, this method tends to measure lower minimum ignition temperatures than the other test methods.

Recently, the Bundesanstalt für Materialprüfung [18] developed a modified BAM furnace with a few improvements with respect to the older BAM furnace. With the modified version the manual dispersion system consisting of a rubber bulb, was replaced by an automatic dust dispersion system. Also, the simple explosion vent was replaced with an explosion cap. The difference between the vent of the older furnace and the explosion cap of the newer furnace results in a more efficient and complete enclosure of the furnace volume. As such the dispersion of the dust is more homogeneous and the ignition probability is higher, compared to the older version of the furnace. Figure 2.6 displays the new BAM furnace.

Furthermore the visual criterion for a dust ignition was replaced by a set of thermocouples which measure any large temperature increase due to dust ignition. The newer BAM furnace is generally considered as better and more reliable, so in Germany the older version is no longer used. This modified version of the BAM furnace is thus now accepted as the new standard for testing minimum ignition temperatures in Germany [18].
Figure 2.6: The improved BAM furnace [18].

Test Procedure

The test method used to determine the minimum ignition temperature is very similar to the one used for the Godbert-Greenwald furnace, described in the previous section. One difference is that this furnace is heated to the desired temperature, after which the heating is turned off. Because the concave metal disc, to which the dust cloud is directed, is mounted in the middle of the furnace, the disc cools the least fast and therefore becomes the hottest item in the furnace. Temperature differences in the furnace, however, are minimal because the dust is dispersed in the furnace immediately after the heating is switched off. An explosion is determined only by visual means in case of the old BAM furnace and by means of thermocouples in case of the improved BAM furnace. Explosions too weak to cause the explosion vent to swing open are not recorded as such.

Test Method Characteristics

Because this oven is designed with an explosion vent, the dust sample is dispersed in a confined space. Since the airflow of the dispersion pressure wave does not force the dust cloud out of the furnace immediately, the dust has more time to heat up and hence the residence times of the dust in the furnace are increased. Moreover, because the furnace does not have an open end, the temperature is more uniform throughout the whole furnace. One additional advantage of this set-up is that dust concentrations are
closer to their theoretical values (by dividing the weight of dust in the dust holder by the furnace volume), than is the case with the open-ended Godbert-Greenwald furnace.

2.3.3 US Bureau of Mines Furnace

The US Bureau of Mines 1.2-L furnace was developed to compensate for the concentration inaccuracies and temperature profile non-uniformity of the Godbert-Greenwald furnace. It is described by Conti et al [13] and Figure 2.7 shows a schematic of the furnace and its receptacle.

The furnace basically consists of a 1.2 litre volume magnesium-aluminium-combustion chamber with inner dimensions of 10 cm in diameter and 33 cm in height. The chamber is wrapped with a 9.7 m length of 18-gauge Nichrome heating wire. The axial temperature gradient of the furnace is reduced by concentrating the windings toward the ends. The heated chamber is insulated with a layer of ceramic, braided cloth, covered by a sheet of metal shell 30 cm in diameter and 30 cm in height. The remaining outer volume between the wrapped chamber and its outer covering is filled with insulating material to further reduce heat losses. Four access holes pass through the furnace tube, two of which are used for Chromel-Alumel thermocouples to measure and control the furnace temperature. The two other holes can be used for various other purposes, like gas sampling systems or spark electrodes. The dust to be tested is placed in the dispenser, which is placed in the bottom of the furnace only moments before the sequence of ignition test events is started. A fibreglass rupture diaphragm covers the top part of the furnace in order to seal the furnace.

The 6.8 liter furnace, developed in the early nineties by the U.S. Bureau of Mines, can be viewed upon as an improved and larger version of the 1.2 liter furnace and is described by Conti et al [19]. Apart from the larger furnace volume, there are several improvements with respect to the design of the 1.2 liter furnace. These consist, firstly, of thermocouples facilitating improved power control, which enables more precise temperature control and measurement. Also the rupture diaphragm is replaced with a vent window, which swings open at an overpressure of 0.3 bar. The dust dispersion system also is improved by increasing the amount of channels through which the dust is dispersed into the oven. For the rest, the furnace design is identical to its smaller brother.

Test Procedure

The test procedure to determine the minimum ignition temperature of a dust sample is virtually the same as that of the Godbert-Greenwald furnace. The dust dispersion system is automated and, according to experiments carried out by Conti [13], the injected dust remains suspended at a relatively constant concentration for a time scale in the order of seconds, a longer time scale compared to the characteristic ignition delays times. Approximately 60 cm$^3$ of air at 4 bar is used to disperse the dust into the furnace, thus about half of the air initially present in the furnace. The dispersion receptacle is placed in the furnace (thus sealing the furnace volume) only moments before ignition, in order to prevent the dust sample from heating. The criterion for ignition in the thermal ignitability
Figure 2.7: Vertical cross section of the 1.2 litre US Bureau of Mines furnace [13].

tests is both the rupture of the fibreglass diaphragm (at 0.1 – 0.3 bar overpressure for the smaller furnace) and the emission of flames from the top of the furnace.
2.3. MINIMUM IGNITION TEMPERATURE (MIT)

Test Method Characteristics

A large number of deficiencies earlier mentioned (with the Godbert-Greenwald furnace) are effectively removed with the design of a furnace volume enclosed with a rupture diaphragm. As mentioned earlier, tests show that concentration and temperature profiles in the furnace remain constant for a time sufficiently long enough to ensure steady state conditions during the ignition of the dust.

2.3.4 Comparison of the Furnaces

Hensel [20] measured the minimum ignition temperatures for several dusts with different measuring techniques. The different measurement techniques used were the standard and modified Godbert-Greenwald furnaces, and the old and new version of the BAM furnace. From the results of Hensel the following details surface. For more than 90 % of the dusts, the minimum ignition temperature measured in the BAM furnaces were lower than the corresponding values of the same dusts in the Godbert-Greenwald furnaces. This difference may be due to the fact that the particle residence time in the BAM oven is considerably longer than the residence time in the Godbert-Greenwald oven. This extra residence time allows for powder devolatilisation, leading to the formation of flammable vapors, which remain enclosed in the BAM furnace due to its closed construction. It are these flammable vapors which subsequently ignite. Such flammable vapors have less chance of formation in the Godbert-Greenwald oven due to its open construction and shorter particle residence time.

In case of homogeneously igniting dusts, pyrolysis, evaporation and devolatilization processes occur on the particle surface and within the particles. Hence, instead of purely solid dust particles, one is igniting a mixture of dust particles and flammable vapors/gases. For heterogeneously igniting particles (e.g. several metal dusts), ignition takes place on the particle surface since a corresponding flammable gas phase is not or hardly present. The combination of the two characteristics of the BAM furnace, i.e. the longer residence time of and the possibility of accumulation of flammable vapors, largely explains the lower minimum ignition temperatures measured with the BAM furnaces compared to the Godbert-Greenwald furnaces.

In the longer version of the Godbert-Greenwald furnace the minimum ignition temperature is slightly lower or equal for homogeneously igniting dusts, compared to the original Godbert-Greenwald furnace. For heterogeneously igniting dusts the minimum ignition temperature is considerably lower for the longer version. For instance, aluminum powder in the short and long version has a minimum ignition temperature of 560 °C and 515 °C, respectively. The mechanisms responsible for the homogeneous ignition mode clearly hardly benefit from the increased residence time. For heterogeneously igniting dusts, where ignition needs to take place on the surface of the particles, the increased residence time allows the particles to be exposed to the high temperature in the furnace. In other words, there is more time for the particles to reach thermal equilibrium temperature with the furnace temperature, resulting in a lowered measured minimum ignition temperature.

With the BAM furnaces the exact opposite effect is observed. For heterogeneously
igniting dusts there is no significant difference in ignition temperatures between the two versions. But for homogeneously igniting dusts there are clear differences, with the newer BAM furnace giving lower temperatures. However, this difference should be ascribed more to the improved dust dispersion techniques and diagnostics for determining ignition, than to differences in ignition modes.

Conti and Cashdollar [13] measured the minimum ignition temperatures of several powders in both versions of the US Bureau of Mines furnaces. The measured data is, however, scattered, and no solid conclusions can be drawn from the experiments. Some homogeneously igniting dusts have lower ignition temperatures in the bigger vessel, whereas others have higher values.

There is no direct comparison available between all the furnaces mentioned in the previous sections. Although some powders were used both by Conti and Cashdollar [13] and by Hensel [20], a comparison is difficult. Subtle differences between the same powders, like different particle size distributions can strongly affect the experimental values. Even with the same piece of equipment, huge differences are possible. For example, the minimum ignition temperature of polyethylene is reported to be 470 °C by Eckhoff [2], whereas Mittal [15] claims the value to be 600 °C. In this case, both dust samples had comparable particle size distributions and were measured in a regular Godbert-Greenwald furnace. This example shows the difficulties that arise when trying to draw conclusions from minimum ignition temperatures originating from different sources and determined under different circumstances, even when measuring the same powder and using identical equipment.

2.4 Minimum Ignition Energy (MIE)

The determination of the minimum ignition energy, as mentioned in the standards, is done by means of a spark as the energy source. The minimum ignition energy of a dust is usually determined by dispersing the dust into a volume containing two or three electrodes, between which a capacitor discharge is triggered after the elapse of a predetermined delay time. Three standards exist, sometimes differing in subtle items like the test vessel used and the number of electrodes applied, to ensure the lowest possible spark energy required for ignition. In general there is considerable overlap between the different standards.

Test Method Characteristics

The apparatus described by the British Standard BS 5958 [21] is shown in Figure 2.8 and comprises of a 1.2 liter so-called Hartmann tube as test vessel and a two-electrode discharge system. The two electrodes, each 2 mm in diameter, have an inter-electrode gap width of 6 mm. A high-voltage DC supply raises the potential of the capacitor until a spark occurs. The cycle is then repeated, giving a series of sparks, each of the same energy. A current-limiting resistor is included in the circuit. The potential across the capacitor is measured by an electrostatic voltmeter with the decoupling resistor in series. Sparks of any energy level from 1 mJ upwards can be readily produced using this circuit.
by varying the value of the capacitor, and if it necessary, the discharge voltage. The setting for sparks of the required energy is determined before any dust is placed in the ignition chamber. A capacitor of the appropriate value is chosen, and a voltage in the range of 10 kV to 30 kV is selected. The voltage and the electrode separation are then adjusted by trial and error until sparks of the required energy occur at the electrodes. In order to perform an ignition test, the high-voltage electrode is connected to earth, and the required quantity of the dust is placed in a dispersion cup. The DC voltage supply is then switched into the circuit, and, as sparks start to pass between the electrodes, the dust is dispersed by an air jet.

![Diagram of Hartmann tube](image)

**Figure 2.8:** The Hartmann tube used for determination of the minimum ignition energy of dust as prescribed by the British Standard 5958 [21].

Both the International Electrotechnical Commission (IEC) [22] and the Verein Deutscher Ingenieure (VDI) [23] recommend the use of the Hartmann tube, as well as the use of the 20 liter explosion sphere [2]. The VDI further recommends the use of the 1 m³ explosion vessel, although this is considered to be impractical. The IEC in fact approves any test vessel to be used, provided these vessels satisfy several described calibration requirements. The IEC mentions three possible electric discharge circuits to be used. The British Standard circuit mentioned above is one of them and is designated as the trickle-charging circuit. In one of the alternative circuits, a third electrode is present perpendicular to the discharge gap. A small amount of energy stored in the main capacitor is used to pre-ionize the discharge gap, hereby reducing the resistance in the gap and facilitating the main electric discharge.
Factors influencing the spark determined MIE

The methods for creating sparks to ignite dust/air mixtures are straightforward. The goal is these methods is to determine the minimum ignition energy. However, this is dependent on many factors, some of which are not considered by the standards. The most important are mentioned here [24, 25]:

- Spark discharge duration and turbulence level
- Size and shape of electrodes
- Electrode gap

The influence of the spark discharge duration was investigated by Kono et al [26]. Depending on propane concentration in stagnant air, the discharge duration varied between 40 and 70 μs. In flowing systems [26, 27] the optimum discharge duration was found to depend, besides on fuel concentration, on the turbulence level. This can be understood as follows. The higher the turbulence level, the easier the heat of the plasma is dissipated and the lower the ignition probability. Hence the properties of the gas (ionization potential, conductivity, flow) dictate the optimum spark duration. With suspended dust clouds, the presence of the particles poses an additional difficulty.

The size and shape of the electrodes can critically affect both the quenching distance and the ignition energy through their influence on the heat loss from the spark kernel to the electrodes. The quenching distance is in this specific case defined as the maximum distance between the electrodes, that just prevents flame propagation. Ballal and Levebvre [27] found that both the quenching distance and the ignition energy increased with increasing electrode diameter. They concluded that the ignition energy will be reduced if the electrode material has low thermal conductivity and a high wear resistance. In their work, they selected and examined a wide range of materials to use as the electrode material, and they concluded that stainless steel was the most suitable one, as it combines low thermal conductivity with high wear resistance. The latter effect can be understood as follows. Which each plasma formed, the electrode tips are slightly deformed due to melting of the metal in question. The higher the wear resistance of the metal, the smaller this (microscopic) effect will be.

Kono et al [26] found that the electrode shape affects the minimum ignition energy. They performed an experiment to establish the effect of the electrode configuration using a spark gap width of 1.0 mm and a mixture of 3.0 % propane. Using an electrode with greater diameter increased the value of the ignition energy. This can be explained as follows. The electrical energy density at the end point of the electrode with a smaller diameter is higher than that of a larger electrode diameter. Hence, gas-breakdown in the spark gap using electrodes with smaller diameter will be easier as the electrode diameter decreases. An additional effect is that with a larger electrode diameter, the heat loss will increase due to a larger exposed metal area.

The next important parameter to consider is the electrode gap width. Ballal and Levebvre [28] studied the effect of the spark gap width on the ignition energy with various
inert gases. They found that the minimum ignition energy decreases with increasing electrode gap-width until a certain value. They subsequently looked at the electrode configuration and observed that by locating the electrodes with their axes parallel to the direction of the flow, the measured ignition energies were found to be lower than those measured with the electrodes perpendicular to the flow. However, when the electrodes were mounted normal to the flow, it is easier to adjust the gap between the electrodes. With the latter electrode configuration, the measured ignition energy value is also more consistent and repeatable.

2.5 Discussion

The minimum ignition temperature as function of particle size, as determined in the standardized furnaces, is influenced by the ignition mechanism of the substance in question.

Intrinsic heterogeneously igniting particles, like metals, show an increase in ignition temperature with increasing particle size [9, 2, 29, 30]. This can be understood as follows. As the particle size increases, the residence time (Godbert-Greenwald), or the suspension time (BAM), decreases, and hence the time available for the particle, or at least the critical particle surface layer, to reach the ignition temperature decreases. With critical particle surface layer is meant that heat does not have sufficient time to be transported throughout the particle volume, and reaction occurs at the particle surface, resulting in ignition. In the furnaces, temperature gradients within metal particles are small [31]. Due to the lower operating temperature of the BAM furnace, data supporting this observation exists, but is less abundant than for the Godbert-Greenwald furnace.

The dependence of intrinsic homogeneously igniting particles is more complex, see Figure 2.9 [32, 7]. Please note in this figure that the lean flammability limit is the lower limit of the range of dust concentrations in air, at which the dust/air mixture is just able to sustain flame propagation.

Based on the results of Hertzberg et al [32], Annamalai et al [8] conclude that for small, intrinsic homogeneously igniting particles in dilute clouds, the homogeneous ignition mechanism dominates. This is caused by the collective effect of the volatile particles. As the concentration of particles increases (denser clouds), the collective effects gain in strength, and the deviation from the horizontal shifts upwards at larger particle diameters [15]. Hertzberg and co-workers state that as the particle size increases, the ignition mechanism shifts to heterogeneous. However, a practical limitation might also contribute to the apparent shift in ignition mechanism with increasing particle size. Hertzberg et al [32] performed the tests in the 1.2 liter Bureau of Mines furnace. As the particle size increases, the possibility of demixing (settling of particles) increases, and in order to maintain the same level of ignition probability the temperature needs to increase. Furthermore, as the particle size increases, the number of particles decreases when the total dispersed mass is kept constant. Hence, for large, intrinsic homogeneously igniting particles, residence time is also important to correctly assess the ignition behaviour and temperature. The above mentioned ignition behaviour for intrinsic homogeneously igniting particles is in accordance with data [2, 30].
Chapter 2. The Phenomenon of Ignition and Its Measurement

Figure 2.9: Ignition temperature as a function of particle size for intrinsic homogeneously igniting particle clouds [32, 7].

The effect of furnace dimension and shape on the minimum ignition temperature was already discussed in a previous section. Summarizing that section, it can be stated that open-ended furnaces, like the Godbert-Greenwald furnace, produce higher minimum ignition temperatures than enclosed furnaces, like the BAM or the US Bureau of Mines furnace. This is due to the production of flammable vapors from settled dust particles at the bottom of the furnace, which, after some time, may also cause ignition at lower temperatures. The powder residence time is determined by the density and size of the dust particles and the furnace shape or length (the former is particular for the BAM furnace, and the latter in particular with the Godbert-Greenwald furnace). Hence the residence time is not a different parameter affecting ignition temperatures, but merely a consequence of furnace design characteristics. It should be stressed here that accurate models exist that show the ignition behaviour of dusts in furnaces, for both homogeneous and heterogeneously igniting particles, by taking the residence time and kinetics of the particles into consideration [33, 34, 35]. Wolanski [36], Hensel and Wuttig [20] and Griesche and Brandt [37] independently investigated the effect of furnace length of the Godbert-Greenwald furnace by increasing the length of the furnace and hence increasing the residence time. As the residence time increased, the minimum ignition temperature was seen to decrease drastically, in most cases even by several hundred degrees centigrade.

In contrast to this wide variation in experimentally determined minimum ignition tem-
2.5. DISCUSSION

Temperatures, the minimum ignition energy as function of particle size, as determined with the standard spark method, is hardly influenced by the ignition mechanism of the substance in question. Both heterogeneously as well as homogeneously igniting particles show an increase in ignition energy with an increase in particle size. This difference, compared to the furnaces, finds its origin in the different heating methods and thus inherent difference in characteristic time scales associated with these techniques (milliseconds for furnaces, while the time scale of a spark is in the order of microseconds).

The determination of the ignition energy is subject to much debate. Generally the minimum ignition energy is calculated with the following equation,

\[ MIE = \frac{CU^2}{2} \]  

(2.2)

where \( C \) is the capacity of the capacitor employed and \( U \) the voltage of that capacitor. Hence, the calculated energy is the energy stored in the capacitor prior to discharge. Since a capacitor will not discharge completely, this energy is not equal the energy discharged in the spark gap. The energy actually discharged in the spark gap, is equal to

\[ MIE = \int_0^{t_d} I Ud\ t \]  

(2.3)

where \( I \) and \( U \) are the current and voltage through the discharge electrode during discharge respectively and \( t_d \) the discharge duration. With each spark formed, part of the energy is not used for igniting the particles, due to the formed shock wave that is associated with the high temperature, high pressure plasma, corona formation, radiation and heat conduction of the electrodes. Hertzberg et al [32] determined that the spark efficiency, defined as the energy transferred to the test mixture divided by the energy initially stored in the capacitor, was in the order of 2 to 60 %. However, what needs to be known is the amount of energy supplied to the particles that is effectively used, i.e. absorbed by the particles, to cause ignition.
List of Symbols

$C$  
Capacity

$I$  
Current

$MIE$  
Minimum Ignition Energy

$T$  
Temperature

$t_d$  
Discharge time

$U$  
Voltage

$V_s$  
Volume of particle

$C_{p,s}$  
Heat capacity of particle

$A^2 s^4 kg^{-1} m^{-2}$

$A$

$k g m^2 s^{-2}$

$K$

$s$

$k g m^2 A^{-1} s^{-3}$

$m^3$

$m^2 s^{-2} K^{-1}$

Greek symbols

$\rho_s$  
Particle density

$kg/m^3$
Chapter 3

State of the art in laser particle ignition

This chapter gives an overview of the current knowledge on laser particle ignition. The most relevant articles are reviewed and lessons learnt from previous research are evaluated and used for designing the laser ignition facility outlined in the next chapter.

3.1 Introduction

With the laser ignition technique it is postulated that the minimum ignition temperature and the minimum ignition energy can be measured simultaneously. In this chapter literature on the laser ignition of particles is critically reviewed to clarify if this goal can be met.

For this purpose, information is acquired to elucidate the mechanism of absorption of electromagnetic radiation by particles as function of, for instance, particle size and wavelength of the electromagnetic radiation. With this information it will become clear how to include the absorption characteristics in the energy balance for a single particle as well as for a number of particles. Furthermore, if the absorption of particles is a function of temperature, this relation also needs to be established.

As mentioned in the previous chapter, the mechanism of ignition (homogeneous vs. heterogeneous) plays a crucial role in the ignition process. Especially for homogeneously igniting particles it is important to know how the pyrolysis and devolatilization processes influence the absorption of laser light. If the influence of these processes is identified, the next step will be to describe these interactions as a function of important parameters, for instance, temperature.

The power density of a laser beam is high. Attention should be paid to achieve homogeneously heating of the particles and to avoid the formation of local hot spots on the particle surface and/or inside the particle. The temperature distribution inside the particle is a function of the heat conductivity of the particle material. Hence the heat capacity and heat conductivity need to be known as function of temperature. As the power
density of the laser beam increases, the possibility of causing air breakdown increases. The maximum power density of the laser beam achievable without air breakdown needs to be established as function of wavelength.

Whenever possible, contactless heating of the particles is most desirable to avoid interaction with other objects (for instance heat sink effects). If contactless heating is possible, this automatically means that the temperature of the particles needs to be measured optically.

3.2 Absorption

Absorption, emission and scattering of radiation by particles play an important role in many engineering applications, environmental systems, astronomy as well as in our daily life. For instance, through scattering of solar radiation, clouds and other aerosols play a role in the Earth’s energy balance that is as important as that of infrared absorbing gases, in influencing climate. Light scattering also enables us to actually see the clouds in the sky.

Several textbooks are available that address the problem of absorption and scattering by particles. This chapter is to a large extent based on the books by Brewster [38], Van de Hulst [39], Bohren and Huffman [40] and Siegel and Howell [41].

The problem of radiation interacting with a particle can be solved by considering a plane, monochromatic wave incident upon a particle of a given shape, size and optical constants and applying Maxwell’s equations [42]. In 1864 James Maxwell published the now famous electromagnetic theory, giving the relation between electric and magnetic fields and optical properties of matter. The Maxwell equations for the macroscopic electromagnetic field may be written as (in SI units):

\[ \nabla \cdot \mathbf{D} = \rho_F \]  \hspace{1cm} (3.1)

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]  \hspace{1cm} (3.2)

\[ \nabla \cdot \mathbf{B} = 0 \]  \hspace{1cm} (3.3)

\[ \nabla \times \mathbf{H} = \mathbf{J}_F + \frac{\partial \mathbf{D}}{\partial t} \]  \hspace{1cm} (3.4)

where \( \mathbf{E} \) is the electric field and \( \mathbf{B} \) the magnetic induction. The electric displacement \( \mathbf{D} \) and magnetic field \( \mathbf{H} \) are defined by

\[ \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \]  \hspace{1cm} (3.5)

\[ \mathbf{H} = \frac{\mathbf{B}}{\mu_0} - \mathbf{M} \]  \hspace{1cm} (3.6)

where \( \mathbf{P} \) is the electric polarization, \( \mathbf{M} \) the magnetization, \( \varepsilon_0 \) the permittivity and \( \mu_0 \) the permeability of free space. These equations are supplemented with a set of constitutive
relations which are assumed (for an isotropic, linear, homogeneous medium) to have the form

\[ J_F = \sigma c E \]  \hspace{1cm} (3.7) \\
\[ B = \mu H \]  \hspace{1cm} (3.8) \\
\[ P = \varepsilon_0 \chi E \]  \hspace{1cm} (3.9)

where \( \sigma \) is the conductivity, \( \mu \) the permeability and \( \chi \) the electric susceptibility.

For a rigorous treatment of the scattering of radiation by a sphere of arbitrary size and optical constants, it is necessary to solve Maxwell’s equations mentioned above. In 1908, based on these equations, Gustav Mie developed his theory, resulting in the most important exactly soluble problem in the theory of absorption and scattering by a spherical particle of arbitrary diameter and complex index of refraction. The solution of the Maxwell equations goes beyond the scope of this overview and the reader is referred to the textbook of Van de Hulst [39]. The resulting expressions for extinction and scattering efficiencies are

\[ Q_e = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n + 1) Re\{a_n + b_n\} \]  \hspace{1cm} (3.10)

\[ Q_s = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2) \]  \hspace{1cm} (3.11)

and

\[ Q_e = Q_s + Q_a \]  \hspace{1cm} (3.12)

where

\[ a_n = \frac{\psi_n'(\tilde{n}x)\psi_n(x) - \tilde{n}\psi_n'(\tilde{n}x)\psi_n'(x)}{\psi_n'(\tilde{n}x)\xi_n(x) - \tilde{n}\psi_n'(\tilde{n}x)\xi_n'(x)} \]  \hspace{1cm} (3.13)

\[ b_n = \frac{\tilde{n}\psi_n'(\tilde{n}x)\psi_n(x) - \psi_n'(\tilde{n}x)\psi_n'(x)}{\tilde{n}\psi_n'(\tilde{n}x)\xi_n(x) - \psi_n'(\tilde{n}x)\xi_n'(x)} \]  \hspace{1cm} (3.14)

where \( \tilde{n} \) denotes the complex index of refraction,

\[ \tilde{n} = n - ik \]  \hspace{1cm} (3.15)

The complex index of refraction and hence the respective efficiencies are a function of temperature. In case the absorption efficiency is close to unity or in case of small temperature intervals, the effect of temperature will be small. However, for a small absorption efficiency in combination with a larger temperature interval (for instance metal particles), the temperature effect can be enormous (factor 1000 and larger) as will be shown in the next section.

The parameter \( x \) is the most important parameter of the Mie theory and is referred to as the particle size parameter, which is the ratio of the circumference of the spherical particle to the wavelength,

\[ x = \frac{\pi d}{\lambda} \]  \hspace{1cm} (3.16)
The functions $\psi_n$ and $\xi_n$ are Ricatti-Bessel functions, which obey the recursion relations

$$
\psi_{n+1}(x) = \frac{2n+1}{x} \psi_n(x) - \psi_{n-1}(x) \quad (3.17)
$$

$$
\chi_{n+1}(x) = \frac{2n+1}{x} \chi_n(x) - \chi_{n-1}(x) \quad (3.18)
$$

where

$$
\xi_n = \psi_n - i \chi_n \quad (3.19)
$$

$$
\psi_{-1}(x) = \cos x \quad \psi_0(x) = \sin x \quad (3.20)
$$

$$
\xi_{-1}(x) = -\sin x \quad \xi_0(x) = \cos x \quad (3.21)
$$

In order to be able to evaluate the scattering and absorption of radiation by a sphere, one can develop a computer program using the above mentioned equations. The only input parameters needed for such a program are the (complex) index of refraction of the particle and surrounding medium, the particle size, and the wavelength of the light. The output parameters that can be calculated are then the absorption, scattering, extinction, backscattering and radiation pressure efficiencies, the scattering angle and the albedo. The latter parameter is the ratio of scattering efficiency to extinction efficiency, which in turn, as mentioned above, is the sum of the absorption and scattering efficiencies. One can also use the book of Wickramasinghe [43]. In this book the computations have already been done and are presented in the form of a set of tables, giving results for the various light scattering functions for spherical and cylindrical particles for various values of the complex index of refraction and size parameter. In this review both the book of Wickramasinghe and an in-house developed computer program, called MIE5xQ [44], were used.

This chapter will focus on the state of the art in laser light absorption and consequent heating and ignition of particles. Albeit laser interactions with particulate matter is more than just absorption, heating and ignition, issues concerning swelling, shrinkage, devolatilization, evaporation and pyrolysis will not be dealt with in this chapter.

### 3.3 Heating

As mentioned in the previous section, it can be difficult to find optical constants at ambient conditions in literature, let alone as function of temperature. Qiu et al [45] tried to overcome this problem by using approximate methods to estimate the optical constants as well as their temperature dependence. Qiu et al show the basic principles of laser radiation incident on a particle. Due to the lack of engineering information regarding radiation absorption of particles during processes like laser cladding, they performed a numerical analysis to characterize the internal absorption of infrared laser light ($\lambda = 10.6 \mu m$) in metallic particles.

The local radiation absorption distribution of nickel particles of different particle size and the absorption efficiencies of aluminum, nickel and chromium particles of different
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particle sizes were determined, assuming that the particles did not have a thin metal oxide layer, by solving the Poynting vector (see Appendix B). Convection and conduction of heat was not taken into consideration, and the particles were assumed to be irradiated from one side only. The optical properties of the metals were evaluated using Drude's free electron theory, although care should be taken when applying this theory (see Appendix A).

Table 3.1: Complex index of refraction of aluminum, nickel and chromium determined with Drude's free electron theory and from literature

<table>
<thead>
<tr>
<th>Metal</th>
<th>Drude</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>k</td>
</tr>
<tr>
<td>Al</td>
<td>27.3</td>
<td>93.8</td>
</tr>
<tr>
<td>Cr</td>
<td>9.4</td>
<td>26.7</td>
</tr>
<tr>
<td>Ni</td>
<td>10.2</td>
<td>39.6</td>
</tr>
</tbody>
</table>

Figure 3.1 shows the spherical coordinate system used to evaluate the absorption characteristics in the metal particles. Note that the laser beam travels along the Z-axis. The cross-sectional area in the Y-Z plane is studied. The local distribution patterns were evaluated as a function of the particle size parameter and the skin-depth parameter ($\beta$). The latter parameter characterizes the mean free photon path length inside the particle and is defined as the ratio of particle diameter to the radiation skin depth ($\delta$). The incident wave is assumed to be a plane wave.

\[ \beta = \frac{d}{2\delta} \]  

(3.22)

with

\[ \delta = \frac{\lambda}{4\pi k} \]  

(3.23)
For small particles the radiation is bent around the particle surface, due to diffraction. The absorption at the back of the particle almost reaches the same value as that at the front of the particle, see Figure 3.2. This bending of radiation can be explained using Huygens' principle. Huygens visualized the effect by assuming that all points of the primary wave front were centers of secondary spherical waves. The position of the wave front at a later time is the envelope of all these secondary waves. The larger the particle size parameter the less pronounced this effect becomes. In other words, the curved surface of the sphere acts as a lens to focus the incident wave within the sphere. This figure also shows that the radiation skin depth is very small for metallic particles.

Figure 3.2: Internal intensity \((\text{V/m}^2)\) distribution of a 0.1 \(\mu\text{m}\) \((x = 0.03)\) nickel particle. The incident plane wave propagates in the positive z-direction. The polarization of the wave is perpendicular with reference to the x - z plane. Literature values for the complex index of refraction were used (Table 3.1).

Qiu et al [45] calculated the absorption efficiencies at three different temperatures, using an specified equation for the temperature dependence of the free electron in Drude's
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theory, for all metals considered (see also Appendix A):

\[ \gamma = \gamma_0 [1 + \alpha (T - T_0)] \]  

(3.24)

The absorption efficiencies for nickel particles of different particle size at the three
temperatures were compared to the absorption efficiency of a flat nickel surface with the same
cross-sectional area as the spheres in question. Due to the diffraction effect, the absolute
absorption efficiency of a spherical particle is larger than that of the flat surface. The
results show that the absorption efficiency can be normalized with respect to temperature,
independent of the particle size, using the relation for the emissivity at normal incidence
for a flat metallic surface:

\[ \epsilon_n(T) = \frac{4n}{(n + 1)^2 + k^2} \]  

(3.25)

\[ \frac{Q_a(T) - Q_a(T_0)}{Q_a(T_0)} = \frac{\epsilon_n(T) - \epsilon_n(T_0)}{\epsilon_n(T_0)} \]  

(3.26)

where \( T_0 \) is a reference temperature.

Despite the simplicity of the normalization procedure, although limited to metals only,
the complex index of refraction has to be known at the given temperatures. One could
use Drude’s theory, but, as pointed out in Appendix A, Drude’s theory can not be used
for all metals. If Drude’s theory is used, one can also apply the computer program and
calculate the efficiencies directly instead of the normalization procedure proposed by Qiu
et al [45].

Pustovalov and Bobuchenko [48] were one of the first research groups to recognize the
importance of incorporating the temperature dependence of the thermophysical properties
and optical constants of the particles which undergo high-temperature processes. To
illustrate this temperature dependence, they present the complex index of refraction of
aluminum oxide in the temperature range of 300 - 2800 K (Table 3.2). In Figure 3.3 the
absorption efficiency of spherical aluminum oxide particles, irradiated with a wavelength
of 1.06 \( \mu \text{m} \) is given. As can be seen from this figure, the absorption efficiency increases
approximately a factor 25000 as the temperature increases from 300 K to 2800 K. Note
that aluminum oxide melts at 2340 K.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Optical constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n )</td>
</tr>
<tr>
<td>300</td>
<td>1.755</td>
</tr>
<tr>
<td>900</td>
<td>1.770</td>
</tr>
<tr>
<td>1700</td>
<td>1.791</td>
</tr>
<tr>
<td>2300</td>
<td>1.809</td>
</tr>
<tr>
<td>2403</td>
<td>1.809</td>
</tr>
<tr>
<td>2800</td>
<td>1.829</td>
</tr>
</tbody>
</table>
Pustovalov and Bobuchenko propose a normalization formula for their data to describe the dependence of the absorption efficiency on particle size and optical parameters at a given temperature

$$Q_\alpha = \frac{4\pi kd}{\lambda} \left[ 1 - \exp \left( -\frac{\lambda}{4\pi kd} \right) \right]$$  \hspace{1cm} (3.27)

As indicated by Pustovalov and Bobuchenko, this normalization procedure only applies for \( k \ll 1 \) and \( n \approx \) constant. This approximation averages the resonance oscillations (concept of resonance oscillations will be explained later in this section) and has an error of \( \leq 20\% \). As expected, since aluminum oxide is not a metal, the normalization procedure proposed by Qiu [45] does not hold. As stated before, although these methods are useful, direct use of the computer program is recommended. Furthermore it can be seen that especially when the particle melts, there is a significant rise in the absorption efficiency of about one order of magnitude.

![Graph](image)

**Figure 3.3:** Absorption efficiency for given aluminum oxide particle sizes as function of temperature and \( \lambda = 1.06 \, \mu m \).

The governing set of equations and boundary conditions used by Pustovalov and
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Bobuchenko needed to solve the problem of laser heating of a single particle are:

\[
\frac{\partial (\rho C_{p,s} T)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \lambda_s \frac{\partial T}{\partial r} \right)
\]

(3.28)

with

\[
\forall r \quad t = 0 \quad T = T_\infty
\]

(3.29)

\[
\forall t \quad r = 0 \quad \frac{\partial T}{\partial r} = 0
\]

(3.30)

\[
\forall t \quad r = R \quad \frac{\partial (\lambda_s T)}{\partial r} = \frac{Q_0 I_0}{4} - h(T - T_\infty) - \epsilon_m \sigma (T^4 - T_\infty^4)
\]

(3.31)

The last boundary condition is valid in case the radiation skin depth is much smaller than the diameter of the particle. Note that the absorption efficiency is cross-sectional based (factor 4). For the heat transfer coefficient, \( h \), the Nusselt number for free convection is used:

\[
\frac{h d}{\lambda_s} = 2 + 0.59 \left( \frac{\alpha \rho c_p g (T_R - T_\infty)}{\eta \nu T_\infty} \right)^{\frac{1}{2}} \left( \frac{C_p g \eta_g}{\lambda_s} \right)^{\frac{1}{3}}
\]

(3.32)

A quasi stationary solution is obtained for diffusive-convective heat and mass transfer of a particle with the diffusion and heat transfer coefficients incorporated as function of temperature. It was assumed that the particles were heated uniformly. The time required for a quasi-stationary temperature profile within the particle is in the order of microseconds for particles in the order of 10 \( \mu m \). Hence the assumption of a uniform temperature distribution over the particle volume is valid. The model was validated by comparing the obtained results with experimental data on the evaporation of a water droplet under intense radiation of a carbon dioxide laser. In Figure 3.4 the heating and evaporation of aluminum particles of various diameter subjected to various laser intensities is depicted. All parameters in the model were calculated as function of temperature, when applicable. The particles are seen to quickly heat up until reaching the melting temperature. At that temperature the particles melt and during that process the temperature does not increase, until the particles are completely melted. Before and during melting, the evaporation of aluminum is absent. After melting, the liquid droplets of aluminum attain their steady state temperatures more quickly due to the increased laser light absorption until the particles are fully vaporized. During the melting period the density of the particle was found to decrease from 2700 to 2350 \( kg/m^3 \), meaning that the particle size needs to increase, which was confirmed by their model. This increase in particle diameter leads to an additional increase in absorption efficiency (in the order of 40 percent) due to the fact that the absorption efficiency is particle size dependent. On the other hand, during the evaporation step, the particle size will reduce due to evaporation and hence the absorption decreases, causing the particle to cool down until solidification. The model was subsequently expanded to incorporate the combustion of a solid boron particle in air.

Spjut et al [49] used limestone particles with diameters in the range 10 - 50 \( \mu m \) which were irradiated by a \( CO_2 \) laser (\( \lambda = 10.64 \mu m \)). Limestone is thermodynamically stable in its calcite form [50] and its properties are presented in Table 3.3.
Figure 3.4: Aluminum particle temperature as function of time for (1) 5 μm, (2-4) 20 μm and (5) 50 μm in case the radiation intensity in MW/cm² equals (4) 0.1, (1,2,5) 0.5, (3) 1.0 and with (6) 0.5 μm, 10 MW/cm². The solid curves represent the calculated temperatures and the dashed curves are experimental results [48].

Table 3.3: Thermophysical properties and optical constants of calcite.

<table>
<thead>
<tr>
<th>Property</th>
<th>value</th>
<th>unit</th>
<th>range</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_m$</td>
<td>0.96</td>
<td>-</td>
<td>*</td>
<td>[51]</td>
</tr>
<tr>
<td>$C_{p,s}$</td>
<td>$1044.3 + 0.219T - 25.92 \cdot 10^6 \ T^{-2}$</td>
<td>J/kg/K</td>
<td>298 - 1000 K</td>
<td>[52]</td>
</tr>
<tr>
<td>$\bar{n}$</td>
<td>1.65 - 0.026i</td>
<td>-</td>
<td>n.a.</td>
<td>[53, 54]</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>$2715.1 - 2.0 \cdot 10^{-3} \ T - 4.85 \cdot 10^{-5} \ T^2$</td>
<td>kg/m³</td>
<td>298 - 973 K</td>
<td>[55]</td>
</tr>
<tr>
<td>$\lambda_s$</td>
<td>$11.76 - 3.9 \cdot 10^{-2} \ T + 3.76 \cdot 10^{-5} \ T^2$</td>
<td>W/m/K</td>
<td>298 - 523 K</td>
<td>[56]</td>
</tr>
</tbody>
</table>

*) Effect of temperature on emissivity negligible

For sake of simplicity, Spjut et al assumed the absorption efficiency to be equal to 1
and neglected the heat loss due to thermal radiation, reducing the energy balance to:

\[ \rho_s C_{p,s} V \frac{dT}{dt} = \frac{\pi d^2 I_0}{4} - 2\pi dh(T - T_\infty) \]  

(3.33)

which can be analytically solved to:

\[ (T - T_\infty) = \theta_{eq} \left( 1 - \exp \left[ -\left( \frac{t}{\tau} \right) \right] \right) \]  

(3.34)

with

\[ \theta_{eq} = \frac{I_0 d}{8h} \]  

(3.35)

and

\[ \tau = \frac{\rho_s C_{p,s} d^2}{12h} \]  

(3.36)

With this set of equations two response characteristics of the calcite particles were modeled, i.e., the time needed for the particles to reach a fixed equilibrium temperature (500, 1000 and 1500 K) and the laser radiation flux required to reach a given temperature in air as function of particle size. It was shown that smaller particles require higher fluxes than larger particles and that the actual flux required could be obtained by dividing the modeled laser flux by the actual absorption efficiency. The followed methodology has some errors. From a practical point of view, calcite decomposes at 1171 K [50] and because of this an equilibrium temperature of 1500 K is not realistic. The chosen particle size range is critical in the sense that resonance effects between the internal and external electromagnetic field are dominant, as can be seen in Figure 3.5. As such, temperature gradients will appear within the particle, a phenomenon underestimated by Spjut et al. This shows that, despite the ease of the model of Spjut et al, in order to model the interaction of electromagnetic radiation with particles, all relevant properties need to be taken into account.

Foss and Davis [57] studied the transient laser heating of a small spherical particle. The effects of conduction, convection and radiation are studied and possibly occurring photophoretic forces are discussed. Photophoretic forces are caused by internal temperature gradients. The gas in the direct vicinity of the particle will be heated differently depending on the local absorption characteristic of the particle and hence particle surface temperature. Due to a difference in kinetic energy between cooler and hotter gas molecules, the photophoretic force will be directed towards the cooler gas molecules. Hence special attention was paid to the nonuniform internal heat source due to laser light absorption and the non-linear radiation heat transfer at the particle surface. The numerical problem solved by Foss and Davis can be described by the following relations:

\[ \rho_s C_{p,s} \frac{\partial T}{\partial t} - \nabla \cdot (\kappa \nabla T) = Q(r; \theta, \phi) \]  

(3.37)

The assumptions made are that the material properties are temperature dependent, the gas phase material properties spatially invariant and particle rotation around its axis is
**Figure 3.5:** Absorption efficiency of calcite particles as function of particle diameter ($\lambda = 10.64 \ \mu m$).

absent. For the heat source, $Q$, the time averaged Poynting vector is used, see Appendix B. The boundary condition at the particle surface is given by:

$$\forall t \quad r = R \quad -\kappa(T)\frac{dT}{dr} = h(T)(T - T_\infty) + \varepsilon\sigma(T^4 - T_\infty^4) \quad (3.38)$$

To determine the heat transfer coefficient a Taylor expansion of the Nusselt number for the Peclet number was applied.

Four cases were studied. The first is infrared heating ($\lambda_0 = 10.6 \ \mu m$) of a small, strongly absorbing, low conductive carbon particle with a particle size parameter equal to around 6. It is shown (Figure 3.6a) that all the absorption takes place at the surface of the particle and a small peak appears at the shadow side of the particle (180°) due to the lens working of the particle. The second case assumes the same particle exposed to visible radiation ($\lambda_0 = 488 \ \text{nm}$) and hence a large particle size parameter ($x = 128.75$) due to a significant reduction in wavelength. The penetration of the laser light is limited to the skin depth and hence is in the order of nanometers (Figure 3.6b). For the third case a weakly absorbing silicate glass particle with a large particle size parameter ($x = 128.75$) in the same visible laser source as case two was assumed. The absorption of laser light is concentrated at the shadow side of the particle due to focusing lens working of the particle (Figure 3.6c). The shadow side of the particle will therefore have a higher temperature than the illuminated side and thus negative photophoresis effects will take place. In case the particle size parameter is reduced to 38.3, second order resonance effects are observed (second order in terms of two peaks in the radial direction) in the particle and the front...
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(Figure 3.6d) and shadow side show about the same order of absorption. Foss and Davis conclude that in order to reduce the magnitude of the photophoretic force, in practice the particle should be irradiated from two, opposite sides. It should be noted that in the figures presented so far, only the interaction of electromagnetic waves with the particles is considered. Heat transfer is not considered.

![Figure 3.6](image)

**Figure 3.6:** Electromagnetic field characteristics of carbon particles [(a) and (b)] and silicate particles [(c) and (d)] with different particle size parameters (see text). The incident plane wave propagates in the positive z-direction. The polarization of the wave is perpendicular with reference to the x-z plane.

For inclusion of the heat transfer, the above mentioned general equations were solved in
a standard finite difference method as it solves the equations implicitly in one direction by using the explicit values in the other direction [57]. The computational methods were validated by solving the equations numerically for one specific point using Green’s function. From the results it could be seen that relatively strong absorbing, conductive particles (carbon) have small and smooth temperature gradients within the particle, compared to weakly absorbing, poor conductive silicate particles. It was shown that, depending on the absorption properties, laser intensity, particle size and particle material properties, particles of several tens of micrometers in diameter will reach their steady state values in less than one millisecond. Hence, laser heating is a fast and effective method for heating up particles.

Monazam and co-workers [58, 59] used a 50 W continuous wave (cw) CO₂ laser to heat SpheroCarb particles with diameters between 50 and 150 μm. SpheroCarb particles are spherical, amorphous carbon particles with an elemental carbon content of 95% on a dry basis. The particles were suspended in an electrodynamic balance and were heated with laser pulses of 3 ms at a repetition rate of 100 Hz. The laser beam coming from the laser was split in two beams to uniformly heat the particles from both sides. The experimental setup was used to show the determination of the heat capacity by the pulsed laser heating of the particles and continuously measuring the temperature of the particles. From the periodic temperature oscillations accompanying the heating and cooling cycles of the particle, the heat capacity can be determined. The particle surface temperature was measured using a single-wavelength pyrometer.

The heating and cooling cycles of the particles were modeled using Equations 3.37 and 3.38. For the heat transfer it is assumed that the Nusselt number for convection in a stagnant medium was applicable (\(Nu = 2\)). Applying the Nusselt number for free convection, showed that the heat transfer coefficient would increase, depending on particle size with 3 to 9 percent. The incident radiation was assumed to be homogeneously absorbed over the entire particle surface. Although not correct, Foss [57] showed that the heat conduction inside the particle is of such order that the temperature gradients within the particle are small. This was confirmed by the model of Monazam that showed that the maximum gradient during the cycle was in the order of 30 K and time-averaged in the order of 15 K. This error will be compensated for by not using the free convection Nusselt number. The set of equations was put in non-dimensional form and solved using an implicit Crank-Nicholson scheme. To determine the stability of the numerical solution a sensitivity analysis of the model parameters was performed and included the incident laser intensity, pulse duration, gas thermal conductivity and particle diameter among others. Monazam and co-workers show through their model that the dominant factor in the energy balance of the particle is the amount of energy absorbed by the particle. Under steady-state conditions this term is about 3 to 4 times larger than the convective term in the energy balance. The radiation term is an order of magnitude lower than the convective term in the temperature interval employed (800 - 1250 K).

The particle surface temperature at the beginning of the experiment increased several hundred Kelvin during one laser pulse. Varying the gas composition in the electrodynamic balance will result in different steady state temperatures of the particles and hence the
temperature dependence of the heat capacity can be determined. In Figure 3.7 the measured steady state particle surface temperature is compared to the modeled temperature predictions with the heat capacity of the particle as a fit parameter. The fitted heated capacity compared well to literature values with an accuracy of within 10 percent.

![Graph showing surface temperature over time](image)

**Figure 3.7**: Measured steady state particle surface temperatures (dots) compared to modeled temperature predictions (solid line) with the heat capacity as fit parameter for a Spherocarb particle [59].

The method applied is only applicable to non-volatile substances. Volatile particles will devolatalize and may even start swelling. A size change leads to morphological resonances as light waves within the particle undergo constructive and destructive interactions and hence differences in absorption characteristics. Swelling particles will undergo density differences, causing another uncertainty in the determination of the heat capacity. Due to the transient changing composition of heated volatile particles, several pseudo steady state temperatures can be reached, obstructing a unambiguous determination of the heat capacity.

Widmann and Davis [60] analyzed the data of Monazam and co-workers to incorporate the non-uniform absorption and hence heating of the particles. The numerical model explained in more detail the origin of some of the discrepancies found by Monazam and co-workers.

Tuntomo et al [61] studied the internal distribution of radiant energy to elucidate the absorbed radiant energy in fuel droplets to enhance the efficiency of a spray combustion system and the safety of medical irradiation treatment of cancerous cells. For the latter
goal, the absorbed energy should be uniformly delivered to the cell instead of localised peaks. For this purpose the classical electromagnetic wave theory was used as well as the geometric optics approach. The latter method was used because of its ease of use and to determine the restrictions of the approximate technique. For the electromagnetic wave theory the same methodology was adopted as adopted by Qiu et al [45]. Special attention was given to the location of the highest concentration of absorbed radiant energy as a function of particle size parameter and complex index of refraction applicable to fuels cells and tissue cells. In Figure 3.8, depending on particle size parameter and complex index of refraction, a map can be made comprising uniform heating (difference between minimum and maximum not more than 10 percent), particle front heating and particle back heating (Huygens principle). As can be seen, for a fixed complex index of refraction, the larger the particle size parameter, the more nonuniform the distribution of the absorbed light becomes. This is highlighted in Figure 3.9. Comparison is made with the geometric optics approach. As is known [38] the geometric optics approach is only valid in case $x \gg 1$ and $x|n-1| \gg 1$ and as such the top two distributions of the geometric optics approach are seriously deviating from the actual (electromagnetic wave) distributions. This discrepancy is due to diffraction (top picture) that occurs with small particle size parameters as well as resonance effects (middle picture) which are not considered by the geometric optics approach.
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approach.

\[ m = 1.5 + 0.1 \]
\[ x = 0.5 \]

\[ m = 1.5 + 0.1 \]
\[ x = 10.0 \]

\[ m = 1.5 + 0.1 \]
\[ x = 100.0 \]

\[ m = 1.5 + 0.1 \]
\[ x = 0.5 \]

\[ m = 1.5 + 0.1 \]
\[ x = 10.0 \]

\[ m = 1.5 + 0.1 \]
\[ x = 100.0 \]

(a) (b)

Figure 3.9: Comparison of the internal absorption distribution obtained via (a) the electromagnetic wave theory and (b) the geometric optics approximation for various particle size parameters [61].

Maloney et al [62] looked at the coal devolatilization process at high heating rates. Coal particles, suspended in an electrodynamic balance were heated with a Nd:YAG laser from opposite sides to ensure uniform heating. Delivered fluxes were in the order of 10 to 11 MW/m². Heating rates of the coal particles, varying in particle size between 110 and 127 μm, were in the order of 10⁵ K/s with laser pulses varying from 3 to 10 ms. Particle surface temperatures were measured using a black-body calibrated, single-wavelength pyrometer. For the modeling the same methodology as Monazam et al [58, 59] was adopted. It was shown that the coal particles started to rotate just after the start of the heating pulse (1.6 - 1.8 ms) with surface temperatures of about 900 K. This rotation is primarily due to the evolution of volatile gases that act as localized jets on the particle surface. After 3 to 4 ms after the start of the laser pulse, intense volatile evolution occurred and the particles started to swell up to 30 percent of their original size. No ignition was observed.
This can be understood as follows. With increasing distance from the particle surface the temperature decreases, lowering the probability of ignition. The agreement between the model and the experimental results of Maloney et al was poor. This is probably caused by inconclusive particle property data and oversimplification of the model in relation to the devolatilization process. The fact that neither the particles nor the gas phase surrounding the particles ignited can likely be contributed to the devolatilization process, as follows. The particles have an intrinsic homogeneous ignition mode. The evolution of flammable gases continued after irradiation by the laser pulse ended. It can be assumed that the concentration of oxygen near the particle surface and in the pores of the particles is insufficient to allow combustion (i.e., concentration of flammable vapor phase greater than the upper explosion limit). The evolved gases were therefore not within the flammable range and/or the absorption efficiency of the gases at this wavelength was insufficient (similar to a small oil droplet that evaporates without ignition, see Section 2.2). More detailed information is, however, required to elucidate the observed results with more certainty.

Astaf’eva [63, 64, 65, 66, 67] published several articles on modeling the interaction of laser light with particles, most notable two-layered particles. This research is especially of interest when studying the ignition of metallic particles that naturally have a thin oxide layer. It was shown that under high laser intensity (> \(10^{10} \text{ W/m}^2\)) gradients in the core of the particle (polystyrene particles with an aluminum shell) prior to melting can be in the order of several hundred degrees centigrade. As soon as somewhere in or on the particle surface the melting point temperature of the substance in question was reached, the calculations were stopped. Typical times were in the order of nanoseconds. It should be noted that Astaf’eva and co-workers considered one-sided heating only. All particles in the models were dispersed in an inert environment. For the two-layered particles the particle size, shell size (directly related to the penetration skin depth) and the radiation intensity influence the degree of non-uniformity. It was shown that for the highly conductive layer (the shell of the particle) the temperature gradient is small compared to the low conductive core of the particle. For metallic particles the oxide layer is thin and has a high penetration depth and high absorption efficiency compared to the pure metallic particles. As such the effect of the oxide layer was considered to be negligible on the heating process of the metallic core.

Longtin et al [68] modeled the heating dependence of one-sided irradiated, highly absorbing particles (platinum) as a function of pulse duration to obtain a uniform temperature distribution inside the particles (\(T_{\text{max}}/T_{\text{avg}} = 1.0\)). It was shown that, as the particle size increases a factor ten, the minimum pulse duration increased a factor hundred. For a 10 \(\mu\text{m}\) particle the minimum pulse duration was 2 \(\mu\text{s}\).

### 3.4 Ignition

Qu et al [69] studied the ignition and combustion of single coal particles subjected to heating from a carbon dioxide laser. The particles were spread onto the center of a silicate plate, see Figure 3.10. Low laser power (1.66 - 2.96 \(\text{MW/m}^2\)) was used to prevent the
ignition of the volatile gases surrounding the particles. This can be understood as follows. The lower the laser power, the more time available for the mass transfer mechanisms to dilute the evolved gases and hence prevent occurrence of a homogeneous, gas phase ignition. The heating rate of the particles was in the order of 3000 K/s for the highest laser power used. Graphite and coal particles in the size range of 100 to 550 micron were used. The atmosphere in the test chamber could be varied in oxygen concentration between 0 and 100 percent. A typical ignition and subsequent sustained combustion process of a graphite particle can be seen in Figure 3.11.

Figure 3.10: Experimental set-up used by Qu et al [69].

In phase II, designated the ignition stage by Qu et al, the oxidation reactions of the particles accelerate, and the rate of pyrolysis will exponentially increase during this period until sustained combustion is reached, phase III. When the atmosphere in the test chamber was replaced by pure nitrogen it could be seen that volatile coal particles reached their equilibrium temperature faster (200 to 1200 ms depending on volatile matter) than the graphite particles (around 1300 ms), confirmed by modeling the laser heating process of the particles with aid of Equations 3.37 and 3.38. The higher absorption efficiency of coal and the change in size and thus density of the coal particles due to swelling contribute to the more rapid heating of the coal particles. No results on the ignition temperature of the various coal grades and/or as function of particle size were given.

Zhang et al [5, 70] used a continuous 1.2 W Nd:YAG laser (wavelength 1.06 μm) with a variable output power to heat 6 different coal ranks, varying in volatile matter content, see Table 3.4. With aid of an optical fiber the radiation was delivered to the particles of
Figure 3.11: Temperature transient of a laser heated particle. Stage I, initial heating; stage II, ignition; stage III, sustained combustion. Stages of a 200 μm graphite particle in 50 % oxygen [69].

different sizes. The core of the fiber, delivering the laser power, had a diameter of 100 μm. After exiting the fiber, the beam expanded with an angle of 16.8 °C. The purpose of the research was to determine the minimum required optical power (in W) to ignite the particles as function of coal rank and particle size. The particles were sieved into three size fractions, i.e. 45 - 63, 75 - 90 and 106 - 125 μm, respectively. By moistening the end of the fiber, the particle to be ignited was "attached" to the fiber end. After ignition and combustion of the particle in question, the fiber was cleaved to ensure a clean fiber end for the next experiment. The optical output from the fiber, measured with a calorimeter, was fixed at 150 mW, equivalent to 18 MW/m². The ignition of a particle was defined as a visually observed flash, irrespective of the controlling mechanism (heterogeneous or homogeneous).

Three different phenomena were observed:

- The coal rank with the highest volatile matter (VM) content required the shortest heating time, i.e. in the order of 10 ms. Smoke was emitted from the heated particle after turning on the laser, believed to be condensation of volatile matter outside the particle. The smoke emission was followed by ignition, creating a yellow flame that enveloped the particle. Subsequently the yellow flame and the particle became a brightly combusting ball.

- Coal 1 and 2 ignited on the particle surface after about 15 ms with a bright flash. A small amount of smoke was emitted from the particle before ignition. After ignition the smoke emission increased considerably and the oxidation process continued as
Table 3.4: Analysis of the six different coal ranks [70].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size fraction (μm)</th>
<th>Moisture (%)</th>
<th>Ash (%)</th>
<th>VM (%)</th>
<th>Fixed Carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal 1</td>
<td>45 - 63</td>
<td>3.1</td>
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<td>0.7</td>
<td>0.7</td>
<td>98.4</td>
</tr>
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</table>

A yellow flame. Somewhat later the smoke emission ceased and the yellow flame turned into a bright flame on the particle surface.

- The coals with the lowest volatile matter content required the longest radiation period (20 ms) before ignition was observed as a flash on the particle surface. No smoke emission was observed and the particle burned brightly.

A schematic of these three ignition modes can be found in Chapter 2, Figure 2.2. Please note that the ignition delay times mentioned above are related to the particle size fraction of 75 – 90 μm. The critical amount of laser power required to achieve ignition was determined by varying the power level in steps of 5 mW such that in at least 10 successive attempts the particles attached to the fiber did not ignite. In Figure 3.12 the results are shown for coal 1 and char 1. It was found that the required optical power decreased with an increase in volatile matter content and a decrease in particle size. The results are summarized in Table 3.5.

The determined laser power is high and can not be regarded as the power absorbed by the particle. There are several effects that play a role in this heating process. The fiber itself can act as a heat sink while the particle is heated from one side only. The radiation emerging from the fiber does not necessarily have a uniform distribution. The expanding beam also needs to be taken into consideration as was done by Zhang and co-workers. Unfortunately the particle surface temperature was not measured and the
Figure 3.12: Critical optical powder required for ignition of Coal 1 (top) and Char 1 (bottom). Solid dots indicate non-ignition, open dots indicate ignition. Please note that the results are related to the largest particle in the given size fraction. [5].

Table 3.5: Critical laser power to visually observe ignition. The value given is related to the the largest particle in the given size fraction [70].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Critical Optical power (mW)</th>
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<tr>
<td></td>
<td>Size fraction µm</td>
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<td>65</td>
</tr>
<tr>
<td>Petroleum coke</td>
<td>190</td>
</tr>
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</table>

The data provided make the recalculation of the actual ignition temperature with a sufficient level of confidence impossible.

Chen et al [71, 72] used a partly transparent upward-flow wind tunnel in which particles of known size were dropped. The flow in the test facility was laminar and the oxidising gas was at room temperature. A pulsed Nd:YAG laser was used as the ignition source. The laser operated at a frequency of 5 Hz, a laser pulse of approximately 150 µs and a pulse energy variable up to 720 mJ. The residual energy left in the beam after the
first passage through the tunnel was, using two prisms, returned into the tunnel through the same focal point. It was estimated that 60 % of the initial pulse energy reached the focal point with the first pass and about 40 % with the second pass. Ignition was detected by means of a photomultiplier tube. The set-up is depicted in Figure 3.13. Particles of carbon, anthracite and high-volatile bituminous coal were used for the ignition experiments. Using Equations 3.28 to 3.31 and assuming the absorption efficiency equal to 0.8, the temperature distribution within the particle was modeled. The model assumed one-sided heating of the particle. It was shown that for a 150 μm particle the temperature gradient inside for the given pulse duration was in the order of 1000 K. As the particle size decreased, the temperature gradient decreased in steepness. After switching off the laser (end of laser pulse) the gradient inside the particle disappeared after about 400 μs. As the particle size decreased or the laser pulse energy decreased the time required for reaching equilibrium also decreased. However, their model did not include the transition to oxidation processes, since the modeled surface temperature due to absorption only was in some cases well in excess of 2000 K. Chen et al. state that a possible explanation for this would be the too short laser pulse for any significant reaction to take place, because heating is confined to the particle surface. However, for heterogeneously igniting particles, ignition will always take place at the particle surface, since no other reaction locations are possible. The statement by Chen et al. that oxidation reactions do not play a significant role during heating is correct and this is confirmed by their experiments. However, the surface temperatures are considered to be on the high side, especially since the gaseous environment were oxygen enriched atmospheres (75 % oxygen or higher). In a subsequent model oxidation processes are taken into account to establish the ignition criterion, defined by Chen et al. as that temperature of the particle above which the heat generation due to reaction exceeds the heat losses. This critical temperature was about 1600 K. This modeled critical (ignition) temperature is regarded to be on the high side.

Typical signals from the photomultiplier tubes are shown in Figure 3.14. In the top picture, for the carbon particle, the first peak, arbitrarily set at 5 ms, corresponds to the rapid heating of the particle surface. The rapid drop corresponds to the laser being turned off and rapidly decreasing particle surface. After some time another signal increase is observed, attributed to combustion of the particle. As mentioned by Chen et al., the picture suggests that there is a certain delay time between heating and ignition. However, this was explained to be caused by operational aspects of the photomultiplier tube. As the temperature increases, the emitted light from a particle will shift to shorter wavelengths. Since the photomultiplier tubes respond to light in the range of 300 to 650 nm, it would be expected that the second peak would be higher than the first one. However, to prevent saturation of the tubes, the operating voltage of the tubes was changed such that saturation did not occur and hence the strange behaviour of the tube during the heating period of the particle. However, laser induced sparking (see Chapter 4) and hence formation of a plasma should not be ruled out and could possibly explain the phenomena observed by the tubes.

It was observed that anthracite particles fragmented upon heating by the laser pulse. This was ascribed to the large temperature gradients within the particles. The carbon
Figure 3.13: Experimental set-up used by Chen et al [71, 72] for their laser ignition experiments.

particles, however, were found not the shatter. This was explained by either the gradients were less severe or that the tensile strength of the anthracite particles is lower. The latter explanation seems to be more likely. The high-volatile bituminous coal was seen to ignite homogeneously. With an oxygen concentration of 75 % the ignition temperature was measured to be 1050 K. This deviates strongly from the above mentioned modeled ignition temperatures. It was also observed that several closely spaced particles ignited, creating a large burning volatile cloud that subsequently ignited more particles until a cloud containing tens of particles burned steadily, since the feeding of particles continued during this phenomenon. From these observations it can be concluded that more than one particle needs to ignite in order to ignite an entire particle cloud.

Pogodaev [73] determined the heating times with a carbon dioxide laser, required to ignite coal particles that were spread on a silver-coated object. The laser power used was in the order of 2 MW/m². The particles were first seen to ignite with a flash that lasted for several milliseconds followed by an extinction phenomenon and further increase in temperature. This is typical for the homogeneous ignition pathway. The first flash is caused by the burning volatile cloud around the particle while the subsequent phenomenon is char burning. It was shown that one-sided heating of the coal particles led to the particles being propelled away from the direction of the laser beam with a velocity in the order of up to 6 m/s upon ignition and subsequent combustion. As the particle surface
became more irregular, the possibility of particle fragmentation was seen to increase, due to the formation of local hot spots. It was shown that particles with a diameter in the order of 1 micron only burn after ignition as long as they are continuously irradiated by the laser. This is due to the larger heat losses compared to heat production of the very small particles, relative to larger particles.

Bukaty and Sutorikhin [74] reported results on laser ignition and subsequent combustion of soot and coal particles with aid of a carbon dioxide laser varying in intensities between 1.3 and 2.1 \( MW/m^2 \). The particle diameter varied between 20 to 250 \( \mu m \). It was shown that a minimum laser intensity was required to reach ignition as a function of particle size. This minimum increased with decreasing particle size. As the particle diameter and hence the particle size parameter decreases, the absorption efficiency also decreases. As the laser intensity increased, the tendency of fragmentation of the particles increased, practically irrespective of particle size.

Liebman et al [75] levitated magnesium particles in an electrodynamic levitator in the size of 28 to 120 \( \mu m \) and irradiated them with a pulsed Nd:YAG laser. The critical
laser intensity was seen to increase with increasing particle size, due to the higher mass of the particles and thus high heat capacity. The Nd:YAG laser, having an unknown pulse energy, had a pulse width of 900 $\mu$s. The laser output pulse was seen to be composed of several spikes lasting several microseconds on the oscilloscope. This kind of behaviour could indicate laser induced sparking (see Chapter 4) although this was not as such noticed by the authors. The levitated particles were seen to slowly rotate with a speed of about 1 cm/s, meaning that for the duration of the laser pulse the particle moved about 10 microns. While heating the particles, the ignition was accompanied by a fast growth of the luminous zone, larger than the particle diameter itself. The authors concluded that a considerable amount of magnesium was vaporized prior to ignition and that ignition took place in the vapor phase. Also fragmentation of the particles was observed, contributing to the formation of the luminous zone, due to large temperature gradients (150 K for the largest particle diameter) existing within the particles. Ignition temperature was believed to be equal to the boiling point of magnesium (1400 K). Particle motion in the direction of the laser beam was observed and ascribed to the nonuniform heating, vaporization and ignition of the particles. The absorption efficiency was fixed at 0.3. However, the absorption efficiency was calculated using Fresnel type of equations for flat surfaces [41]. Recalculating the absorption efficiency for the particles under the given conditions with the program developed by Boxman [44] gives values in the order of 0.08, slightly particle size dependent. This is almost of factor 4 less than the value the authors used. The use of a strong Nd:YAG laser is known to create so-called laser induced sparks. These sparks can fragment particles and form a plasma. In most cases "seeding material" in the air facilitates the formation of the plasma. In this case, the magnesium particles can act as seeding material and the particles will be engulfed in the plasma, where temperatures will be well above the boiling point of magnesium. Since multiple spikes where seen on the oscilloscope, a different heating mechanism (absorption versus creation of hot plasma) can be responsible for the observed phenomena.

Mohan and Williams [76] experimentally determined the ignition and combustion mechanisms of crystalline and amorphous boron, and hypothetical models were derived to explain the observed phenomena. The study was of practical interest because of the possible use of boron in rocket propulsion systems. Roughly spherical particles were held at the tip of a glass fiber and ignited by means of a 1 J, 600 $\mu$s Nd:YAG laser pulse. Mixtures of oxygen and argon in mole ratios of 20/80 and 50/50 in the pressure range of 0.75 to 1.5 atmosphere were used as gaseous environments. Boron particles were seen to spin with a speed of around 250 rps, caused by the nonuniform heating and burning of the particles. The particles had diameters in the range 50 to 150 $\mu$m. Boron has the feature of a sharply decreasing thermal diffusivity as the temperature increases and hence facilitating the creation of steeper and steeper temperature gradients within the particle as the particle is being heated. In the boron oxide that is formed during oxidation, the oxygen transport is not rate controlling, but the transport of the oxide itself to the atmosphere very much so. This layer plays a dominant role in the ignition sequence. For a boron particle initially at ambient temperature and pressure, the modeled ignition temperature is constant up to 200 $\mu$m. With further increasing particle diameter the ignition
3.4. **IGNITION**

As the initial temperature of the gaseous environment increases, the particle diameter up to which the ignition temperature remains constant, decreases. This behaviour is attributed to two different oxidation mechanisms, the low and high temperature oxidation mechanisms. The thickness of the oxide layer therefore influences the ignition behaviour.

Wong et al [77] suspended char particles in an electrodynamic balance and heated the particles from one side with a carbon dioxide laser pulse of 420 ms. The particles used were 158 to 210 μm Spherocarb particles and 200 to 300 μm char particles from a bituminous coal. The achieved heating rates were in the order of 4500 K/s. The particle surface temperature was measured using a dual-color pyrometer. As soon as the particles ignited they dropped out of the balance. The ignition process was modeled using Semenov’s thermal explosion theory, that states that in order to have ignition the heat of reaction should equal or exceed the heat losses. The carbon dioxide laser beam intensity had a donut shaped profile, compared to the traditional Gaussian profile. The reasoning for this beam mode was that thermophoretic and photophoretic forces, due to heating, will push the particle away from that part of the beam where the intensity is highest. In case of the donut shaped profile the particle will remain in the low-intensity center of the beam. However, the profile influences the modeling of the beam, due to the clear non-uniform profile. As such the absorption efficiency of the particles was determined by heating the particles in a nitrogen environment and by fitting a model to the acquired temperature profile with the absorption efficiency as the fitting parameter. In Figure 3.15a the temperature traces in different gaseous environments are depicted. The oxygen concentration in the levitator was increased stepwise by intervals of 5%. Spherocarb particles ignited in an atmosphere containing 40 % oxygen. In case of 20 % oxygen, it can be seen that the steady state temperature is higher than in a pure nitrogen atmosphere. This was ascribed to slow surface oxidation reactions that increased the surface temperature. As can be seen from the bottom picture, as soon as the particle ignites and starts burning, the stability decreases due to loss of unified charge and hence drops out of the levitator. In Figure 3.15b the temperature traces of a 300 μm char particle are depicted. In the middle picture, a dip is observed in the temperature trace. This is caused by the movement of the uneven char particle in and out the focus of the pyrometer. No explanation for the duration of the ignition delay time was given by the authors. It is believed that the duration is composed of two effects, i.e., that of oxygen depletion and the emission of pyrolysis products near and at the particle surface. The delay time will have to decrease as the oxygen concentration is increased. No data is available to confirm this hypothesis.

Marion et al [78] and Legrand et al [79] ignited and combusted electro dynamically levitated aluminum particles in air under high pressure. Ignition and combustion behaviour of aluminum particles is of special interest since it is being used as an additive in rocket propulsion formulations, hence the high pressures applied in this study. To achieve these high pressures, the electrodynamic balance was placed in a high pressure chamber, allowing optical access. A 20 W carbon dioxide laser was used as the heating source and the optical system allowed dual-sided heating of the particles. A two-color pyrometer was used to measure the signals coming from the particle without recalculating this to a
Figure 3.15: Temperature traces for (a) 198 µm Spherocarb particle and (b) 300 µm char particle in different gaseous media. Solid lines present measured temperature traces and dashed lines represent the temperatures Wong et al calculated with their model [77].

particle surface temperature. Particle diameters varied between 35 and 70 µm. Ignition was seen to start locally somewhere on the particle surface and spread over the entire surface in less than 1 ms.
3.5 Conclusions

Studies on laser heating of single particles are well documented. No articles were found that include the laser heating of multiple particles. Information on laser ignition of single particles is difficult to find and only one article mentions the laser ignition of multiple particles, although this was not within the scope of that particular study.

The complex index of refraction should be known as a function of wavelength and temperature in order to model the heating process correctly. Approximate techniques estimating the optical constants are useful within their limited applicability range, but even there prone to considerable errors. Alternatively the absorption efficiency can be measured by placing the particles in question in an inert environment and fitting the model to the data points with the absorption efficiency as a fit parameter, under the conditions that the particles do not swell and that under atmospheric conditions the devolatilization and pyrolysis processes do not interfere. Other characteristics of the substance, such as density and conductivity, need to be known as function of temperature. Taking this into consideration, the temperature dependent properties are reasonably well documented for metals, metal oxides, alloys, carbon and a few organic substances. Oxides are irrelevant in this discussion since they are already in an oxidized state and will therefore not ignite. Alloys can be considered after the pure components composing these alloys are studied.

The particles should exhibit a large skin depth to avoid local hot spots that can destabilize or even fragment the particles. Alternatively, the particles should be small (maximum 10 micron) to make up for the small skin depth or have a high conductivity. Most organic particles have a high skin depth, but a low conductivity. Metals have a high conductivity, but a small skin depth. However, the conductivity of most metals is more than appropriate enough to equalize the temperature within the particle under laser heating, despite the small skin depth. In case of small skin depth and low conductivity, small particles seem logical, but this depends on the particle size parameter. If the particle size parameter is close to unity, resonance oscillations will occur within the particle, facilitating hot spot formation. Furthermore, the smaller the particles, the smaller the absorption efficiency. In order to avoid photohoretic forces, the particles needs to be heated from an even number of beams from multiple, opposite directions. From a practical point of view, a two beam construction is easily created and has proven to be appropriate.

The model for single particle laser heating is established and proves to be an accurate representation of the observed phenomena, as long as the temperature dependencies are carefully considered. The thermal radiation term can be neglected in cases temperatures are below circa 1000 °C. The absorption term can be up to one order of magnitude larger than the convective heat loss term, depending on particle properties (size, absorption efficiency) and laser intensity. For high conductive particles in the size range considered (up to 1000 μm) the characteristic time to reach steady state is smaller than 1 millisecond. For the experimental facility this means that the laser pulse required to reach the ignition point should be longer than 1 millisecond to facilitate the internal conduction processes, avoiding large temperature gradients. Furthermore, the smaller the pulse duration, the higher to probability of laser induced sparks. Nd:YAG lasers are generally operated in the
pulse mode, with laser pulses generally lower than 1 millisecond. These lasers are therefore less appropriate for ignition studies. The profile of the beam should approximate that of a planar wave as much as possible to ensure a uniform energy distribution across the beam cross section. Changes in particle size during heating are undesirable. Swelling of particles with increasing temperature will always occur, due to the volumetric expansion. With organic particles the swelling due to devolatilization and pyrolysis, hereby emitting gases, is several orders of magnitude larger than their natural volumetric expansion. This will affect the absorption characteristics, heat capacity and so on. Most metal particles are not affected by these processes. The effect of naturally present oxide layers on metal particles on the absorption characteristics and heat transport processes has proven to be negligible.

The most appropriate experimental set-up will comprise a levitating device. Herewith non-particle related transport phenomena (like heat sink effects) are avoided. The electrodynamic balance is useful for heating purposes, but the particles leave the instrument as they reach their ignition point, because of loss of a unified charge that ensures their levitating capabilities. To increase the stability of the particles, the shape of the particles needs to be as spherical as possible. This shape requirement will also lower the fragmentation possibility of the particles. With non-contact experiments required, an optical temperature measurement device is needed to measure the particle (surface) temperature.

Thusfar ignition temperatures of single particles were not established, but at best minimum optical power levels required for ignition were determined. The required optical power is wavelength dependent, because of the specific absorption bands of the heated objects in question. The applicability of the values is therefore limited.

**List of Symbols**

\[
\begin{align*}
  a_n & \quad \text{Mie coefficients} \\
  B & \quad \text{Magnetic induction} \\
  b_n & \quad \text{Mie coefficients} \\
  C_{p,g} & \quad \text{Heat capacity of bulk gas} \\
  C_{p,s} & \quad \text{Heat capacity of particle} \\
  c & \quad \text{Speed of light} \\
  D & \quad \text{Electric displacement} \\
  d & \quad \text{Particle size} \\
  E & \quad \text{Electric field vector} \\
  g & \quad \text{Gravitational acceleration} \\
  H & \quad \text{Magnetic field vector} \\
  h & \quad \text{Heat transfer coefficient} \\
  I_0 & \quad \text{Initial intensity laser light} \\
  J_F & \quad \text{Free charge current density vector} \\
  k & \quad \text{Imaginary part refractive index} \\
  M & \quad \text{Magnetization}
\end{align*}
\]
3.5. CONCLUSIONS

\[ \tilde{n} \quad \text{Complex index of refraction} \]
\[ n \quad \text{Real part refractive index} \]
\[ P \quad \text{Electric polarization} \]
\[ p \quad \text{Skin-depth parameter} \]
\[ Q \quad \text{Heat source term} \]
\[ Q_a \quad \text{Absorption efficiency} \]
\[ Q_e \quad \text{Extinction efficiency} \]
\[ Q_s \quad \text{Scattering efficiency} \]
\[ R \quad \text{Particle radius} \]
\[ r \quad \text{Radial coordinate} \]
\[ S \quad \text{Normalized source function} \]
\[ T \quad \text{Temperature} \]
\[ T_\infty \quad \text{Temperature of gas bulk} \]
\[ T_0 \quad \text{Reference temperature Drude's model} \]
\[ t \quad \text{Time} \]
\[ x \quad \text{Particle size parameter} \]

**Greek symbols**

\[ \alpha \quad \text{Temperature coefficient} \quad K^{-1} \]
\[ \beta \quad \text{Radiation skin depth parameter} \quad - \]
\[ \gamma \quad \text{Relaxation frequency free electron} \quad s^{-1} \]
\[ \gamma_0 \quad \text{Initial relaxation frequency} \quad s^{-1} \]
\[ \delta \quad \text{Radiation skin-depth} \quad m \]
\[ \epsilon \quad \text{Complex dielectric function} \quad - \]
\[ \epsilon_0 \quad \text{Electric permittivity of free space} \quad A^2 s^4 kg^{-1} m^{-3} \]
\[ \epsilon' \quad \text{Real part dielectric function} \quad - \]
\[ \epsilon'' \quad \text{Imaginary part dielectric function} \quad - \]
\[ \epsilon_b \quad \text{Bound component dielectric function} \quad - \]
\[ \epsilon_b' \quad \text{Real part bound dielectric function} \quad - \]
\[ \epsilon_f \quad \text{Free component dielectric function} \quad - \]
\[ \epsilon_f' \quad \text{Real part free dielectric function} \quad - \]
\[ \epsilon_f'' \quad \text{Imaginary free dielectric function} \quad - \]
\[ \epsilon_m \quad \text{Emissivity of particle} \quad - \]
\[ \epsilon_n \quad \text{Emissivity at normal incidence} \quad - \]
\[ \phi \quad \text{Spherical coordinate} \quad - \]
\[ \eta_g \quad \text{Dynamic viscosity of bulk gas} \quad kg m^{-1} s^{-1} \]
\[ \kappa \quad \text{Thermal conductivity} \quad kg m s^{-3} K^{-1} \]
\[ \lambda \quad \text{Wavelength laser light} \quad m \]
\[ \lambda_g \quad \text{Thermal conductivity of bulk gas} \quad kg m s^{-3} K^{-1} \]
\[ \lambda_s \quad \text{Thermal conductivity of particle} \quad kg m s^{-3} K^{-1} \]
\[ \mu \quad \text{Magnetic permeability} \quad kga^{-2} s^{-2} \]
\[ \mu_0 \quad \text{Magnetic permeability of free space} \quad kga^{-2} s^{-2} \]
\[ \xi_n \quad \text{Ricatti-Bessel function} \quad - \]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<tr>
<td>$\rho_g$</td>
<td>Density of bulk gas</td>
<td>$kg m^{-3}$</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Density of particle</td>
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<td>$\chi$</td>
<td>Electric susceptibility</td>
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<tr>
<td>$\chi_n$</td>
<td>Ricatti-Bessel function</td>
<td>–</td>
</tr>
<tr>
<td>$\psi_n$</td>
<td>Ricatti-Bessel function</td>
<td>–</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Circular frequency of laser light</td>
<td>$s^{-1}$</td>
</tr>
<tr>
<td>$\omega_p$</td>
<td>Plasma frequency of free electron</td>
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Chapter 4

Development of the Laser Ignition Facility

The findings from the previous chapter are used to create the most optimal experimental set-up. The advantages and disadvantages of the separate elements of the set-up will be discussed, determining the feasible experimental program.

4.1 Acoustic levitation

4.1.1 Introduction

The use of levitators for contactless, non-intrusive processing has a long history. The electrostatic levitator was the first levitator to be developed. In 1909 Millikan [80, 81] measured the charges of oil droplets in air by finding the electric field which balances each drop against its weight. King [82] was the first to develop the rigorous theory of acoustic levitation. This work will be used for as the basis for the next section.

4.1.2 Working principle of the acoustic levitator

Acoustic levitation [83] is a technique that enables contactless levitation of samples by means of a standing sound wave. By means of a piezoelectric crystal a piston is brought into vibration which causes a sound wave. A reflector is present opposite to the vibrating piston. The reflector can be moved along the z-axis by means of the micrometer adjustment screw, which enables the variation of the distance between the vibrating piston and the reflector. When the distance between the vibrating piston and the reflector is a multiple of the half of the wavelength of the sound wave, a standing wave will appear, see Figure 4.1. Solid (but also liquid) samples with effective diameters of less than half the wavelength of the sound wave will be contactlessly levitated below the pressure nodes as a result of axial radiation pressure and radial Bernoulli stress. The axial force in the levitator is also known as the levitation force because it provides the necessary force to
compensate gravity during levitation. Under the assumption of a planar sound wave, the acoustic levitation force in a gaseous environment for particles significantly smaller than the wavelength can be derived as follows [84, 85]:

\[ F_l = \frac{5}{6} (\pi R^2) \rho_p \nu_p^2 (kR) \sin(2kz) \]  \hspace{1cm} (4.1)

Rewriting this equation and balancing the resultant equation with the gravitational force gives

\[ F_l = \frac{5}{8} k \rho_p \nu_p^2 V_p \sin(2kz) = g \rho_p V_p \]  \hspace{1cm} (4.2)

where \( k \) is the wave number according to

\[ k = \frac{2\pi}{\lambda} \]  \hspace{1cm} (4.3)

Because samples of interest have a finite size, a correction should be made. Leung et al [86] calculated the size factor by not taking the limit \( x \to 0 \) for the surface integration leading to the levitation force. The size factor is given by

\[ f(x) = \frac{3}{x^2} \left( \frac{\sin x}{x} - \cos x \right) \]  \hspace{1cm} (4.4)

where \( x \) is the dimensionless sample radius and is calculated by

\[ x = 2kR \]  \hspace{1cm} (4.5)
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Equation 4.2 can now be rewritten as

\[
F_i = \frac{5}{6} (\pi R^2) \rho g \nu_g^2 (kR) \sin(2kz) f(x) = g \rho_p V_p
\]  
(4.6)

A sample under levitation is not located exactly in the pressure nodes, as noted before, but is slightly displaced downward. When inspecting Equation 4.2 this is logical because at \( z = 0 \) the resulting levitation force is zero and gravitation is not compensated for (see Figure 4.2). The displacement can be calculated using

\[
z = \frac{1}{2k} \sin^{-1} \left[ 8 \frac{\rho g}{k} \left( \frac{\rho_p \nu_g^2}{k} \right)^{-1} \frac{1}{f(x)} \right] \leq \frac{\lambda}{8}
\]  
(4.7)

The fact that the maximum displacement is \( \frac{\lambda}{8} \) follows from the fact that at this point the levitation force is maximal in a given sound field. When the displacement would be larger no extra stability is gained because the levitation force decreases with increasing displacement.

![Diagram of acoustic pressure, velocity, and levitation force in an ultrasonic standing wave](image)

Figure 4.2: Acoustic pressure, velocity and levitation force in an ultrasonic standing wave [83].

The sound field in the levitator was assumed to consist of a plane wave. This is not entirely true due to the limited dimensions of the vibrating piston. The sound field is divergent in nature which causes a radial force on the sample. This radial force is significantly smaller than the axial force, but provides the necessary force to locate the sample in one point. This force is calculated by its ratio to the levitation force, using the relation given by Lierke [87]:

\[
\frac{F_i}{F_r} = 4.35 \frac{k \sin 2kz}{k_r \sin k_r r}
\]  
(4.8)
For the size of the levitated samples a minimum, a maximum and an optimum exists. The optimum is found by differentiation of Equation 4.6 to the dimensionless sample diameter $x$:

$$
\frac{dF_1}{dx} = \frac{15}{6} \pi R^2 \rho g v_2^2 \sin(2kz) \frac{d}{dx} \left[ \frac{1}{x} \left( \frac{\sin(x)}{x} - \cos(x) \right) \right] = 0
$$

(4.9)

This results in an optimal sample diameter of one third of the applied wavelength.

$$
d_{\text{p,opt}} = \frac{\lambda}{3} = \frac{c}{3f_\lambda}
$$

(4.10)

**Acoustic streaming**

Between the nodes and antinodes in the ultrasonic levitator a finite pressure difference is present. Inevitably this results in flow, in this particular case better known as acoustic streaming.

The acoustic streaming phenomenon near a solid boundary can be described with Nyborg’s theory [88, 89]. For this purpose the second-order momentum equation is written as

$$
\nu_g \nabla^2 u_2 = \nabla p_2 - F
$$

(4.11)

with

$$
F = -\rho_g \nabla \cdot (u_1 u_1) = -\rho_g (u_1 \cdot \nabla u_1 + (u_\nabla \cdot u_1))
$$

(4.12)

in which $\nu_g$ is the viscosity of the medium, $u_2$ and $p_2$ are the steady second-order velocity and pressure, respectively, $\rho_g$ is the constant medium density, $u_1$ is the first-order particle velocity. The velocities are taken as the average over a wave cycle, $u_1$ is irrotational everywhere and furthermore:

$$
\nabla \times F = 0
$$

(4.13)

The viscosity outside the boundary layer can be neglected, since most of the dissipation occurs inside the boundary layer, which is a fair assumption since primary interest is focused on a standing wave in an enclosure of a finite volume, such that wave attenuation in the bulk is not important. The momentum equation for streaming is therefore:

$$
\nu_g \nabla^2 u_2 = \nabla P
$$

(4.14)

together with

$$
\nabla \cdot u_2 = 0
$$

(4.15)

we have obtained the equations for steady streaming. The following task is the determination of the boundary conditions.

On the surface where the acoustic velocity has tangential components such that friction occurs and a thin boundary layer exists:

$$
u_2 = u_L
$$

(4.16)
where the limiting velocity \( \mathbf{u}_L \) is tangential to the surface. However, on the surface where the acoustic velocity does not have tangential components the no-slip condition is imposed:

\[
\mathbf{u}_2 = 0
\]  

(4.17)

The function \( \mathbf{u}_L \) contains information of compressibility. In deriving Equations 4.11 or 4.14 it has been assumed that the Reynolds number \( Re \) for the steady streaming flow is sufficiently small.

With the general equations mentioned above, we will now calculate the outer streaming around a sphere in a plane standing wave. The \( z \) axis passes through the center of the sphere with radius \( R \) and points along the direction of vibration. The origin of the coordinate system is at the velocity antinode closest to the sphere. To find \( \mathbf{u}_L \), the velocity on the sphere surface needs to be determined. Let the acoustic pressure of the incident wave be

\[
p_i = Re[p_{i0}\exp(-i\omega t)]
\]  

(4.18)

where

\[
p_{i0} = A\sin kz = A\sin(kr\cos \theta + z)
\]  

(4.19)

in which \( Z \) is the \( z \) coordinate of the sphere and \( k = \omega / c \). We need to find the scattered field

\[
p_s = Re[p_{s0}\exp(-i\omega t)]
\]  

(4.20)

such that the normal derivative \( (\partial p / \partial n) \) of the total field on the rigid sphere is zero. We only need to know the pressure field on the sphere surface because the velocity does not have a normal component there. This gives:

\[
p_{a0} = A\left[ \sin kZ + \frac{3}{2}(kR)\cos kZ\cos \theta - \frac{5}{6}(kR)^2\sin kZ\cos^2 \theta - \frac{2}{9}(kR)^2\sin kZ \right]
\]  

(4.21)

Obviously, the velocity does not have a \( \phi \) component. For the velocity on the particle surface the following relation can be derived

\[
\mathbf{u}_1 = Re[u_{a0}\mathbf{e}_\theta \exp(-i\omega t)]
\]  

(4.22)

resulting in

\[
u_{a0} = -3kA(2i\omega p_0)^{-1}\left[ \cos kZ\sin \theta - \frac{10}{9}(kR)\sin kZ\cos \theta \sin \theta \right]
\]  

(4.23)

and subsequently the following relation is obtained:

\[
\mathbf{u}_L = -45A^2(16\omega R \rho_s c^3)^{-1}\left[ \cos^2 kZ\sin \theta \cos \theta - \frac{2}{9}(kR)\sin kZ\cos kZ\sin \theta (13\cos^2 \theta - 3) \right]
\]  

(4.24)

The term with the factor \( kR \) on the right side represents the compressibility effect arising from the displacement of the sphere from the velocity antinode.
Because of the continuity equation (Equation 4.15) and the absence of the \( \phi \) component, \( u_2 \) can be treated in terms of a scalar function \( \Phi \) as

\[
 u_2 = \nabla \times \nabla \times (\Phi \mathbf{r}) \tag{4.25}
\]

where \( \mathbf{r} \) is the position vector of a spatial point. Substituting Equation 4.25 in Equation 4.11 and taking the curl of both sides we obtain

\[
 \nabla^2 \nabla^2 \Phi = 0 \tag{4.26}
\]

Then, from Equation 4.25,

\[
 u_2 = \frac{1}{r} \frac{\partial \Phi}{\partial r} + \frac{\partial^2 \Phi}{\partial r \partial \Theta} \tag{4.27}
\]

and

\[
 u_2 = \frac{L^2 \Phi}{r} \tag{4.28}
\]

where

\[
 L^2 = -\frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \sin \Theta \frac{\partial}{\partial \Theta} \tag{4.29}
\]

is an operator that has the Legendre polynomials \( P_n \) as its eigenfunctions with the corresponding eigenvalues \( n(n + 1) \).

Since \( u_2 = 0 \) and \( u_2 = u_L \) on the sphere surface the boundary conditions for \( \Phi \) at \( r = R \) are:

\[
 \Phi = 0 \tag{4.30}
\]

and

\[
 \frac{\partial^2 \Phi}{\partial r \partial \Theta} = u_L \tag{4.31}
\]

As \( r \to \infty \), \( \Phi \) does not approach zero. The solution is:

\[
 \Phi = \frac{45 A^2}{32 \omega p_k c^2} \left[ \frac{1}{3} \cos^2 k Z \left( \frac{R}{r} \right)^3 \right] P_2(\cos \Theta) + \frac{4}{45} (kR) \sin k Z \cos k Z \left[ 1 - \left( \frac{R}{r} \right)^2 \right] P_1(\cos \Theta) - \frac{52}{135} (kR) \sin k Z \cos k Z \times \left[ \left( \frac{R}{r} \right)^2 - \left( \frac{R}{r} \right)^4 \right] P_3(\cos \Theta) \tag{4.32}
\]

such that

\[
 u_2 = \frac{45 A^2}{32 \omega R p_k c^2} \left[ \frac{2}{3} \cos^2 k Z \left( \frac{R}{r} \right)^4 \frac{\partial P_2}{\partial \Theta} \right] + \frac{4}{45} (kR) \sin k Z \cos k Z \left[ \left( \frac{R}{r} \right)^3 + \frac{R}{r} \frac{\partial P_1}{\partial \Theta} \right] - \frac{52}{135} (kR) \sin k Z \cos k Z \left[ 3 \left( \frac{R}{r} \right)^5 - \left( \frac{R}{r} \right)^3 \right] \frac{\partial P_3}{\partial \Theta} \tag{4.33}
\]
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\[ w_2 = \frac{45A^2}{32\omega R_0^2 c^2} \left[ 2\cos^2kZ \left( \frac{R}{r} \right)^2 - \left( \frac{R}{r} \right)^4 \right] P_2(\cos\Theta) \]
\[ + \frac{8}{45} (kR)\text{sinkZcoskZ} \left[ \frac{R}{r} - \left( \frac{R}{r} \right)^3 \right] P_1(\cos\Theta) \]
\[ - \frac{208}{45} (kR)\text{sinkZcoskZ} \times \left[ \left( \frac{R}{r} \right)^3 - \left( \frac{R}{r} \right)^5 \right] P_3(\cos\Theta) \] (4.34)

In order to show this in graphical form the Stokes stream function \( \psi \) is introduced:

\[ u_2 = -\frac{1}{r \sin\Theta} \frac{\partial \psi}{\partial r} \] (4.35)

and

\[ w_2 = -\frac{1}{r^2 \sin\Theta} \frac{\partial \psi}{\partial \Theta} \] (4.36)

The function can be shown to be

\[ \psi = \frac{45A^2R}{32\omega p_0^2 c^2} \left[ \frac{1}{3} \cos^2kZ \left[ 1 - \left( \frac{R}{r} \right)^2 \right] \sin\Theta \frac{\partial P_2}{\partial \Theta} \right. \]
\[ + \frac{4}{45} (kR)\text{sinkZcoskZ} \left[ \frac{r}{R} - \frac{R}{r} \right] \sin\Theta \frac{\partial P_1}{\partial \Theta} \]
\[ \left. - \frac{52}{135} (kR)\text{sinkZcoskZ} \left[ \frac{R}{r} - \left( \frac{R}{r} \right)^3 \right] \sin\Theta \frac{\partial P_3}{\partial \Theta} \right] \] (4.37)

The streamlines are plotted for the cases a spherical particle is positioned in the center of a velocity antinode (Figure 4.3) and positioned midway a velocity node and velocity antinode (Figure 4.4) respectively.

Due to acoustic streaming the heat and mass transfer from and to particles in a levitator will be enhanced, as function of position, i.e., at the equator of the sphere the transfer will assume a maximum while at the poles the transfer will be lowest. For heat and mass transfer ([90, 91, 92, 93]), the average enhancement (averaged over the particle surface) amounts a factor 5 to 10 over the normal diffusion regime.

4.1.3 The Dantec/Invent levitator

The Dantec/Invent ultrasonic levitator [83] works at a frequency of 58 kHz in ambient air. Hence the wavelength is approximately 5.9 mm. According to theory, the largest particle to be suspended is in the order of 3 mm, while the smallest particle is around 15 \( \mu \)m. The levitator is designed for applications with solid and liquid samples with densities in the range of 0.5 – 2.0 g/cm\(^3\). The large dynamic range of the levitation force allows however short time levitation experiments with heavy samples having significantly higher densities. In the levitator a maximum of 7 pressure nodes exist and hence a maximum of 7 particles can be levitated simultaneously. Only the inner three pressure nodes can be used for stable levitation. The outer four nodes are influenced by destabilising effects
from the transducer and the reflector. Particles with diameters larger or equal to two thirds of the wavelength can not be levitated.

Due to sound absorption, a radial and axial temperature profile exists, similar to the energy density profile in the standing wave field. As a result thereof, a levitated particle will be heated up to the equilibrium temperature existing at the levitation position. These temperature effects are usually small and negligible. With the current frequency of 58
kHz, a temperature increase at the pressure nodes of maximum 0.5 °C is possible [83].

4.1.4 Two-dimensional levitator

One can argue that one single particle does not make a dust cloud and hence a single particle levitator, as described in section 4.1.3, is not answering the initial questions on dust particle cloud ignition. However, as will be shown in the later chapters, the concept of single particle ignition experiments actually forms the core of all ignition concepts, regardless of the ignition source. In collaboration with the group of Apfel [94] an improved

Figure 4.5: Two-dimensional Acousto-electric levitator.

version of their two-dimensional acousto-electric levitator was fabricated [95], see Figure 4.5. The two-dimensional levitator is composed of three major parts: an acoustic system, an electromagnetic system and an observation system. The acoustic system has a horn shaped sandwich transducer, a focusing reflector and a test chamber. Their structures are illustrated in Figure 4.5. The transducer consists of two aluminum hollow cylinders, one aluminum horn and two 2 inch diameter, 1/8 inch thickness PZT hollow disks (Channel Industries, Inc., CA). All of these elements are held together by a central bolt. The resonance frequency of this transducer is 27 kHz. The total wavelength of the transducer is about one wavelength. An 1.75 inch diameter, 1/8 inch thickness aluminum disk is attached to the tip of the horn to increase the radiation area. The design of the reflector has to meet two requirements: it should provide a method to detect the sound pressure during the experiments, and the observation of the test sample from the top should be possible. As shown in Figure 4.6, a small glass window is built at the apex of the reflector.
Between the glass plate and the shell of the reflector there is a poly-vinylidene fluoride film (Atochem North America, Inc., Pa) which works as an acoustic probe. The PVDF is connected to an oscilloscope for the monitoring of the maximum stability of the standing wave. A small hole is cut at the center of the PVDF probe thereby permitting the observation of the test sample from the top. The observation and recording of the test sample is accomplished with the use of a CCD camera, which is connected to a television. Both the acoustic transducer and reflector are placed inside a test chamber. This chamber is carefully sealed with a thin sheet of plastic wrap. Hence the acoustic wave can propagate from the inside to the outside. The alignment between the transducer and reflector is accomplished by micro-positioners. The whole acoustic system is seated on a vibration-isolated table. The transducer is connected to a function generator, which in its turn is connected to an amplifier. The function generator generates the required frequency needed for the optimum standing wave within the levitator. The amplifier produces the required radiant pressure for levitation. The function generator is also connected to the oscilloscope. The electromagnetic system exists of a high voltage supply that can generate up to 3000 Volts. The positive pole is connected to the reflector and the ground pole (negative pole) is connected to the amplifier and thus connected to the function generator and oscilloscope. Through this way the transducer is connected to the ground and has a charge of 0 Volt. By charging the reflector an electric voltage is obtained between the tip of the transducer and the reflector.
4.1.5 Three-dimensional levitator

The two-dimensional levitator is a clear improvement over the single particle levitator in terms of simulating a dust cloud. In order to obtain the missing third dimension, two approaches can be followed. The first approach is described by Colver et al [96], albeit the technique used is not a pure levitation technique as described in the previous sections. The so-called Electrostatic Particulate Suspension (EPS) method produces steady-state clouds of high uniformity as confirmed by using laser beam attenuation techniques in both horizontal as vertical direction, see Figure 4.7. The suspension is sustained by accelerating particles between parallel plate electrodes. The test section vibrates to facilitate the break-up of clusters of cohesive particles. The method can be used for insulating powders exhibiting a finite surface conductivity and to high conductivity metals. The particles in the test chamber can have velocities up to 10 m/s, but generally have a velocity in the order of 1 m/s. The disadvantages of this method are the latter characteristic of the method, i.e. it can not be determined for how long the particle or particles remained in the laser beam and as such the amount of energy absorbed by the particle or particles can not be determined. Secondly, the dust concentration in the test chamber necessarily needs to be low to avoid charge shielding and hence facilitate an optimum suspension degree. Thirdly the reproducibility of the method is low. The inherent velocity of the particles increases the heat losses of the heated particles and hence lowers the ignition probability of the particles. The second approach relies on a more complex set-up and returns to the original levitation methodology of the single particle levitator. In collaboration with Koptenko from Applied Acoustic Technologies Ltd. [97] a technical feasibility study on the creation of an acoustic three-dimensional levitator was performed as well as that a first matrix levitator, the Matrix Levitator Technology Demonstrator (MLTD), was built and demonstrated.

In the most favorable configuration the three-dimensional levitator needs to be capable of levitating a discrete three dimensional array of particles, 10 to 1000 \( \mu \)m in diameter, densities up to 3 g/cc, a total number of particles in the order of 100 and an adjustable interparticle distance (thus particle concentration). The gaseous atmosphere in the levitator can contain up to 50 percent oxygen. The equipment should therefore be resistant against such atmospheres as well as the burning particles that will appear once ignited. The arrangement of the particles will be \((x:y:z)\) 4 : 4 : 4 minimum and 10 : 10 : 6 maximum. The interparticle distance will have a value between 3 and 20. This arrangement can be either cubical or cylindrical. The latter is more convenient for designing the acoustic side of the equipment since acoustic transducers and the corresponding acoustic field tend to have a cylindrical type of symmetry.

In order to position a discrete array of solid particles an acoustic field is required that resembles as close as possible a standing wave field created by plane waves. In the horizontal plane, at any given vertical coordinate, there are pressure variations. Thus the pressure field consists of interlaced infinite horizontal planes of minimum and maximum pressure nodes spaced at a distance of a quarter of the wavelength. Theoretically, the minimum distance in the horizontal plane, between those particles is a quarter of the wavelength. Since the minimum distance between the particles in the vertical plane is
half the wavelength, the reflectors need to be spaced at half the wavelength as well. This is purely theoretical, since no one yet managed to produce waves resembling plane waves with a pressure amplitude of any significance.

In practice it is customary to use a sound projector with a flat face plate to transmit the sound vibration into the fluid or to employ a plate vibrating flexurally. However, the sound field produced by either plate has a complex structure in radial as well as vertical direction. The shape of this field, number and position of local minima and maxima are generally a function of the wavenumber and the emitting face radius. In this specific case, since the sound frequency has to be varied, this introduces an additional degree of complexity. It can be shown theoretically that the flexurally vibrating plate performs satisfactorily at one given frequency, but the acoustic field will fluctuate strongly when changing the frequency. The flat face plate produces an axisymmetric field with a field intensity that varies in the horizontal plane as a function of a Bessel function of zero order. Consequently, the strength of the potential wells drops as a function of distance from the vertical axis and thus introduces a variation in the vertical position of the particles. The higher the pressure gradient in radial direction, the larger the variation becomes and hence distorting the array. As a solution a third option can thus be considered by applying a
4.1. ACOUSTIC LEVITATION

combination of the sound projector and reflector both curved in such a way that the sound field is more uniformly distributed in the frequency range applied here. The latter solution is more complicated to model and to build, but it is more promising in terms of particle stability and array linearity.

The main obstacle in this levitator is the development of a transducer with a variable frequency to accommodate for the different interparticle distances foreseen in the levitator, while maintaining sufficient power emitted by the transducer to levitate the particles. It is envisioned that a frequency shift of around 40 to 50 kHz is required for this purpose. Furthermore, for each transducer working frequency applied, the shape of the reflector needs to be adjusted slightly to facilitate the reflection of the acoustic wave. In order to position a 4 by 4 by 4 array of 1 mm particles of intermediate density at 65 kHz, the transducer must produce a sound pressure level of 159 dB (or 1808 Pa), which is about three times more than a conventional, off-the-shelf, transducer. Furthermore it needs a very high mechanical quality and corresponding narrow band in frequency.

The demonstration levitator, the so-called Matrix Levitator Technology Demonstrator (MLTD), differs from the ultimate device to be built in two aspects. The MLTD is an open structure device. There is no enclosure around a levitation chamber, so air currents which exist in the room, and air currents arousing from breathing and from moving things around may, sometimes, affect the stability of particles. Another factor contributing into particle instability is vibration from moving or turning the MLTD. Sometimes such disturbances may result in particle escaping the potential well. Secondly the transducer and reflector assembly are not custom made but rather "pressed into service". The resultant acoustic field is far from ideal, which leads to potential wells being much weaker then they could be made with custom-made transducers and reflectors. Tolerances in the MLTD are far below what they should be and alignments are very coarse indeed. This also greatly contributes to particle instability. The transducer driving frequency was 67.874 kHz. This corresponds to a wavelength equal 5.1 mm. Thus, in the vertical plane (Z), particle centers will be separated by 2.6 mm. The particles used in MLTD were low density (Styrofoam) particles from 2.2 mm to 2.4 mm in diameter. The coarse shape was another contributor to particle instability since it would induce particle rotation in a standing acoustic wave under certain conditions. The use of Styrofoam particles as test particles is common in acoustic levitation. It offers a great degree of convenience with handling and many things can be tried without large efforts. The lateral dimensions (X and Y) were correspondingly \( X = 15.0 \text{ mm} \) and \( Y = 12.6 \text{ mm} \) between the reflector centers, where \( X \) is taken as axis which goes from left to right (towards the Z scale on the right side) and \( Y \) goes from the observer. This all gives an array grid size \( (X \times Y \times Z) \) as \( 15 \text{ mm} \times 12.6 \text{ mm} \times 2.6 \text{ mm} \) or in particle sizes as \( 6.5 \times 5.5 \times 1.1 \). The lateral dimensions are not dictated by acoustics but merely by the position of convenient spots on the support structure to place reflectors as well as by reflector sizes.
CHAPTER 4. DEVELOPMENT OF THE LASER IGNITION FACILITY

Figure 4.8: Design of the Transducer and Reflector.

4.2 Laser heating

4.2.1 Introduction

Using a laser as a heating source has many potential advantages over conventional heating sources (ovens) like, for instance, its high reproducibility and the possibility of applying high heating rates. Furthermore, as pointed out by Romney [98, 99], it is of particular interest for comparing conventional ignition sources to laser ignition, whether high-temperature sources ignite particles by creating radicals or simply by addition of thermal energy, with the reactants subsequently generating radicals. However, a disadvantage of using a laser as a heating/ignition source is the need to know the scattering and especially the absorption characteristics of the particles in question, in order to be able to include the laser energy input term in the heat balance in a proper way. Finding the optical constants of the material and wavelength in question is one of the most tedious problems encountered in this matter, not to mention to find the optical constants as a function of temperature.

In practice, there are three types of laser, based on wavelength, that can be used for ignition purposes [100, 101, 102], i.e.,

- UV laser. Generally operate in the region between 153 and roughly 350 nm. With this laser photo-dissociation of, in general, oxidiser molecules is targeted.
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- Nd:YAG laser, both in pulsed as continuous wave mode. YAG lasers are predominantly used in the pulsed mode for spectroscopic purposes. In this mode, when focusing the beam, breakdown of the gaseous medium is possible forming a plasma. In literature this plasma producing process is generally referred to as laser induced sparking. The plasma subsequently heats the particles to ignition. In continuous mode, laser induced sparking is less likely. Absorption bands of targeted particles are needed at 1.06 \( \mu m \). Although generally present, the absorption characteristics are not as strong as with the next laser type.

- Carbon dioxide. Wavelength of 10.6 \( \mu m \). All organic substances have absorption bands at this wavelength as do most non-organic compounds, although less strong as their organic counterparts. This laser heats the targeted particles by absorption.

4.2.2 UV laser

With a UV laser highly reactive oxygen radicals are formed. These radicals will initiate a rapid chemical chain reaction with the targeted particle, will recombine to oxygen or recombine with oxygen to form ozone that subsequently can attack the particle. In order to create the radicals the wavelength of the laser must match the resonance frequency of the, in this case, oxygen molecule in order to dissociate the molecule. For oxygen this means the use of either the Fluorine laser (\( F_2 \)) with a wavelength of 157 nm or the Argon fluoride laser (\( ArF \)) with a wavelength of 193 nm. Since the goal of these lasers is the dissociation of chemical bonds, the required energy will be low and generally in the order of microJoules. Another advantage is that UV lasers can also be used at low pressures and close to the flammability limits. As far as could be traced in open literature no studies on the ignition of solid particles have been undertaken. Mostly interest in photochemical ignition is based on hydrogen/oxygen fueled propulsion systems [103, 104, 105, 106]. With both the Argon fluoride laser and the Fluorine laser molecular oxygen can be dissociated, although the absorption of molecular oxygen at 157 nm is so strong that the penetration depth of the laser beam is rather small and hence not useful in most practical applications. Aside from dissociating molecular oxygen, sensitizers/additives can be added to ignite the flammable mixtures, like gaseous ammonia, that dissociates in \( NH_2 \) and \( H \) with an Argon fluoride laser, and ozone that dissociates in molecular oxygen and oxygen radicals with a Krypton fluoride laser (\( \lambda = 248 \) nm). In some cases fuels are dissociated, like for instance ethyne (\( C_2H_2 \)) that produces several reactive intermediate species like CH, H and C radicals and \( C^+ \) ions under the action of an Argon fluoride laser. Mostly the \( H \) radicals produced with any of the techniques combine with molecular oxygen to form highly reactive \( O \) and \( OH \) radicals.

4.2.3 Nd:YAG laser

A pulsed Nd:YAG laser will, if the energy density is high enough, produces a plasma, generally called a laser induced spark owing to its resemblance to electrical sparks. Upon creation of (any) spark, a shock wave is produced and the formed plasma emits radiation
and heat through conduction. All three energy types from the laser spark can facilitate ignition. An average laser induced spark can locally achieve temperatures in the order of $10^6$ K and pressures in the order of $10^3$ atmosphere. Matching the resonance frequency with the wavelength of the laser is not required as long as the energy density is high enough to create the plasma. Several examples of the application of the Nd:YAG laser for igniting solid particles are mentioned in Chapter 3. Control of the amount of energy deposited in the focal volume is difficult. The part of the laser pulse that is not absorbed can not be utilized. The residual energy from the laser pulse that did not participate in the creation of the plasma needs to be measured in order to quantify the amount of energy deposited in the plasma. The created shock waves can be very strong, strong enough for instance the blow out a flame on a Bunsen burner or to initiate a direct detonation (without transition from a deflagration) of detonable gaseous mixtures.

Because of its absorption band independence of the targeted species and its high reliability, Nd:YAG laser were also used for propulsion purposes [107, 108, 109]. Because the laser induced sparks can also ignite very lean flammable mixtures, studies were performed on improving the fuel economy and emission characteristics of spark ignition engines, hereby replacing the spark plug by a compact Nd:YAG laser. At first glance no benefit can be found in this. However, a laser beam can be split in several beams and hence ignite the flammable mixture in several locations within the engine cylinder, reducing the total combustion time significantly.

Breakdown of aerosol media is governed by the molecular absorption, the absorption and scattering by the aerosol particles and the flow field of the fluid. Any laser type can cause breakdown, as long as the energy density in the beam is higher than the threshold value for breakdown of the fluid. This is governed by the pulse energy, pulse duration and focal length of the focusing lens. The energy density is in its turn governed by the wavelength of the laser, the pulse duration and energy of the pulse. The shorter the wavelength and pulse duration and the higher the energy, the easier breakdown will be accomplished. As a rule of thumb it can be assumed that a minimum power density in the order of $10^{10}$ W/cm² is required to create a spark. The laser spark can be formed through two processes [110]: the multiphoton ionization process or the electron cascade process. With the multiphoton process a molecule absorbs a number of photons until the ionization potential of the molecule is exceeded, hereby ionizing the molecule. This process is only possible when the collision rate of the molecule is low, thus at low pressures. The lower the wavelength of the laser the higher the chance of exceeding the ionization potential of the molecule and the lower the number of required photons are to reach the ionization potential. With the cascade process "seeding" electrons are required. These electrons absorb photons, hereby increasing their kinetic energy. Upon impact with a molecule, electrons are liberated from this molecule. The number of free electrons will increase and an avalanche effect is generated, causing the gas to breakdown. The seeding electrons in general find their origin from impurities in the gas phase, like (organic) aerosol particles. In practical applications the later process will dominate the formation of laser induced sparks.
4.2.4 Carbon dioxide laser

With a carbon dioxide laser the goal is to increase the kinetic energy of molecules in either translational, rotational or vibrational form, causing bond breakage and subsequent chemical reactions can take place. Matching of the resonance frequency of the molecular bonds with the wavelength of the laser is required, but less troublesome as with the UV laser. Applications of the carbon dioxide laser are mentioned in Chapter 3.

4.3 Temperature Measurement of Particles

4.3.1 Introduction

It is known [111, 112, 113] that a substance having a temperature above the absolute zero emits radiant energy as a result of the finite kinetic energy of the molecules and atoms, giving rise to vibrating behaviour. As the temperature increases, the kinetic energy increases and hence the emission per unit area of the substance will increase. The emittance of the substance will occur over a wide range of wavelengths, the spectral emittance being a function of temperature, see Figure 4.9. As can be seen from this figure, the lower the temperature the more the detectable emittance will shift to longer wavelengths. The visible portion of the spectrum is indicated by the shaded part of the figure.

The radiance emitted by a blackbody, at any wavelength, is a function of the absolute temperature only and can be described by Planck’s Law, see Equation 4.38. A blackbody is defined as an ideal body that absorbs all incident radiation for all wavelengths and for all angles of incidence. Being at thermal equilibrium it emits the maximum radiant energy.

\[
R^b = \frac{c_1}{\lambda^5 \left( \exp \left( \frac{c_2}{\lambda T} \right) - 1 \right)} \quad (4.38)
\]

with

\[
c_1 = 8\pi hc^2 = 4.993 \cdot 10^{-24} \text{(Jm)} \quad (4.39)
\]

and

\[
c_2 = \frac{hc}{k_b} = 1.4388 \cdot 10^{-2} \text{(mK)} \quad (4.40)
\]

Integrating Equation 4.38 over all wavelengths, the Stefan-Boltzmann law is obtained. In terms of spectral radiance, Equation 4.38 becomes:

\[
R^b_\lambda = \frac{c_1}{\pi \lambda^5 \left( \exp \left( \frac{c_2}{\lambda T} \right) - 1 \right)} \quad (4.41)
\]

with

\[
c_1 = 2\pi hc^2 \quad (4.42)
\]

In Figure 4.9 the spectral emittance of a blackbody as function of temperature and wavelength is given. As mentioned before, a blackbody is an ideal emitter. In practice a
certain body emits spectral radiance depending on its emissivity that in its turn depends on temperature and wavelength. The spectral radiance for any body can therefore be defined as:

$$R_{\lambda}(T) = \epsilon_{\lambda}(T) R_{\lambda}^{b}(T)$$  \hspace{1cm} (4.43)

or

$$\epsilon_{\lambda}(T) = \frac{R_{\lambda}(T)}{R_{\lambda}^{b}(T)}$$  \hspace{1cm} (4.44)

where $R_{\lambda}(T)$ is the spectral radiance of a non-blackbody. In order to optically measure the temperature, information on the emissivity and the radiant distribution of the emitting body is required.

![Figure 4.9: Black body radiance versus wavelength [113.]](image)

With a dual-color pyrometer, as mentioned in Chapter 3, the emitted radiation is split in two beams and led through two separate defined wavelength filters. For the radiance
of these two beams the following relations hold. For wavelength 1:

\[ R_{\lambda_1} = \frac{\varepsilon_1 c_1}{\lambda_1^5 \exp \left( \frac{\varepsilon_2}{\lambda_1 T} \right)} \]  

(4.45)

and for wavelength 2

\[ R_{\lambda_2} = \frac{\varepsilon_2 c_1}{\lambda_2^5 \exp \left( \frac{\varepsilon_2}{\lambda_2 T} \right)} \]  

(4.46)

Dividing Equation 4.46 by Equation 4.45 gives:

\[ \frac{R_{\lambda_2}}{R_{\lambda_1}} = \frac{\varepsilon_2}{\varepsilon_1} \left( \frac{\lambda_1}{\lambda_2} \right)^5 \exp \left[ \frac{c_2}{T} \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) \right] \]  

(4.47)

and hence the temperature can be calculated as:

\[ \frac{1}{T} = \left\{ \ln \left[ \frac{\varepsilon_1}{\varepsilon_2} \left( \frac{\lambda_2}{\lambda_1} \right)^5 \frac{R_{\lambda_2}}{R_{\lambda_1}} \right] \right\} \left[ c_2 \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) \right]^{-1} \]  

(4.48)

Adding more filters specific for other wavelengths, the accuracy of the measurements will increase [113]. However, even with a three-color system, the experimental set-up will already become very complex. First of all the analysis of the measurements is not straightforward. Three equations for the spectral emittance, similar to Equation 4.45, together with a relation coupling the various emissivities to the respective wavelengths, need to be solved through trial and error with a suitable numerical iteration method. The accuracy obtained with the measurement technique can therefore be eliminated by faulty analysis. Secondly, a dual-color system is already quite accurate, as can be seen from Figure 4.10. As the temperature to be measured of the emitting body increases and hence the shorter the emitted wavelengths, the higher the accuracy.

### 4.3.2 Accufiber's Optical Fiber Thermometer (OFT)

The basic concept (see Figure 4.11) of Accufiber's Optical Fiber Thermometer (OFT) [111, 114, 115, 116] comprises a single crystal sapphire rod which is coated at its tip with a thin film of a precious metal (platinum with 30% rhodium) that acts as the blackbody cavity. This basic concept is meant for direct contact measurements. The emissivity of the precious metal is known as function of temperature. As the cavity is heated, it emits radiant energy that obeys Planck's equation. The sapphire rod transmits the radiant energy to an optical, non-emitting, non-absorbing fiber at low temperature, which in turn transmits the radiation to a remote optical detector. The transmission losses are maximum 1% of the total radiation. The detector converts the radiation to an amplified electrical signal, that is converted in the temperature of the blackbody cavity and hence that of the studied object. With this technique the maximum measurable temperature is about 2000 °C before damaging the thin film and/or the sapphire rod. For laser ignition experiments, physical contact between the sensor and the heated body is impractical. An
alternative exists. The same sapphire rod is optically polished at the end instead of having a thin film of a certain substrate. The sensor is placed in close proximity of the object, which now takes over the role as blackbody cavity. The rest of the system remains the same. The unknown parameter that needs to be given to the system is the emissivity of the measured object as function of temperature and wavelength.

As mentioned in the previous section, the more wavelengths the optical measurement system can analyze, the more accurate the determined temperature can be. When measuring high temperatures \((T > 1500 \text{ K})\), a single-color system is more than accurate enough. However, when measuring lower temperatures, multiple wavelengths are required to obtain the same accuracy. With the Accuﬁber a kind of hybrid dual-color system is applied. Instead of looking at one or more speciﬁc wavelengths, the system combines the analysis of the incoming radiation over a wavelength band between 700 to 1800 nm together with a single-color ﬁlter for higher temperatures. Hence the emissivity coefﬁcient of the targeted object needs to be known for the wavelength band and the single-color wavelength and given as input to the thermometer. The (analog) speed of the OFT is
minimum 10 kHz, the accuracy is 0.2% of full scale or 2 °C. The resolution of the system equals 0.01 °C. The entire system is calibrated with a blackbody furnace traceable to the US National Bureau of Standards. Target emissivities as low as 0.05 can be reliably measured. The very small drift of the silicon photodiode detector is accommodated for by a periodic adjustment operation in which the photodetector is momentarily exposed to a reference of known temperature. Although the photodetector has response times in the order of nanoseconds, a finite integration time is desirable to suppress the effects of photodetector noise. Therefore the minimum response time of the system is in the order of 10 μs. The minimum detectable temperature of the system is related to the detector noise, and, because of attenuation, the minimum detectable temperature depends upon the length of the fiber. With a fiber length of 2 m, the minimum detectable temperature of the system equals 215 °C. Furthermore, the targeted object needs to have a certain finite size in order to record its temperature (minimum radiating area), depending on the emissivity of the object.

The conversion of the electrical signal to an output voltage is executed by a linear amplifier, whose magnitude is a linear function of the electrical signal. The amplifier operates with a selectable gain control to optimally exploit the full dynamic range of the signal from the detector. With a signal processor the output voltage is digitized. The system can also be operated in the analog mode. With aid of an algorithm the signal processor calculates, using Planck's Equation (Equation 4.38), the temperature of the object. The linear amplifier preceding the signal processor reduces the distortion of the electrical signal. The silicon photodiode detector has a response of approximately one electron Volt output for one photon input at any given wavelength. In the detector circuit changes in ambient temperature that influence the accuracy of the silicon photodiode and the filters are accounted for by using a thermistor that supplies the signal processor with
corrections in the spectral response of the filters. In an internal loop of the signal processor these inputs are periodically used for calibrating the system. The optical calibration circuit consists of a standard source lamp configured with beam splitters to insert light into the detector section's optical transmission line where it is transmitted through the fiber to a mirror and reflected back through the optical fiber to the detector.

4.4 Experimental Set-up

Two possible levitation techniques can be used for single particle laser ignition, i.e., the electrodynamic balance and the ultrasonic levitator. There are more levitation techniques available (optical levitation, magnetic levitation, etc) [117, 118], but these techniques are not as well developed as the first two techniques or impracticable. The disadvantage of the ultrasonic technique is primarily the effect of acoustic streaming. This phenomenon increases the heat and mass transfer from and to the particle. Although the heating of the particles will not suffer from this effect, due to the high heating rates achievable with a laser, the mass transport will be influenced. The influence can be such, that an intrinsic homogeneously igniting particle will exhibit a forced heterogeneous ignition pathway. The primary disadvantage of the electrodynamic balance it is loss of unified charge just prior and during ignition. For the same reason, with homogeneously igniting particles, the evolution of volatile gases disrupts the levitation capabilities of the particles prior to ignition in the electrodynamic balance. Looking ahead, scaling up of the ultrasonic system to include multiple particles is more straightforward than that of the electrodynamic system. In the latter case, in order to levitate the particles, particles are charged. However, agglomeration is unavoidable. To avoid this, a hybrid levitation technique, the acousto-electric levitator [94, 95], is required. This method is limited to two dimensions because the acoustic force generates one stable plane (pressure well) for levitation somewhere along the axial axis. Multiple pressure wells at different locations along the axial axis will require acoustic powers that are currently not feasible. Furthermore, even when possible, interparticle distances are difficult to control within each pressure well and between the different pressure wells and it would be more convenient to build a pure acoustic three-dimensional levitator. A three dimensional acoustic levitator is not possible with the current state of the art techniques. The three-dimensional Electrostatic levitator [96] is impracticable for laser ignition experiments for determining the minimum ignition temperature of the igniting particles, due to the inherent velocity of the particles. The particles will move quickly in and out the laser beam as well as the focus of the optical fiber thermometer.

An ultraviolet laser dissociates molecules to start ignition and subsequent combustion. This dissociation starts as soon as the beam leaves the laser, before reaching the particle. Part of the oxygen molecules that are dissociated in the vicinity of the particle surface will attack the surface, while another part will not contribute to the ignition of the particle. As such the quantification of the amount of energy that was efficiently used to create reactive species that contributed to the ignition of the particle is tedious. Furthermore, the ignition principle deviates strongly from that of the current standards, i.e., furnaces
and sparks. With a pulsed Nd:YAG laser the possibility of creating laser induced sparks is present. As with the ultraviolet laser, the quantification of the amount of energy efficiently used for igniting the particle in question is difficult, not alone because of the presence of three "ignition sources", i.e., shock wave, radiation and heat conduction. Since the temperature of the particle surface will be measured, the plasma temperature will dominate the temperature read-out of the thermometer. As such the exact ignition temperature is difficult to assess. A continuous YAG laser as well as a pulsed or continuous carbon dioxide laser can be used to heat particles by absorption. As long as the absorption efficiency of the particle at the wavelength of the given laser is known, the heating problem is exactly soluble. The absorption bands of substances are generally stronger in the wavelength range of the carbon dioxide laser than those in the range of the Nd:YAG laser.

To measure the particle surface temperature an optical system is required with a high sampling frequency, accuracy and resolution. From literature it is known that a two-color pyrometer will adequate measure the surface temperature for both low, medium and high temperatures, under the condition that the emissivity is known as function of temperature for the wavelengths of the pyrometer detectors in question.

4.5 Conclusions

Based on the previous sections and the conclusions of Chapters 2 and 3, the ignition facility is configured as follows, see Figure 4.12. The ultrasonic levitator and the optical fiber thermometer are described in Sections 4.1 and 4.3 respectively. Determining the particle sizes to be levitated, the following points need to be considered. The levitator can stably levitate particles with diameters between 15 and roughly 3000 μm, having densities up to 2500 kg/m³. In dust explosion science, generally particle sizes up to 500 μm are considered. The minimum particle size is determined by the practical possibility to insert particles of known size in the levitator as well as that the smaller the particles the lower the absorption efficiency and the higher the probability of resonance oscillations within the particle. The latter effect is dictated by the particle size parameter and hence the wavelength of the laser. To ensure particle stability the particles should be as spherical as possible. The to be levitated particle sizes will therefore be in the range from 150 to 750 μm.

Accufiber's optical fiber thermometer is the state of the art optical thermometer, having a high sampling frequency and resolution. An off-the-shelf system is preferred over a self assembled system for obvious reasons. The measurable temperature interval is between 200 and 2000 °C, appropriate for the laser ignition experiments. The thermometer requires precise knowledge of the emissivity of the studied materials as a function of temperature and wavelength. Planck's equation (Eqn. 4.38) is in principal only valid under vacuum. However, air and other gases have an emissivity coefficient close to one, making the optical measurement system reliable. As previously concluded, heating times need to be longer than approximately 1 ms. The sampling frequency of 10 kHz is sufficient. The calibration of the optical thermometer is checked by measuring the temperature of a hot wire at steady state and checking the temperature with that of a type "J" thermocouple.
Figure 4.12: Laser ignition facility for determining the minimum ignition energy and minimum ignition temperature. Components: (1) Carbon dioxide laser; (2) Ultrasonic levitator; (3) ZnSe 50 % beam splitter; (4) Gold mirror; (5) ZnSe focusing lens and (6) Optical fiber thermometer.

Using several combinations of voltage and current, different steady state temperatures between 400 and 800 °C were determined. Deviation on average was 1.7 °C.

The carbon dioxide laser employed is a 60 W Synrad sealed-off system that can be operated in both the pulsed as continuous mode. Maximum pulse frequency is 5 kHz. The nominal laser output is 60 W with (constant) "interpeak" powers up to 100 W, depending on the number of operating hours. The zinc selenide lenses with anti-reflection coatings and the mirrors are compatible with the infrared laser beam. The splitting efficiency of the zinc selenide beam splitter is checked with a power meter. The energy irradiated on the particles is determined after the lenses, to incorporate all losses of the optics. The spatial intensity distribution of the beams were mapped using a calibrated laser beam diagnostics IR camera system. The intensity was found to vary less than 8 percent over the cross section of the targeted particle diameter cross section. The cross section of the laser beam is hereby larger than the particle cross sectional area. The maximum intensity of the focal point of each beam using this optical system is in the order of 2.0 · 10^8 W/m². This is on the limit where, depending on particle size, fragmentation becomes feasible. The particles are heated from two sides to ensure uniform heating. The two beams are nearly opposite to each other to prevent interference of the two laser beams as well as unwanted reflections. The particles will be subject to a small force in the direction perpendicular to the laser beams due to the small angle of the two beams (170° contrary to 180°).
4.5. CONCLUSIONS

To assess the advantages and disadvantages of the laser ignition philosophy for determining the minimum ignition energy and minimum ignition temperature, the properties and behaviour of the target species should be known as accurately as possible. This includes, besides the obvious properties like density and conductivity, the complex index of refraction and emissivity as function of temperature. The particles should not considerably change in size during the heating process, due to swelling or shrinkage. Furthermore, reliable reference information should be available to establish the proof of concept as well as to elucidate the differences measured with the current standard techniques as mentioned in Chapter 2. These material requirements focus attention to metals. Taking those metals and substances that are generally considered in dust explosion science, possible candidates are beryllium, magnesium, zirconium, titanium, iron, nickel and aluminum as well as boron. From these, beryllium and boron are disregarded due to toxicological reasons. As mentioned in Chapter 3, the effect of the oxide layer on the laser heating process is negligible.

**List of Symbols**

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>Speed of light</td>
<td>$\text{ms}^{-1}$</td>
</tr>
<tr>
<td>$c_1$</td>
<td>Constant of Planck Equation</td>
<td>$\text{kgm}^3\text{s}^{-2}$</td>
</tr>
<tr>
<td>$c_2$</td>
<td>Constant of Planck Equation</td>
<td>$\text{mK}$</td>
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<tr>
<td>$d_{p,\text{opt}}$</td>
<td>Optimum levitation particle size</td>
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<tr>
<td>$F$</td>
<td>Acoustic streaming force</td>
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<tr>
<td>$F_L$</td>
<td>Levitation force</td>
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<tr>
<td>$F_r$</td>
<td>Radial force</td>
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<tr>
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<tr>
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### Symbols

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<tr>
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### Greek Symbols

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<td>$\theta$</td>
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<tr>
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<tr>
<td>$\rho_g$</td>
<td>Density of surrounding gas</td>
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<tr>
<td>$\omega$</td>
<td>Circular frequency of sound wave</td>
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Chapter 5
Absorption by Multiple Particles

This chapter explains the interaction of planar electromagnetic waves with multiple particles using the so-called T-Matrix method. The T-Matrix method is derived and validated for a single particle and consequently expanded to include more particles.

5.1 Introduction

Modeling the ignition of multiple particles, heated by electromagnetic radiation, is required to understand the collective effect of the particles. Not so much in sense of multiple scattering effects that will contribute to the heating of the particles. Multiple scattering can be disregarded in this respect, although the mathematical equations need to be considered to enable convergence of the model. More importantly, when a laser beam passes through a cloud of particles, the intensity of the laser beam will change as a function of position. This will affect the absorption capabilities of the particles that are positioned deeper into the cloud and hence the ignition probability of that given cloud. In this chapter the efforts are described to model the absorption of multiple particles in a fixed array by electromagnetic radiation.

As described by Mischenko et al [119] there are several methods that have found extensive practical applications to compute scattered electromagnetic fields. The most important methods are briefly mentioned below.

The Separation of Variables Method for single homogeneous, isotropic spheroids is accurate when particle size parameters (ratio of circumferential diameter to wavelength) are not larger than approximately 20. This is especially true for absorbing particles. As the name of the method already indicates, it is only applicable to spheroids. However, for those particles the method will produce very accurate results.

The Finite Element Method has as advantages that it permits the modeling of arbitrarily shaped and inhomogeneous particles. The method is simple in concept and execution. It solves the vector Helmholtz equation subject to boundary conditions at the particle surface. With this method, approximate absorbing boundary conditions have to be imposed at the outer boundary of the computational domain in order to suppress wave reflections.
back into the domain and permit all outward-propagating numerical wave analogs to exit the domain almost as if the domain were infinite. However, the calculations are rather time consuming, since the computations are spread over the entire computational domain instead of being confined to the scatterer(s). Hence this method is limited to particle size parameters less than 10. The finite spatial discretization and the approximate absorbing boundary condition mean low numerical accuracy.

The Method of Moments is the most developed method of the Integral Equation Methods family. Closely related is the Discrete Dipole Approximation. Both methods can be applied to inhomogeneous, anisotropic, and optically active scatterers. The accuracy is low and the computational effort increases significantly with increasing particle size parameter. Mostly the methods are used for particle size parameters not exceeding unity.

The T-Matrix Method is based on expanding the incident field in vector spherical wave functions regular at the origin and expanding the scattered field outside a circumscribing sphere of the scatterer in the vector spherical wave functions regular at infinity. For spheres the T-Matrix Method formulas are reduced to those of the Mie theory. The method can be applied to any arbitrary shape of one or more particles, even without axial symmetry like cubes. The method is highly accurate, fast, and applicable to particles with particle size parameters exceeding 100. The elements of the T-matrix are independent of the incident and scattered fields and depend only on the shape, size parameter and refractive index of the scattering particle and on its orientation with respect to the reference frame. As such the T-matrix needs to be computed only once and then can be used in computations for any direction of light incidence and scattering. The disadvantage of the method is that it will become less efficient as the particles have large aspect ratios.

In potentially explosive dusts the shape of the particles can vary widely. One can have dusts consisting of spherical particles, but also porous particles (e.g. pollen), particles shaped like needles (e.g. polyurethane) and particles shaped like cubes (e.g. sugar). This requirement rules out the use of the Separation of Variables Method. However, it should also be mentioned that from a practical point of view, the more spherical the particles, the higher the stability of the particles in the ultrasonic levitator (Section 4.1) in terms of degree of stationary ability. Since non-spherical particles will also be used in the ignition tests, the requirement stands. The most important requirement, however, is determined by particle size. The particle size generally encountered in potentially explosive dusts varies between submicron up to roughly 500 micron. With the use of the carbon dioxide laser, the particle size parameter can therefore vary up to 150. This leaves the T-matrix method as the only method fit for the job. Under these circumstances, also the computational efficiency of the T-matrix is better compared to the other methods. For instance, the T-matrix method explicitly incorporates the external field. With the Finite Element Method the external field needs to be defined additionally. Assume an array of ten by ten by ten corn starch particles. It is known [120] that corn starch reaches a maximum explosion pressure at a concentration of 1000 gram per cubic meter. Assuming that corn starch has a density of 1100 per cubic meter, the aforementioned array will have an interparticle distance of ten particle diameters. The corn starch particle diameter is about two times the wavelength of the carbon dioxide laser. In order to make a mesh for
the finite element method one needs about 15 cells per length of wavelength. Restricting the "far-field" by only one interparticle distance, one will end up with a grid consisting of about 210 million cells for this particular array. As one will like to expand the far field to larger distances and use larger particle sizes, the number of cells will increase exponentially. On the other hand, contrary to the T-Matrix Method, the matrices in case of the Finite Element Method may not be completely filled, making the inversion step less time consuming. From these considerations it is apparent that the T-Matrix method has prevailing advantages over the other methods. In the following sections the T-matrix method will be explained.

5.2 History

"It is now, I believe, generally admitted that the light which we receive from the clear sky is due, in one way, or another, to small suspended particles which divert the light from its regular course." [121] This, the first sentence of the first paper of Lord Rayleigh on the origin of the blue color of the sky, was the starting point of his investigation of the theoretical and practical aspects of light-scattering. The oscillating electric field of light traversing any real medium induces oscillating electric moments in the particles composing it. Provided the frequency of the induced oscillations is far from the natural frequency of the electrons, these in turn act as secondary sources of radiation of the same wavelength, the scattered light. There is also a small component of the incident-light beam absorbed, raising the molecules to higher energy states, which is re-emitted changed into certain specific wavelengths, as the Raman spectra. This radiation, however, is usually several orders of magnitude smaller, and may be neglected. Rayleigh’s original treatment was for independent transparent particles that are optically isotropic and small compared with the incident wavelengths. When, however, the particles become bigger, i.e. same order or greater than the wavelength, this theory no longer holds. For spherical particles and the electromagnetic scattering for a single sphere one has to make use of the Mie theory developed by Gustav Mie in 1908 [122], which was 35 years after Maxwell formulated the fundamental equations of electromagnetic wave theory [42].

For a problem involving multiple particles the situation is more complex [121]. One can imagine that the influence of each particle on each other particle makes it quite complicated. The simplest case is the multiple scattering by two spheres, which was treated first by Trinks in 1935 [123].

5.3 Scattering by a Single Sphere

5.3.1 Introduction

Here we consider the scattering of a plane electromagnetic wave by a single sphere. The basic concepts that are needed to describe the behaviour of electromagnetic fields are
described. First the source-free Maxwell’s equations are given. Second these equations
will be considered for coordinates that are suitable to the geometry of the sphere, i.e. spherical coordinates will be introduced. The analysis will be done in the frequency-domain, i.e. s-domain representation assuming \( \exp(-i\omega t) \) time dependence [121].

5.3.2 Maxwell’s Equations

The source-free Maxwell’s equations are given by:

\[
-\nabla \times \mathbf{H} + s\varepsilon \mathbf{E} = 0, \tag{5.1}
\]

\[
\nabla \times \mathbf{E} + s\mu \mathbf{H} = 0, \tag{5.2}
\]

where \( s = -i\omega \) and \( \varepsilon \) and \( \mu \) are the complex permittivity and permeability, respectively. Furthermore, the total electric and magnetic field can be written in a transverse magnetic (TM) and a transverse electric (TE) contribution [124],

\[
\mathbf{H} = \mathbf{H}^{TM} + \mathbf{H}^{TE}, \tag{5.3}
\]

\[
\mathbf{E} = \mathbf{E}^{TM} + \mathbf{E}^{TE}. \tag{5.4}
\]

This decomposition is unique; see Bouwkamp and Casimir [125]. They have proved that any electromagnetic field satisfying Maxwell’s equations in the empty space between two concentric spheres is completely determined by its radial components \( E_r \) and \( H_r \). In this case, these vector wave equations in three dimensions can be reduced to the scalar wave equations, because we are considering a homogeneous, isotropic medium. Debye [126] showed that this is best done by introducing the Debye potential \( \pi_e, \pi_m \) to characterize the TM and TE waves, respectively, i.e.

\[
\mathbf{H}^{TM} = \nabla \times r\pi_e, \tag{5.5}
\]

\[
\mathbf{E}^{TE} = \nabla \times r\pi_m. \tag{5.6}
\]

From Maxwell’s source-free Equations (5.1-5.2), the vector wave equation for the electric field can be found by substituting the expression for the magnetic field into the expression for the electric field. Using this and the vector identity,

\[
\nabla \times \nabla \times \mathbf{E} = \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E}, \tag{5.7}
\]

where \( \nabla \cdot \mathbf{E} = 0 \) for a homogeneous, isotropic and source-free medium, the vector wave equation can be written as

\[
(\nabla^2 + k^2)\mathbf{E} = 0, \tag{5.8}
\]

where \( k^2 = \omega^2\varepsilon\mu \). Similarly we have

\[
(\nabla^2 + k^2)\mathbf{H} = 0, \tag{5.9}
\]

With \( \mathbf{H}^{TM} = \nabla \times r\pi_e \), we observe that Equation (5.9) can be satisfied when \( \pi_e \) satisfies the scalar Helmholtz equation

\[
(\nabla^2 + k^2)\pi_e = 0 \tag{5.10}
\]
Similarly from Equations (5.8) and (5.6) it follows that $\pi_m$ has to satisfy the scalar Helmholtz equation

$$ (\nabla^2 + k^2)\pi_m = 0. \quad (5.11) $$

The total electromagnetic field can be written into $TE$ and $TM$ components as follows

$$ H = \nabla \times r\pi_e - \frac{1}{s\mu} \nabla \times \nabla \times r\pi_m, \quad (5.12) $$

$$ E = \nabla \times r\pi_m + \frac{1}{s\varepsilon} \nabla \times \nabla \times r\pi_e. \quad (5.13) $$

Introducing the spherical coordinates, see Figure 5.1, the $(r, \theta, \phi)$-components of these

![Diagram of a sphere with spherical coordinates](image)

**Figure 5.1: Configuration of the sphere**

field quantities are obtained as

$$ E_r = \frac{1}{s\varepsilon} \left( \frac{\partial^2}{\partial r^2} r\pi_e + k^2 r\pi_e \right), \quad (5.14) $$

$$ H_r = -\frac{1}{s\mu} \left( \frac{\partial^2}{\partial r^2} r\pi_m + k^2 r\pi_m \right), \quad (5.15) $$

$$ E_\theta = \frac{1}{s\varepsilon r} \frac{1}{\partial r \partial \theta} r\pi_e + \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} r\pi_m, \quad (5.16) $$
CHAPTER 5. ABSORPTION BY MULTIPLE PARTICLES

\[
H_\theta = -\frac{1}{s\mu r} \frac{\partial^2}{\partial r \partial \theta} r\pi_e + \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \pi_e, \tag{5.17}
\]

\[
E_\phi = \frac{1}{s\epsilon r \sin \theta} \frac{\partial^2}{\partial r \partial \phi} r\pi_e - \frac{\partial}{\partial \theta} \pi_m, \tag{5.18}
\]

\[
H_\phi = -\frac{1}{s\mu r \sin \theta} \frac{\partial^2}{\partial r \partial \phi} r\pi_m - \frac{\partial}{\partial \theta} \pi_e, \tag{5.19}
\]

while the scalar wave equation becomes

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \pi_{e,m}}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \pi_{e,m}}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \pi_{e,m}}{\partial \phi^2} + k^2 \pi_{e,m} = 0. \tag{5.20}
\]

The radius of the scattering sphere is \( r_s \). At \( r = r_s \), the tangential components \( E_\theta, H_\theta, E_\phi \) and \( H_\phi \) are continuous. In order to find boundary conditions for \( \pi_e \) and \( \pi_m \) we write the tangential components as

\[
\begin{bmatrix}
E_\theta \\
E_\phi
\end{bmatrix} = \begin{bmatrix}
\frac{1}{s\epsilon r} \frac{\partial^2}{\partial r \partial \phi} r - \frac{1}{s\mu \sin \theta} \frac{\partial^2}{\partial \phi^2}

\frac{1}{s\mu r \sin \theta} \frac{\partial^2}{\partial r \partial \phi} r + \frac{1}{s\mu \sin \phi} \frac{\partial^2}{\partial \phi^2}
\end{bmatrix} \begin{bmatrix}
\pi_e \\
\pi_m
\end{bmatrix}, \tag{5.21}
\]

\[
\begin{bmatrix}
H_\theta \\
H_\phi
\end{bmatrix} = \begin{bmatrix}
\frac{1}{s\mu \sin \theta} \frac{\partial^2}{\partial \phi^2} - \frac{1}{s\mu r} \frac{\partial^2}{\partial \phi^2} r

- \frac{1}{s\mu \sin \phi} \frac{\partial^2}{\partial \phi^2} r
\end{bmatrix} \begin{bmatrix}
\pi_e \\
\pi_m
\end{bmatrix}. \tag{5.22}
\]

Now this matrix can be decomposed in separate \((\theta, \phi)\)- and \(r\)-components as follows

\[
\begin{bmatrix}
E_\theta \\
E_\phi
\end{bmatrix} = \begin{bmatrix}
\frac{\partial}{\partial \phi} - \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \\
\frac{1}{\sin \theta} \frac{\partial}{\partial \phi}
\end{bmatrix} \begin{bmatrix}
\frac{1}{s\epsilon r} \frac{\partial}{\partial r} r \pi_e \\
0
\end{bmatrix} \begin{bmatrix}
\pi_e \\
\pi_m
\end{bmatrix}, \tag{5.23}
\]

\[
\begin{bmatrix}
H_\theta \\
H_\phi
\end{bmatrix} = \begin{bmatrix}
\frac{\partial}{\partial \phi} - \frac{1}{\sin \phi} \frac{\partial}{\partial \phi} \\
\frac{1}{\sin \phi} \frac{\partial}{\partial \phi}
\end{bmatrix} \begin{bmatrix}
\frac{1}{s\mu r} \frac{\partial}{\partial r} r \pi_e \\
0 - \frac{1}{s\mu} \frac{\partial}{\partial r} r \pi_e
\end{bmatrix} \begin{bmatrix}
\pi_e \\
\pi_m
\end{bmatrix}. \tag{5.24}
\]

From this decomposition we can deduce that for the tangential components to be continuous, \( \pi_e \) and \( \pi_m \) also have to be continuous for \( TM \) and \( TE \)-mode, respectively. Furthermore, the derivative with respect to \( r \) in these equations has to be continuous too. This results in the following four equations

\[
\pi_e = \text{continuous}, \tag{5.25}
\]

\[
\pi_m = \text{continuous}, \tag{5.26}
\]

\[
\frac{1}{\epsilon} \frac{\partial}{\partial r} (r \pi_e) = \text{continuous}, \tag{5.27}
\]

\[
\frac{1}{\mu} \frac{\partial}{\partial r} (r \pi_m) = \text{continuous}. \tag{5.28}
\]

The Helmholtz Equation (5.20) and the boundary conditions, see Equations (5.25-5.28), together with the radiation conditions at infinity describe the unique solutions for \( \pi_e \) and \( \pi_m \). Let us now discuss the scattering problem of a wave by a homogeneous sphere with
permittivity $\varepsilon_1$, permeability $\mu_1$ and radius $r_s$. The total field outside the sphere can be written as an incoming field $\{\mathbf{E}^i, \mathbf{H}^i\}$ and a scattered field $\{\mathbf{E}^s, \mathbf{H}^s\}$ as

\[
\mathbf{E} = \mathbf{E}^i + \mathbf{E}^s, \quad \mathbf{H} = \mathbf{H}^i + \mathbf{H}^s. \tag{5.29}
\]

The field inside the sphere is denoted as $\mathbf{E}^i, \mathbf{H}^i$. Consistent with Equations (5.29-5.30) we also write the potentials $\pi_{e,m}$ in an incident and scattered constituent outside the sphere as

\[
\pi_{e,m} = \pi_{e,m}^i + \pi_{e,m}^s, \tag{5.31}
\]

for $r_s < r < \infty$. Inside the sphere we write the potentials as $\pi_{e,m}^i$. From the boundary conditions, Equations (5.25-5.28), we directly conclude that $\pi_e$ and $\pi_m$ can be written as

\[
\lim_{r \downarrow r_s} \pi_e^i = \lim_{r \downarrow r_s} \left\{ \pi_e^i + \pi_e^s \right\}, \tag{5.32}
\]

\[
\lim_{r \downarrow r_s} \pi_m^i = \lim_{r \downarrow r_s} \left\{ \pi_m^i + \pi_m^s \right\}, \tag{5.33}
\]

\[
\lim_{r \downarrow r_s} \frac{1}{\varepsilon_0} \frac{\partial}{\partial r} (r \pi_e^i) = \lim_{r \downarrow r_s} \left\{ \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} (r \pi_e^i) + \frac{\partial}{\partial r} (r \pi_e^s) \right] \right\}, \tag{5.34}
\]

\[
\lim_{r \downarrow r_s} \frac{1}{\mu_0} \frac{\partial}{\partial r} (r \pi_m^i) = \lim_{r \downarrow r_s} \left\{ \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} (r \pi_m^i) + \frac{\partial}{\partial r} (r \pi_m^s) \right] \right\}, \tag{5.35}
\]

where $\pi_{e,m}^i$ is the total field within the sphere and $\varepsilon_1, \mu_1$ corresponds to the area within the sphere ($r < r_s$) and $\varepsilon_0, \mu_0$ to the area outside the sphere ($r > r_s$). Now we have
these equations and the fact that \( \pi_{e,m} \) is continuous at \( r = r_s \), the boundary conditions are known. To find explicit expressions for \( \pi_{e,m} \) an analysis of the spherical functions is crucial. First we shall perform this analysis; second the reflection and transmission of an incoming wave will be discussed.

### 5.3.3 Separation of variables

Since the configuration is independent of \( \theta \) and \( \phi \), the solution of the Helmholtz equation (5.20) is obtained by separation of variables

\[
\pi_{e,m} = R(r)\Theta(\theta)\Phi(\phi)
\]

The special functions satisfy the following differential equations:

\[
\begin{align*}
\left( \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + k^2 - \frac{n(n+1)}{r^2} \right) R &= 0 \\
\left( \frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} + n(n+1) - \frac{m^2}{\sin^2 \theta} \right) \Theta &= 0 \\
\left( \frac{d^2}{d\phi^2} + m^2 \right) \Phi &= 0
\end{align*}
\]

The requirement that \( \Phi(\phi) \) is single-valued yields the periodicity \( \Phi(\phi + 2\pi) = \Phi(\phi) \). Under this condition, Equation (5.37) can only be solved when \( m \) is an integer. Solutions to Equations (5.37-5.39) are the spherical Bessel functions, \( j_n(kr) \) and \( h_n^{(1)}(kr) \), the associated Legendre polynomials, \( P_n^{ml}(\cos \theta) \), and the harmonic functions, \( \exp(\pm im\phi) \), respectively. Since \( \pi_m \) and \( \pi_e \) are solutions of the scalar wave equation, a particular solution is

\[
\pi_{e,m} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \left[ a_n^{e,n} j_n(kr) + b_n^{e,n} h_n^{(1)}(kr) \right] P_n^{ml}(\cos \theta) \exp(\pm im\phi),
\]

where \( a_n^{e,m} \) and \( b_n^{e,m} \) are constants to be determined.

### 5.3.4 Reflection and Transmission of an Incoming Wave

As shown in Figure 5.2 we need to consider two different regions:

- Region 0 outside the sphere with \( \mu_0 \) and \( \varepsilon_0 \) resulting in a \( k_0 = \omega \sqrt{\varepsilon_0\mu_0} \)
- Region 1 within the sphere with \( \mu_1 \) and \( \varepsilon_1 \) resulting in a \( k_1 = \omega \sqrt{\varepsilon_1\mu_1} \)

The incident and scattered field are limited to region 0, whereas the total field is limited to region 1. The incoming field must be regular and finite within the sphere. From this it follows that the factor \( b_n^{e,m} \) in Equation (5.40) is zero, because the Hankel function is singular at the origin. The incident field is regular at \( r = 0 \), therefore it can be written as

\[
\begin{align*}
\pi_i^e &= \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} a_n^{e,m} j_n(k_0r) P_n^{ml}(\cos \theta) \exp(\pm im\phi), \\
\pi_i^m &= \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} a_n^{m,m} j_n(k_0r) P_n^{ml}(\cos \theta) \exp(\pm im\phi).
\end{align*}
\]
The same analysis for the scattered field, where $h_n^{(1)}(kr)$ is an outgoing wave and singular at $r = 0$, results in:

$$
\pi_e^s = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} b_{m,n}^e h_n^{(1)}(k_0 r) P_n^{\text{im}}(\cos \theta) \exp(i m \phi),
$$

$$
\pi_m^s = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} b_{m,n}^m h_n^{(1)}(k_0 r) P_n^{\text{im}}(\cos \theta) \exp(i m \phi).
$$

And for the total field within the sphere, which must be regular,

$$
\pi_e^t = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} c_{m,n}^e j_n(k_1 r) P_n^{\text{im}}(\cos \theta) \exp(i m \phi),
$$

$$
\pi_m^t = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} c_{m,n}^m j_n(k_1 r) P_n^{\text{im}}(\cos \theta) \exp(i m \phi),
$$

where $a_{n,m}^e, b_{m,n}^e$ and $c_{m,n}^e$ are constants to be determined. Now we have the expressions for $\pi_{e,m}$ in spherical functions, the boundary conditions using these spherical functions are written as follows

$$
c_{m,n}^e j_n(k_1 r_s) = a_{m,n}^e j_n(k_0 r_s) + b_{m,n}^e h_n^{(1)}(k_0 r_s),
$$

$$
c_{m,n}^m j_n(k_1 r_s) = a_{m,n}^m j_n(k_0 r_s) + b_{m,n}^m h_n^{(1)}(k_0 r_s),
$$

$$
\frac{1}{\varepsilon_1} \left[ \frac{\partial}{\partial r} \left( r c_{m,n}^e j_n(k_1 r) \right) \right]_{r=r_s} = \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} \left( r a_{m,n}^e j_n(k_0 r) \right) + \frac{\partial}{\partial r} \left( rb_{m,n}^e h_n^{(1)}(k_0 r) \right) \right]_{r=r_s},
$$

$$
\frac{1}{\mu_1} \left[ \frac{\partial}{\partial r} \left( r c_{m,n}^m j_n(k_1 r) \right) \right]_{r=r_s} = \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} \left( r a_{m,n}^m j_n(k_0 r) \right) + \frac{\partial}{\partial r} \left( rb_{m,n}^m h_n^{(1)}(k_0 r) \right) \right]_{r=r_s}.
$$

Note that these conditions hold for all $m$. Therefore we can introduce the constants $R_{n,m}^e$ and $T_{n,m}$ which are independent of $m$. These coefficients are denoted as the reflection and transmission factors and are introduced through

$$
b_{m,n}^e = a_{m,n}^e R_{n,m}^e,
$$

$$
c_{m,n}^e = a_{m,n}^e T_{n,m}.
$$

From Equations (5.47-5.50) it follows that

$$
T_{n}^e j_n(k_1 r_s) = R_{n}^e h_n^{(1)}(k_0 r_s) + j_n(k_0 r_s),
$$

$$
T_{n}^m j_n(k_1 r_s) = R_{n}^m h_n^{(1)}(k_0 r_s) + j_n(k_0 r_s),
$$

$$
\frac{1}{\varepsilon_1} \left[ T_{n}^e \frac{\partial}{\partial r} j_n(k_1 r) \right]_{r=r_s} = \frac{1}{\varepsilon_0} \left[ R_{n}^e \frac{\partial}{\partial r} h_n^{(1)}(k_0 r) + \frac{\partial}{\partial r} j_n(k_0 r) \right]_{r=r_s},
$$

$$
\frac{1}{\mu_1} \left[ T_{n}^m \frac{\partial}{\partial r} j_n(k_1 r) \right]_{r=r_s} = \frac{1}{\mu_0} \left[ R_{n}^m \frac{\partial}{\partial r} h_n^{(1)}(k_0 r) + \frac{\partial}{\partial r} j_n(k_0 r) \right]_{r=r_s}.
Using these equations expressions for $R_n^e$, $T_n^e$ and $R_n^m$, $T_n^m$ can be found as

\[
R_n^e = \frac{j_n(k_0 r_s) \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} r j_n(k_1 r) \right]_{r=r_s} - j_n(k_1 r_s) \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} r j_n(k_0 r) \right]_{r=r_s}}{j_n(k_1 r_s) \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} r j_n(k_0 r) \right]_{r=r_s} - h_n^{(1)}(k_0 r_s) \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} r j_n(k_1 r) \right]_{r=r_s}}, \tag{5.57}
\]

\[
T_n^e = \frac{j_n(k_0 r_s) \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} r h_n^{(1)}(k_0 r) \right]_{r=r_s} - h_n^{(1)}(k_0 r_s) \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} r j_n(k_1 r) \right]_{r=r_s}}{j_n(k_1 r_s) \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} r h_n^{(1)}(k_0 r) \right]_{r=r_s} - h_n^{(1)}(k_0 r_s) \frac{1}{\varepsilon_0} \left[ \frac{\partial}{\partial r} r j_n(k_1 r) \right]_{r=r_s}}, \tag{5.58}
\]

\[
R_n^m = \frac{j_n(k_0 r_s) \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} r j_n(k_1 r) \right]_{r=r_s} - j_n(k_1 r_s) \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} r j_n(k_0 r) \right]_{r=r_s}}{j_n(k_1 r_s) \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} r j_n(k_0 r) \right]_{r=r_s} - h_n^{(1)}(k_0 r_s) \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} r j_n(k_1 r) \right]_{r=r_s}}, \tag{5.59}
\]

\[
T_n^m = \frac{j_n(k_0 r_s) \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} r h_n^{(1)}(k_0 r) \right]_{r=r_s} - h_n^{(1)}(k_0 r_s) \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} r j_n(k_1 r) \right]_{r=r_s}}{j_n(k_1 r_s) \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} r h_n^{(1)}(k_0 r) \right]_{r=r_s} - h_n^{(1)}(k_0 r_s) \frac{1}{\mu_0} \left[ \frac{\partial}{\partial r} r j_n(k_1 r) \right]_{r=r_s}}. \tag{5.60}
\]

To make these equations better readable, the following functions will be introduced:

\[
\hat{J}_n(x) = x j_n(x) \tag{5.61}
\]

\[
\hat{H}_n^{(1)}(x) = x h_n^{(1)}(x) \tag{5.62}
\]

If we use these relations for Equations (5.57-5.60) it follows that:

\[
R_n^e = \frac{\sqrt{\varepsilon_0 \mu_1} \hat{J}_n(k_0 r_s) \hat{J}_n^{(1)}(k_1 r_s) - \sqrt{\varepsilon_1 \mu_0} \hat{J}_n(k_1 r_s) \hat{J}_n^{(1)}(k_0 r_s)}{\sqrt{\varepsilon_1 \mu_0} \hat{J}_n(k_1 r_s) \hat{J}_n^{(1)}(k_0 r_s) - \sqrt{\varepsilon_0 \mu_1} \hat{J}_n^{(1)}(k_0 r_s) \hat{J}_n^{(1)}(k_1 r_s)}, \tag{5.63}
\]

\[
T_n^e = \frac{\varepsilon_1 \mu_0 \hat{J}_n(k_1 r_s) \hat{H}_n^{(1)}(k_0 r_s) - \varepsilon_0 \mu_1 \hat{J}_n^{(1)}(k_0 r_s) \hat{J}_n^{(1)}(k_1 r_s)}{\varepsilon_0 \mu_1 \hat{J}_n(k_0 r_s) \hat{H}_n^{(1)}(k_1 r_s) - \varepsilon_1 \mu_0 \hat{J}_n^{(1)}(k_0 r_s) \hat{J}_n^{(1)}(k_1 r_s)}, \tag{5.64}
\]

\[
R_n^m = \frac{\sqrt{\varepsilon_0 \mu_1} \hat{J}_n(k_0 r_s) \hat{J}_n^{(1)}(k_1 r_s) - \sqrt{\varepsilon_1 \mu_0} \hat{J}_n(k_1 r_s) \hat{J}_n^{(1)}(k_0 r_s)}{\sqrt{\varepsilon_0 \mu_1} \hat{J}_n(k_0 r_s) \hat{J}_n^{(1)}(k_1 r_s) - \varepsilon_1 \mu_0 \hat{J}_n^{(1)}(k_0 r_s) \hat{J}_n^{(1)}(k_1 r_s)}, \tag{5.65}
\]

\[
T_n^m = \frac{i \mu_1 \sqrt{\varepsilon_0} \hat{J}_n(k_1 r_s) \hat{H}_n^{(1)}(k_0 r_s) - \varepsilon_0 \mu_1 \hat{J}_n^{(1)}(k_0 r_s) \hat{H}_n^{(1)}(k_1 r_s)}{i \mu_0 \sqrt{\varepsilon_1} \hat{J}_n(k_0 r_s) \hat{H}_n^{(1)}(k_1 r_s) - \varepsilon_1 \mu_0 \hat{J}_n^{(1)}(k_0 r_s) \hat{H}_n^{(1)}(k_1 r_s)}. \tag{5.66}
\]

The Wronskian for spherical functions has been used to simplify $T_n^m$. The Wronskian of spherical Bessel functions is given by:

\[
\hat{J}_n(k_1 r_s) \hat{H}_n^{(1)}(k_1 r_s) - \hat{J}_n^{(1)}(k_1 r_s) \hat{H}_n^{(1)}(k_1 r_s) = i \tag{5.67}
\]

### 5.3.5 Substitution of $\pi_{e,m}$ in the Field Components

Now we have explicit expressions for $\pi_e$ and $\pi_m$, these can be substituted in the field components $E_{r,\theta,\phi}$ and $H_{r,\theta,\phi}$ from Equations (5.14-5.19). From these expressions and using the scalar Helmholtz equation, see Equation (5.40), we can find the expressions for
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the field components. From the scalar wave equation and the general equation for the Bessel functions, see Equation (5.37), we have

\[
\frac{\partial^2}{\partial r^2} r \pi_{e,m} = - \left[ k^2 - \frac{n(n+1)}{r^2} \right] r \pi_{e,m},
\]

(5.68)

which for the particular solution results in

\[
H_r = \frac{1}{s \mu} \frac{n(n+1)}{r} \pi_m,
\]

(5.69)

\[
E_r = \frac{1}{s \varepsilon} \frac{n(n+1)}{r} \pi_e.
\]

(5.70)

As mentioned earlier the incident and scattered field are limited to region 0, whereas the total field is limited to region 1. Now the analysis for the TM case, where only \( \pi_e \) plays a role will be done. The incident field is obtained as

\[
H_{0,r}^{\text{i}} = 0,
\]

(5.71)

\[
H_{0,\theta}^{\text{i}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{im}{\sin \theta} P_n^{(m)}(\cos \theta) j_n(k_0 r) a_{m,n}^e \exp(i m \phi),
\]

(5.72)

\[
H_{0,\phi}^{\text{i}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} - \frac{\partial}{\partial \theta} P_n^{(m)}(\cos \theta) j_n(k_0 r) a_{m,n}^e \exp(i m \phi),
\]

(5.73)

\[
E_{0,r}^{\text{i}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s \varepsilon_0} \frac{n(n+1)}{r} P_n^{(m)}(\cos \theta) j_n(k_0 r) a_{m,n}^e \exp(i m \phi),
\]

(5.74)

\[
E_{0,\theta}^{\text{i}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s \varepsilon_0} \frac{\partial}{\partial \theta} P_n^{(m)}(\cos \theta) \frac{1}{r} \frac{\partial}{\partial r} j_n(k_0 r) a_{m,n}^e \exp(i m \phi),
\]

(5.75)

\[
E_{0,\phi}^{\text{i}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s \varepsilon_0 \sin \theta} \frac{im}{r} P_n^{(m)}(\cos \theta) \frac{1}{r} \frac{\partial}{\partial r} j_n(k_0 r) a_{m,n}^e \exp(i m \phi),
\]

(5.76)

while the scattered field is obtained as

\[
H_{0,r}^{\text{s}} = 0,
\]

(5.77)

\[
H_{0,\theta}^{\text{s}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{im}{\sin \theta} P_n^{(m)}(\cos \theta) R_n h_n^{(1)}(k_0 r) a_{m,n}^e \exp(i m \phi),
\]

(5.78)

\[
H_{0,\phi}^{\text{s}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} - \frac{\partial}{\partial \theta} P_n^{(m)}(\cos \theta) R_n h_n^{(1)}(k_0 r) a_{m,n}^e \exp(i m \phi),
\]

(5.79)

\[
E_{0,r}^{\text{s}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s \varepsilon_0} \frac{n(n+1)}{r} P_n^{(m)}(\cos \theta) R_n h_n^{(1)}(k_0 r) a_{m,n}^e \exp(i m \phi),
\]

(5.80)

\[
E_{0,\theta}^{\text{s}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s \varepsilon_0} \frac{\partial}{\partial \theta} P_n^{(m)}(\cos \theta) \frac{1}{r} \frac{\partial}{\partial r} R_n h_n^{(1)}(k_0 r) a_{m,n}^e \exp(i m \phi),
\]

(5.81)

\[
E_{0,\phi}^{\text{s}} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s \varepsilon_0} \frac{im}{\sin \theta} P_n^{(m)}(\cos \theta) \frac{1}{r} \frac{\partial}{\partial r} R_n h_n^{(1)}(k_0 r) a_{m,n}^e \exp(i m \phi).
\]

(5.82)
The field inside the sphere is obtained as

\[
H^{n,t}_{1,r} = 0, \quad (5.83)
\]

\[
H^{e,t}_{1,\theta} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{im}{\sin \theta} \frac{1}{s_{\xi_1}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{\partial}{\partial \theta} j_n(k_1 r) a^m_{m,n} \exp(im\phi), \quad (5.84)
\]

\[
H^{m,t}_{1,\phi} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{\partial}{\partial \theta} P_n^{m} \cos \theta \frac{1}{r} \frac{\partial}{\partial r} j_n(k_1 r) a^m_{m,n} \exp(im\phi), \quad (5.85)
\]

\[
E^{n,t}_{1,r} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\xi_1}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} j_n(k_1 r) a^m_{m,n} \exp(im\phi), \quad (5.86)
\]

\[
E^{e,t}_{1,\theta} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\xi_1}} \frac{n(n+1)}{\sin \theta} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} j_n(k_1 r) a^m_{m,n} \exp(im\phi), \quad (5.87)
\]

\[
E^{m,t}_{1,\phi} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\xi_1}} \frac{n(n+1)}{\sin \theta} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} j_n(k_1 r) a^m_{m,n} \exp(im\phi). \quad (5.88)
\]

Second, for the TE-case, where only \( \pi_m \) plays a role, the incident field is

\[
H^{m,i}_{0,r} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\mu_0}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} j_n(k_0 r) a^m_{m,n} \exp(im\phi), \quad (5.89)
\]

\[
H^{m,i}_{0,\theta} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\mu_0}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} j_n(k_0 r) a^m_{m,n} \exp(im\phi), \quad (5.90)
\]

\[
H^{m,i}_{0,\phi} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\mu_0}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} j_n(k_0 r) a^m_{m,n} \exp(im\phi), \quad (5.91)
\]

\[
E^{m,i}_{0,r} = 0, \quad (5.92)
\]

\[
E^{m,i}_{0,\theta} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\mu_0}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} j_n(k_0 r) a^m_{m,n} \exp(im\phi), \quad (5.93)
\]

\[
E^{m,i}_{0,\phi} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\mu_0}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} j_n(k_0 r) a^m_{m,n} \exp(im\phi), \quad (5.94)
\]

and the scattered field is written as

\[
H^{m,s}_{0,r} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\mu_0}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} h_n(1)(k_0 r) a^m_{m,n} \exp(im\phi), \quad (5.95)
\]

\[
H^{m,s}_{0,\theta} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\mu_0}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} h_n(1)(k_0 r) a^m_{m,n} \exp(im\phi), \quad (5.96)
\]

\[
H^{m,s}_{0,\phi} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\mu_0}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} h_n(1)(k_0 r) a^m_{m,n} \exp(im\phi), \quad (5.97)
\]

\[
E^{m,s}_{0,r} = 0, \quad (5.98)
\]

\[
E^{m,s}_{0,\theta} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{1}{s_{\mu_0}} \frac{n(n+1)}{r} P_n^{m} \cos \theta \frac{1}{r} \frac{1}{\partial r} h_n(1)(k_0 r) a^m_{m,n} \exp(im\phi), \quad (5.99)
\]
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\[ E_{0,\phi}^{\infty,\infty} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} -\frac{\partial}{\partial \theta} P_n^{lm}(\cos \theta)P_n^{m}(k_0 r) j_n^{(1)}(k_0 r)a_{m,n}^m \exp(i m \phi). \]  

(5.100)

And the field inside the sphere is

\[ H_{1,r}^{\infty,\infty} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} -\frac{1}{s \mu_1} \frac{n(n+1)}{r} P_n^{lm}(\cos \theta)T_n^{m} j_n^{(1)}(k_1 r)a_{m,n}^m \exp(i m \phi), \]  

(5.101)

\[ H_{1,\theta}^{\infty,\infty} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} -\frac{1}{s \mu_1} \frac{\partial}{\partial \theta} P_n^{lm}(\cos \theta)T_n^{m} \frac{1}{r} \frac{\partial}{\partial r} r j_n^{(1)}(k_1 r)a_{m,n}^m \exp(i m \phi), \]  

(5.102)

\[ H_{1,\phi}^{\infty,\infty} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} -\frac{1}{s \mu_1} \frac{\partial}{\partial \theta} P_n^{lm}(\cos \theta)T_n^{m} \frac{1}{r} j_n^{(1)}(k_1 r)a_{m,n}^m \exp(i m \phi), \]  

(5.103)

\[ E_{1,r}^{\infty,\infty} = 0, \]  

(5.104)

\[ E_{1,\theta}^{\infty,\infty} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} \frac{im}{\sin \theta} P_n^{lm}(\cos \theta)T_n^{m} j_n^{(1)}(k_1 r)a_{m,n}^m \exp(i m \phi), \]  

(5.105)

\[ E_{1,\phi}^{\infty,\infty} = \sum_{n=0}^{+\infty} \sum_{m=-\infty}^{+\infty} -\frac{\partial}{\partial \theta} P_n^{lm}(\cos \theta)T_n^{m} j_n^{(1)}(k_1 r)a_{m,n}^m \exp(i m \phi). \]  

(5.106)

Now we have determined the field components, we only have to find an expression for the constant \(a_{m,n}^m\). This will be done in the next section.

5.3.6 Orthogonality Relations & Expansion of Plane Waves

Let \( P \) be a point on a sphere as shown in Figure 5.3 whose coordinates with respect to a fixed rectangular reference system are \( \theta \) and \( \phi \). A second point \( Q \) on the sphere has the coordinates \( \theta' \) and \( \phi' \). The angle made by the axis \( OP \) with the axis \( OQ \) is \( \gamma \). The harmonics at \( P \) referred to the new polar axis \( OQ \) are of the form \( P_n(\cos \gamma) \) which can be expanded in terms of the coordinates \( \theta, \phi, \theta', \phi' \). We now assume for \( P_n(\cos \gamma) \) an expansion of the form:

\[ P_n(\cos \gamma) = \sum_{m=-\infty}^{+\infty} a_m \exp(i m \phi) P_n^{lm}(\cos \theta), \]  

(5.107)

in which \( \cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi') \). The orthogonality relations for \( P_n^{lm}(\eta) \) are given by [127]:

\[ \int_{-1}^{1} P_n^{lm}(\eta) P_m^{lm}(\eta) d\eta = 0, \]  

(5.108)

\[ \int_{-1}^{1} [P_n^{lm}(\eta)]^2 d\eta = \frac{2(n + |m|)!}{(2n + 1)(n - |m|)!}. \]  

(5.109)

We first consider an axis that coincides with the direction of the wave. Since the wave is symmetrical about this axis, we write

\[ \exp(ikr \cos \gamma) = \sum_{n=0}^{\infty} \beta_n J_n(kr) P_n(\cos \gamma). \]  

(5.110)
The coefficients are determined by multiplying both sides by $P_n(\cos \gamma) \sin \gamma$ and integrating with respect to $\gamma$ from 0 to $\pi$. Using the orthogonality relations of the Legendre polynomials, the following relation results:

$$\beta_n j_n(kr) = \frac{2n + 1}{2} \int_0^\pi \exp(ikr \cos \gamma) P_n(\cos \gamma) \sin \gamma d\gamma$$

(5.111)

To remove the $r$-dependence from this relation, differentiate both sides with respect to $\rho = kr$ and then put $\rho = 0$. From Stratton [127] it follows that

$$\left[ \frac{d^n j_n(\rho)}{d\rho^n} \right]_{\rho=0} = \frac{2^n(n!)^2}{(2n + 1)!}$$

(5.112)

which results in the following equation:

$$\frac{2^n(n!)^2}{(2n + 1)!} \beta_n = \frac{2n + 1}{2} \epsilon^n \int_0^\pi \cos^n \gamma P_n(\cos \gamma) \sin \gamma d\gamma$$

(5.113)

The integral on the right can be found using Rodrigues' Formula [128], i.e.,

$$P_n(\cos \gamma) = \frac{1}{2^n n!} \frac{d^n(\cos^2 \gamma - 1)^n}{d \cos^n \gamma},$$

(5.114)
eventually resulting in $\beta_n = (2n + 1)i^n$, or
\[
\exp(ikr \cos \gamma) = \sum_{n=0}^{\infty} (2n + 1)i^n j_n(kr) P_n(\cos \gamma)
\] (5.115)

### Addition Theorem

For an arbitrary axis of coincidence we may want to introduce the addition theorem for the Legendre polynomials. Stratton [127] showed that if an arbitrary function on the surface of a sphere $g(\theta, \phi)$, and all its first and second derivatives are continuous, then $g(\theta, \phi)$ can be represented by an absolutely convergent series of surface harmonics,

\[
g(\theta, \phi) = \sum_{n=0}^{\infty} \sum_{m=-\infty}^{\infty} (A_{nm} \exp(i m \phi) P_n^m(\cos \theta)),
\] (5.116)

whose coefficients are determined by

\[
A_{n0} = \frac{2n + 1}{4\pi} \int_0^{2\pi} \int_0^\pi g(\theta, \phi) P_n(\cos \theta) \sin \theta d\theta d\phi,
\] (5.117)

\[
A_{nm} = \frac{2n + 1}{4\pi} \frac{(n - |m|)!}{(n + |m|)!} \int_0^{2\pi} \int_0^\pi g(\theta, \phi) P_n^m(\cos \theta) \exp(i m \phi) \sin \theta d\theta d\phi,
\] (5.118)

where it is clear that $A_{n0}$ is the expression resulting from the case that $m = 0$. Using this expansion theorem at the pole, $\theta = 0$, results in:

\[
g(\theta, \phi)_{\theta=0} = \sum_{n=0}^{\infty} A_{n0} = \frac{1}{4\pi} \sum_{n=0}^{\infty} (2n + 1) \int_0^{2\pi} \int_0^\pi g(\theta, \phi) P_n(\cos \theta) \sin \theta d\theta d\phi,
\] (5.119)

because $P_n(1) = 1$ and $P_n^m(1) = 0$. Since $\cos \gamma$ is nothing else than a function of $\theta$ and $\phi$, we could say that $P_n(\cos \gamma)$ is a spherical surface harmonic of degree $n$, i.e. $Y_n(\theta, \phi)$. Then in virtue of the orthogonality relations, the sum in (5.119) reduces to a single term and we obtain the formula

\[
\int_0^{2\pi} \int_0^\pi Y_n(\theta, \phi) P_n(\cos \theta) \sin \theta d\theta d\phi = \frac{4\pi}{2n + 1} [Y_n(\theta, \phi)]_{\theta=0}
\] (5.120)

This results in

\[
\int_0^{2\pi} \int_0^\pi P_n(\cos \gamma) P_n^m(\cos \theta) \exp(i m \phi) \sin \theta d\theta d\phi = \frac{4\pi}{(2n + 1)} [P_n^m(\cos \theta) \exp(i m \phi)]_{\gamma=0}
\] (5.121)

\[
= \frac{4\pi}{(2n + 1)} P_n^m(\cos \theta) \exp(i m \phi)
\]

Since when $\gamma = 0$, $\theta = \theta'$, $\phi = \phi'$. But from Equation (5.107) and the orthogonality relations, we obtain

\[
\int_0^{2\pi} \int_0^\pi P_n(\cos \gamma) P_n^m(\cos \theta) \exp(i m \phi) \sin \theta d\theta d\phi = \frac{2\pi}{(2n + 1)} \frac{(n + |m|)!}{(n - |m|)!} c_m
\] (5.122)
Using these equations, we find for $\alpha_m$:

$$\alpha_m = \frac{(n - |m|)!}{(n + |m|)!} P_n^{|m|}(\cos \theta') \exp(im\phi')$$  \hspace{1cm} (5.123)

This analysis finally results in the entire plane wave expansion from an arbitrary axis as:

$$\exp(ikr \cos \gamma) = \sum_{n=0}^{\infty} (2n+1)i^n j_n(kr) \sum_{m=-n}^{n} \frac{(n - |m|)!}{(n + m)!} P_n^{|m|}(\cos \theta') P_n^{|m|}(\cos \theta) \exp(im(\phi - \phi')).$$  \hspace{1cm} (5.124)

This is the expansion of a scalar plane wave. However, we need the expansion of a vectorial plane wave. This is discussed in the next subsection.

### 5.3.7 Expansion of a Plane Wave in Vector Spherical Harmonics

Now we have the plane wave contribution and noting that only the $m = 1$ azimuthal mode is required for the sphere solution, we can derive the plane-wave expansion in vector spherical coordinates. Here we take a plane $x$-polarized wave, written in spherical polar coordinates as

$$E_x = E_0 \exp(ikr \cos \theta) i_x,$$  \hspace{1cm} (5.125)

where

$$i_x = \sin \theta \cos \phi i_r + \cos \theta \cos \phi i_\theta - \sin \phi i_\phi.$$  \hspace{1cm} (5.126)

When we suppose unit incidence ($E_0 = 1$), the desired expansion of a plane wave in spherical harmonics can be written as

$$E_x = \sum_n \sum_m f_{m,n} m_{m,n}^{(1)} + g_{m,n} n_{m,n}^{(1)}. $$  \hspace{1cm} (5.127)

Here $m$ and $n$ are vector functions which have all required properties of an electromagnetic field as described in Appendix C. Earlier we found expressions of $E$ written in $\pi_\varphi$ and $\pi_m$, viz.,

$$E = \nabla \times r \pi_m + \frac{1}{\varepsilon} \nabla \times \nabla \times r \pi_\varphi.$$  \hspace{1cm} (5.128)

As stated earlier these Debye potentials obey the following relations:

$$\pi_\varphi^i = \sum_n \sum_m a_{m,n}^i \psi_{m,n}^{(1)},$$  \hspace{1cm} (5.129)

$$\pi_m^i = \sum_n \sum_m a_{m,n}^i \psi_{m,n}^{(1)},$$  \hspace{1cm} (5.130)

where $\psi_{m,n}$ are the spherical functions

$$\psi_{m,n}^{(1)} = j_n(k_0 r) P_n^{|m|}(\cos \theta) \exp(im\phi).$$  \hspace{1cm} (5.131)

From Appendix C we know that

$$m_{m,n}^{(1)} = (-1)^m \nabla \times r \psi_{m,n}^{(1)}, \quad n_{m,n}^{(1)} = \frac{(-1)^m}{k} \nabla \times \nabla \times r \psi_{m,n}^{(1)}.$$
By combining Equations (5.127-5.130) with these relations we find expressions for $a_{m,n}^m$ and $a_{m,n}^e$ as:

$$a_{m,n}^m = (-1)^m f_{m,n}, \quad a_{m,n}^e = -i(-1)^m \left( \frac{\varepsilon_0}{\mu_0} \right)^{\frac{1}{2}} g_{m,n}. \quad (5.132)$$

Using again the results of Appendix C, we can write for these coefficients

$$a_{m,n}^m = f_{m,n} = i^{n-1} \frac{2n+1}{2n(n+1)} [\delta_{m,-1} - \delta_{m,1}], \quad (5.133)$$

$$a_{m,n}^e = \left( \frac{\varepsilon_0}{\mu_0} \right)^{\frac{1}{2}} i^n \frac{2n+1}{2n(n+1)} [\delta_{m,-1} + \delta_{m,1}]. \quad (5.134)$$

The same analysis for an incident wave in the case of $y$-polarization yields

$$a_{m,n}^m = f_{m,n} = -i^{n} \frac{2n+1}{2n(n+1)} [\delta_{m,-1} + \delta_{m,1}], \quad (5.135)$$

$$a_{m,n}^e = \left( \frac{\varepsilon_0}{\mu_0} \right)^{\frac{1}{2}} i^{n-1} \frac{2n+1}{2n(n+1)} [\delta_{m,-1} - \delta_{m,1}]. \quad (5.136)$$

### 5.3.8 The Scattered Far-Field Expression

The vector far-field amplitude $\mathbf{F}$ of the scattered field is defined by

$$\mathbf{E}^s(kr) = \mathbf{F} \frac{\exp(ikr)}{r} \quad (5.137)$$

in the limit as $kr \to \infty$. Here we take the definition of the far-field given by Barber and Hill [129]. This facilitates an easy comparison of the results. Only the spherical Hankel function $h_n^{(1)}(kr)$ needs to be considered here, because we use the scattered field component. The following recursion relation for Bessel functions can be used to extract the desired expressions [130],

$$\frac{\nu}{z} u_{\nu}(z) + u'_{\nu}(z) = u_{\nu-1}(z). \quad (5.138)$$

The explicit form can be obtained by replacing $h_n^{(1)}(kr)$ and its derivative in the scattered field components with the asymptotic expressions

$$\lim_{kr \to \infty} h_n^{(1)}(kr) = \frac{i^{-n}}{ikr} \exp(ikr), \quad (5.139)$$

$$\lim_{kr \to \infty} h_{n-1}^{(1)}(kr) = \frac{i^{-n}}{kr} \exp(ikr), \quad (5.140)$$

and neglecting any terms in $1/r^2$. If we now use the recursion relation stated above, the resulting derivative of the first order Hankel function reads as

$$h_n^{(1)}(k_0r) = h_{n-1}^{(1)}(k_0r) - \frac{n}{k_0r} h_n^{(1)}(k_0r). \quad (5.141)$$
In our expression for the scattered field the following relation has been used
\[
\lim_{kr \to \infty} \frac{1}{r} \frac{\partial}{\partial r} rh_n^{(1)}(kr) = i^n \frac{\exp(ikr)}{r}.
\] (5.142)

### 5.3.9 Results for a single sphere

**Scattering simulations**

Since we now have the coefficients for a vectorial plane wave, we can check the theory we have constructed thusfar by computing the far field and compare the numerical results with known results from literature [129]. The intensity function used here is related to the differential scattering cross section \( \sigma_d \), normalized by \( \pi a^2 \), where \( a \) is the sphere radius, and reads as
\[
\frac{\sigma_d}{\pi a^2} = \frac{|kF|^2}{\pi (ka)^2}.
\] (5.143)

The electric field components \( E_\theta \) and \( E_\phi \) will be taken both for \( TM \) and \( TE \) and written in terms of \( kF^T_n, kF^m_n, kF^c_\phi, kF^m_\phi \), respectively. For \( x \)-polarization the far-field expressions read as
\[
kF^x_\theta &= \sum_n i \frac{2n + 1}{2n(n + 1)} \frac{\partial}{\partial \phi} P_n^1(\cos \theta) R_n^c [\exp(-i\phi) + \exp(i\phi)],
\] (5.144)
\[
kF^m_\theta &= \sum_n \frac{2n + 1}{2n(n + 1) \sin \theta} P_n^1(\cos \theta) R_n^m [\exp(-i\phi) + \exp(i\phi)],
\] (5.145)
\[
kF^c_\phi &= \sum_n \frac{2n + 1}{2n(n + 1) \sin \theta} P_n^1(\cos \theta) R_n^c [\exp(-i\phi) - \exp(i\phi)],
\] (5.146)
\[
kF^m_\phi &= \sum_n \frac{2n + 1}{2n(n + 1)} \frac{\partial}{\partial \theta} P_n^1(\cos \theta) R_n^m [\exp(-i\phi) - \exp(i\phi)].
\] (5.147)

The same can be done for the case of \( y \)-polarization and yields
\[
kF^y_\theta &= \sum_n \frac{2n + 1}{2n(n + 1)} \frac{\partial}{\partial \phi} P_n^1(\cos \theta) R_n^c [\exp(-i\phi) - \exp(i\phi)],
\] (5.148)
\[
kF^m_\theta &= \sum_n \frac{2n + 1}{2n(n + 1) \sin \theta} P_n^1(\cos \theta) R_n^m [\exp(-i\phi) - \exp(i\phi)],
\] (5.149)
\[
kF^c_\phi &= \sum_n -\frac{2n + 1}{2n(n + 1) \sin \theta} P_n^1(\cos \theta) R_n^c [\exp(-i\phi) + \exp(i\phi)],
\] (5.150)
\[
kF^m_\phi &= \sum_n \frac{2n + 1}{2n(n + 1)} \frac{\partial}{\partial \theta} P_n^1(\cos \theta) R_n^m [\exp(-i\phi) - \exp(i\phi)].
\] (5.151)

In Figures 5.4, 5.5 and 5.6 we present the scattered intensities \( \frac{\sigma_d}{\pi a^2} \) as a function of \( \theta \), while \( \phi = 0 \). In the computation to arrive at the results of Figures 5.4, 5.5 and 5.6, we have taken the summations in Equations (5.144)-(5.151) from \( n = 1 \) to \( n = 80 \). This relatively high number is necessary for the spherical functions to converge. The plotting increment is 0.01° in all simulations which are shown here.
Figure 5.4: Angular scattered intensity for a sphere with $ka = 50$ and a relative permittivity of 2.25; $x$-polarization results of Barber and Hill [129] (top), our results (bottom).
Figure 5.5: Angular scattered intensity for a sphere with $ka = 50$ and a relative permittivity of 2.25; y-polarization results of Barber and Hill [129] (top), our results (bottom).
Figure 5.6: Angular scattered intensity for a sphere with $ka = 50$ and a relative complex permittivity of $2.2499 + 0.03i$; $x$-polarization results of Barber and Hill [129] (top), our results (bottom).
CHAPTER 5. ABSORPTION BY MULTIPLE PARTICLES

Internal Intensity Distribution

Also the intensity distribution has been calculated along a line through the center of the sphere. The calculated quantity is the intensity function \( I \) given as

\[
I = E \cdot E^* .
\]  

(5.152)

The intensity along a line through the center of the sphere is obtained by varying the ratio \( \frac{\lambda}{\theta} \) from one to zero while the angle \( \theta \) is set to \( 180^\circ \) and then from zero to one while \( \theta \) is set to \( 0^\circ \). One numerical example is shown in Figure 5.7 for parallel polarization. The incident wave propagates from left to right, producing a standing wave pattern within the sphere resulting from interference between the refracted and internally reflected components. Figure 5.7 is for a lossless sphere; Figure 5.8 shows the internal intensity distribution for two different absorbing spheres. The standing-wave pattern pattern is still prominent for an index of refraction of \( 2.2475 + 0.1500i \). However, when the imaginary part is \( 0.3 \), the internal intensity attenuates rapidly from the illuminated side of the sphere. These figures also show the focusing effect due to the curvature of the sphere. From this effect, the larger intensities can be explained as if a focal point exists.

Conclusion

From a comparison of our results with the ones from Barber and Hill [129], we conclude that the results coincide and with this confidence in our results for the scattering by a single sphere, we now continue our discussion with the problem of many spherical scatterers.
5.3. **SCATTERING BY A SINGLE SPHERE**

![Graph](image)

**Figure 5.7**: The internal intensity along the z axis as a function of $\frac{r}{a}$ for a sphere with $ka = 20$ and a relative permittivity of 2.25.

![Graph](image)

**Figure 5.8**: The internal intensity along the z axis as a function of $\frac{r}{a}$ for a sphere with $ka = 20$ and a relative complex permittivity of $2.2475 + 0.1500i$ and $2.2400 + 0.3000i$ for the solid and dashed line, respectively.
5.4 Multiple Scattering

5.4.1 Introduction

In this chapter we will describe the theory of scattering by a number of spherical particles [131, 132, 121]. Although the problem is a vectorial one, for simplicity, we discuss the theory of multiple scattering by considering the scalar version. The actual implementation is carried in complete vectorial form. The main problem in multiple scattering that has to be solved is the interaction between all the objects. The total field impinging on a scatterer consists of the incident field and all scattered fields from the other scatterers.

5.4.2 Problem Configuration

The configuration of a number of spherical scatterers is shown in Figure 5.9. Again, we can write for the total field:

$$\phi = \phi^i + \phi^s$$  \hspace{1cm} (5.153)

Outside the circumscribing sphere we introduce two amplitude vectors $a$ and $f$ for the incident field and the scattered field, respectively, as

$$\phi^i = \sum_{m,n} a_{m,n} \mathcal{Rg} \psi_{m,n}(k_0, r) = a^i \cdot \mathcal{Rg} \psi(k_0, r),$$  \hspace{1cm} (5.154)

$$\phi^s = \sum_{m,n} f_{m,n} \psi_{m,n}(k_0, r) = f^i \cdot \psi(k_0, r),$$  \hspace{1cm} (5.155)

where $\psi$ denote the functional vectors and $a^i$, $f^i$ are the transposed amplitude vectors. In the scalar case the function $\psi_{m,n}$ and $\mathcal{Rg} \psi_{m,n}$ are the outgoing spherical harmonics and their regular parts, respectively [Appendix C]. In three dimensions $\psi(k_0, r)$ is a column vector containing the vector spherical wave functions, which are defined as

$$\psi = [\psi_{-m,1}, \ldots, \psi_{+m,1}, \ldots, \psi_{m,n}, \ldots]^t,$$  \hspace{1cm} (5.156)

where

$$\psi_{m,n}(k_0, r) = [M_{m,n}(r) \quad N_{m,n}(r)].$$  \hspace{1cm} (5.157)

Now we can define a transition matrix which relates the amplitude of the scattered field with the amplitude of the incident field through

$$f = \mathbf{T} \cdot a,$$  \hspace{1cm} (5.158)

where $\mathbf{T}$ denotes the $T$-matrix. We need to find this $T$-matrix to calculate the amplitude of the scattered field, $f$. With the help of the Waterman method [Appendix D] the $T$-matrix for an arbitrary scatterer can be found. However, we do not need this method since for one single spherical particle this matrix can be found exactly. Therefore, a recursive scheme will be discussed which starts with the isolated $T$-matrix, i.e. the $T$-matrix of a single scatterer in free space and calculates this matrix for $2, 3, 4, \ldots, N$ scatterers. Once we know this matrix which comprises all particles, the transition matrix for $N$ spheres, the
scattered field can be found directly. We use Figure 5.10 to clearly illustrate the physical phenomena in multiple scattering. We directly observe that all the interactions between the spheres have to be calculated. Furthermore, the spherical harmonics can only be applied when the origin coincides with the origin of the considered scatterer. Therefore, a translational addition theorem is also needed to shift the results from one origin to the one of the sphere particularly considered.

**Isolated T-Matrix**

The $\overline{T}$-matrix for a single spherical scatterer can be found from the reflection coefficients. For a single sphere the transition matrix is diagonal and consists of the reflection coefficients only, while it is given as

$$\overline{T}_1^{(1)} = \begin{bmatrix} R_n^m & 0 \\ 0 & R_n^c \end{bmatrix}.$$  \hspace{1cm} (5.159)

where $\overline{T}_1^{(1)}$ indicates that this is the isolated matrix of the first scatterer. For example, $\overline{T}_2^{(1)}$ would be the isolated transition matrix of the second spherical scatterer. The reflection coefficients have been described in a previous section, but will be given again for convenience,

$$R_n^c = \frac{\sqrt{\varepsilon_0 \mu_0} \hat{J}_n(k_0 r_s) \hat{H}_n^{(1)}(k_0 r_s) - \sqrt{\varepsilon_1 \mu_0} \hat{J}_n(k_1 r_s) \hat{J}_n(k_0 r_s)}{\sqrt{\varepsilon_0 \mu_0} \hat{J}_n^{*}(k_1 r_s) \hat{H}_n^{(1)*}(k_0 r_s) - \sqrt{\varepsilon_0 \mu_0} \hat{J}_n^{*}(k_1 r_s) \hat{J}_n^{*}(k_0 r_s)},$$

$$R_n^m = \frac{\sqrt{\varepsilon_1 \mu_0} \hat{J}_n(k_0 r_s) \hat{J}_n^{*}(k_1 r_s) - \sqrt{\varepsilon_0 \mu_0} \hat{J}_n(k_0 r_s) \hat{J}_n^{*}(k_0 r_s)}{\sqrt{\varepsilon_0 \mu_1} \hat{J}_n^{*}(k_1 r_s) \hat{H}_n^{(1)*}(k_0 r_s) - \sqrt{\varepsilon_0 \mu_1} \hat{J}_n^{*}(k_1 r_s) \hat{J}_n^{*}(k_0 r_s)}.$$  \hspace{1cm} (5.160)
5.4.3 T-Matrix for Two Scatterers

For a two-scatterer problem, three coordinate systems are introduced. One is a global coordinate system. The others are two local coordinate systems located at the centers of the scatterers. We write the incident field in terms of the global coordinate system as

$$\phi^i(r) = a^t \cdot Rg\psi(k_0, r_0),$$

(5.162)

where $\psi(k_0, r_0)$ represents the outgoing harmonics expressed in the global coordinate system and $a$ is a column vector whose components are the expansion coefficients of the incident wave. When $r_1$ represents the local coordinates of the first scatterer and $r_2$ represents the local coordinates of the second scatterer, the scattered field is expressed as

$$\phi^s(r) = f_1^t \cdot \psi(k_0, r_1) + f_2^t \cdot \psi(k_0, r_2),$$

(5.163)

while the total field in the presence of two scatterers can be expressed as

$$\phi(r) = a^t \cdot Rg\psi(k_0, r_0) + f_1^t \cdot \psi(k_0, r_1) + f_2^t \cdot \psi(k_0, r_2),$$

(5.164)

where $f_1$ and $f_2$ are the unknowns to be determined. The scattered fields from each scatterer, which are the last two terms in the above equation, are written in terms of the outgoing harmonics expressed in the local coordinate systems of the scatterers. In order to find $f_1$ and $f_2$, the following translation formulas, which relate the harmonic functions at two different locations, are needed:

$$\psi(k_0, r_i) = \sum_j \alpha_{ji} \cdot Rg\psi(k_0, r_j) = \alpha_{ji}^d \cdot Rg\psi(k_0, r_j), \quad |r_j| < d_{ij},$$

(5.165)
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\[ \psi(k_0, r_i) = \sum_j \beta_{ij} \cdot \psi(k_0, r_j) = \overline{\beta}_{ij}^t \cdot \psi(k_0, r_j), \quad |r_j| > d_{ij}, \quad (5.166) \]

\[ \Re g \psi(k_0, r_i) = \sum_j \beta_{ij} \cdot \Re g \psi(k_0, r_j) = \overline{\beta}_{ij}^t \cdot \Re g \psi(k_0, r_j), \quad \forall |r_j|, \quad (5.167) \]

where \( d_{ij} \) is the distance between \( O_i \) and \( O_j \), the origins of the \( i \) and \( j \) coordinate systems. Using these formulas, the harmonic expansion of the field of one coordinate system can be expressed in terms of another coordinate system. More about the recursion formulas for the vector addition theorem can be found in Chew [124]. Using the translation formulas of Equations (5.165)-(5.166), the total field outside the scatterers can be expressed in terms of the local coordinate system of the first scatterer as

\[ \phi(r) = [\overline{\beta}_{10} \cdot a]^t \cdot \Re g \psi(k_0, r_1) + f_1^t \cdot \psi(k_0, r_1) + [\overline{\alpha}_{12} \cdot f_2]^t \cdot \Re g \psi(k_0, r_1). \quad (5.168) \]

Notice that this equation is only valid when \( |r_1| < d_{1,2} \) in order to apply (5.165). The first and the third terms in the above can be viewed as the incident field impinging upon scatterer 1, while the second term is the scattered field from scatterer 1. The isolated \( \overline{T} \) matrices, \( \overline{T}_{1(1)} \) and \( \overline{T}_{2(1)} \), for scatterers 1 and 2 are known. Note that we have used the notation that \( \overline{T}_{i(1)} \) is the one-scatterer \( \overline{T} \) matrix (isolated) for the \( i \)-th scatterer. Therefore, we can relate \( f_1 \) to \( a \) and \( f_2 \) using the \( \overline{T}_{1(1)} \) matrix as

\[ f_1 = \overline{T}_{1(1)} \cdot \overline{\beta}_{10} \cdot a + \overline{\alpha}_{12} \cdot f_2. \quad (5.169) \]

Similarly, for scatterer 2, we find

\[ f_2 = \overline{T}_{2(1)} \cdot \overline{\beta}_{20} \cdot a + \overline{\alpha}_{21} \cdot f_1. \quad (5.170) \]

Solving Equations (5.169)-(5.170) for \( f_1 \) and \( f_2 \), we find

\[ f_1 = \left[ I - \overline{T}_{1(1)} \cdot \overline{\alpha}_{12} \cdot \overline{T}_{2(1)} \cdot \overline{\alpha}_{21} \right]^{-1} \cdot \overline{T}_{1(1)} \cdot \left[ \overline{\beta}_{10} + \overline{\alpha}_{12} \cdot \overline{T}_{2(1)} \cdot \overline{\beta}_{20} \right] \cdot a, \quad (5.171) \]

\[ f_2 = \left[ I - \overline{T}_{2(1)} \cdot \overline{\alpha}_{21} \cdot \overline{T}_{1(1)} \cdot \overline{\alpha}_{12} \right]^{-1} \cdot \overline{T}_{2(1)} \cdot \left[ \overline{\beta}_{20} + \overline{\alpha}_{21} \cdot \overline{T}_{1(1)} \cdot \overline{\beta}_{10} \right] \cdot a. \quad (5.172) \]

Now, new \( \overline{T} \) matrices are defined such that

\[ f_1 = \overline{T}_{1(2)} \cdot \overline{\beta}_{10} \cdot a, \quad (5.173) \]

\[ f_2 = \overline{T}_{2(2)} \cdot \overline{\beta}_{20} \cdot a. \quad (5.174) \]

Note that we have introduced here that \( \overline{T}_{i(2)} \) is a two-scatterer \( \overline{T} \) matrix, which relates the total scattered field due to the \( i \)-th scatterer to the incident field amplitude when two scatterers are present. The equations for \( \overline{T}_{i(2)} \) read as follows:

\[ \overline{T}_{1(2)} = \left[ I - \overline{T}_{1(1)} \cdot \overline{\alpha}_{12} \cdot \overline{T}_{2(1)} \cdot \overline{\alpha}_{21} \right]^{-1} \cdot \overline{T}_{1(1)} \cdot \left[ \overline{\beta}_{10} + \overline{\alpha}_{12} \cdot \overline{T}_{2(1)} \cdot \overline{\beta}_{20} \right] \cdot \overline{\beta}_{01}, \quad (5.175) \]

\[ \overline{T}_{2(2)} = \left[ I - \overline{T}_{2(1)} \cdot \overline{\alpha}_{21} \cdot \overline{T}_{1(1)} \cdot \overline{\alpha}_{12} \right]^{-1} \cdot \overline{T}_{2(1)} \cdot \left[ \overline{\beta}_{20} + \overline{\alpha}_{21} \cdot \overline{T}_{1(1)} \cdot \overline{\beta}_{10} \right] \cdot \overline{\beta}_{02}, \quad (5.176) \]

where the relation \( \overline{\beta}_{i0}^{-1} = \overline{\beta}_{0i} \) has been used. Finally, the total field exterior to the scatterers can be written as

\[ \phi(r) = a^t \cdot \Re g \psi(k_0, r_0) + \overline{T}_{1(2)} \cdot \overline{\beta}_{10} \cdot a^t \cdot \psi(k_0, r_1) + \overline{T}_{2(2)} \cdot \overline{\beta}_{20} \cdot a^t \cdot \psi(k_0, r_2). \quad (5.177) \]
Domains of Validity of the Translation Theorem

Before we go to the three- and $N$-scatterer solutions, it is helpful to first take a closer look at the domains of validity of the translation formulas. To make this clear, the figures shown here are two-dimensional. Also, some new definitions will be introduced which will be very helpful in the descriptions of the three- and $N$-scatterer solution. First we take a closer look at the translation formulas, i.e. Equations (5.165)-(5.167) and in particular the first two equations. Second we can clarify these formulas by simply introducing a sphere defined by the radius between the $i$-th and the $j$-th coordinate systems and its origin located at the origin of the $j$-th coordinate system in which we want to express the $i$-th coordinate system. We call this sphere $S_{j,i}$. Now there are two possibilities:

- The observation point $P$ is located within this sphere $S_{j,i}$. If this is true, the field has to be regular inside this sphere, since we can see this as an incoming wave.

- The observation point $P$ is located outside $S_{j,i}$. When this is the case, we are dealing with an 'outgoing wave'.

Notice that in the above we use coordinate systems instead of scatterers, since these formulas are general and one of these coordinate systems can be the global coordinate system without a scatterer centered at its origin.
5.4. MULTIPLE SCATTERING

5.4.4 Extension to Three Scatterers

Now we have discussed the domains of validity of the translation formulas, the three-scatterer solution will be presented. We shall derive the three-scatterer $\mathbf{T}$ matrices directly from the isolated $\mathbf{T}$ matrices, $\mathbf{T}_{i(1)}$, $i = 1, 2, 3$. From the two-scatterer solution we observe that we may express the total field as

$$\phi(r) = \mathbf{a}^t \cdot \mathbf{Rg} \psi(k_0, r_0) + \left[ \mathbf{T}_{1(3)} \cdot \mathbf{B}_{10} \cdot \mathbf{a} \right]^t \cdot \psi(k_0, r_1) +$$

$$\left[ \mathbf{T}_{2(3)} \cdot \mathbf{B}_{20} \cdot \mathbf{a} \right]^t \cdot \psi(k_0, r_2) + \left[ \mathbf{T}_{3(3)} \cdot \mathbf{B}_{30} \cdot \mathbf{a} \right]^t \cdot \psi(k_0, r_3). \quad (5.178)$$

Using the translation formulas, Equations (5.165)-(5.167), the three-scatterer solution can be written in terms of the local coordinate system of the first scatterer as

$$\phi(r) = \left[ \mathbf{\bar{B}}_{10} \cdot \mathbf{a} \right]^t \cdot \mathbf{Rg} \psi(k_0, r_1) + \left[ \mathbf{T}_{1(3)} \cdot \mathbf{\bar{B}}_{10} \cdot \mathbf{a} \right]^t \cdot \psi(k_0, r_1) +$$

$$\left[ \mathbf{\bar{a}}_{12} \cdot \mathbf{T}_{2(3)} \cdot \mathbf{\bar{B}}_{20} \cdot \mathbf{a} \right]^t \cdot \mathbf{Rg} \psi(k_0, r_1) + \left[ \mathbf{\bar{a}}_{13} \cdot \mathbf{T}_{3(3)} \cdot \mathbf{\bar{B}}_{30} \cdot \mathbf{a} \right]^t \cdot \mathbf{Rg} \psi(k_0, r_1). \quad (5.179)$$

Equation (5.179) is valid if $|r_1| < d_{1,2}$ and $|r_1| < d_{1,3}$. So, depending on which scatterer is located nearest to the local coordinate system of the first scatterer, the observation point is located in either $S_{2,1}$ or $S_{3,1}$. If we consider the first and last two terms on the right-hand side of Equation (5.179) as the incident field impinging upon the first scatterer, we have

$$\mathbf{T}_{1(3)} \cdot \mathbf{\bar{B}}_{10} = \mathbf{T}_{1(1)} \cdot \left[ \mathbf{\bar{B}}_{10} + \mathbf{\bar{a}}_{12} \cdot \mathbf{T}_{2(3)} \cdot \mathbf{\bar{B}}_{20} + \mathbf{\bar{a}}_{13} \cdot \mathbf{T}_{3(3)} \cdot \mathbf{\bar{B}}_{30} \right]. \quad (5.180)$$
The same analysis for scatterers 2 and 3 results in
\[
\begin{align*}
\mathbf{T}_{2(3)} \cdot \vec{\beta}_{20} &= \mathbf{T}_{2(1)} \cdot \left[ \vec{\beta}_{20} + \vec{\alpha}_{21} \cdot \mathbf{T}_{1(3)} \cdot \vec{\beta}_{10} + \vec{\alpha}_{23} \cdot \mathbf{T}_{2(3)} \cdot \vec{\beta}_{30} \right], \\
\mathbf{T}_{3(3)} \cdot \vec{\beta}_{30} &= \mathbf{T}_{3(1)} \cdot \left[ \vec{\beta}_{30} + \vec{\alpha}_{31} \cdot \mathbf{T}_{1(3)} \cdot \vec{\beta}_{10} + \vec{\alpha}_{32} \cdot \mathbf{T}_{2(3)} \cdot \vec{\beta}_{20} \right].
\end{align*}
\] (5.181) (5.182)

In order to eliminate \( \mathbf{T}_{2(3)} \cdot \vec{\beta}_{20} \), we first use Equation (5.181) in Equation (5.180), to obtain
\[
\mathbf{T}_{1(3)} \cdot \vec{\beta}_{10} = \mathbf{T}_{1(1)} \cdot \vec{\beta}_{10} + \mathbf{T}_{1(1)} \cdot \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \left[ \bar{\%B} \text{etm}_{20} + \vec{\alpha}_{21} \cdot \mathbf{T}_{1(3)} \cdot \vec{\beta}_{10} + \vec{\alpha}_{23} \cdot \mathbf{T}_{3(3)} \cdot \vec{\beta}_{30} \right] + \mathbf{T}_{1(1)} \cdot \vec{\alpha}_{13} \cdot \mathbf{T}_{3(3)} \cdot \vec{\beta}_{30}. \\
\] (5.183)

Secondly, rearranging Equation (5.183) gives
\[
\left[ \mathbf{I} - \mathbf{T}_{1(1)} \cdot \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \vec{\alpha}_{21} \right] \cdot \mathbf{T}_{1(3)} \cdot \vec{\beta}_{10} = \mathbf{T}_{1(1)} \cdot \left[ \vec{\beta}_{10} + \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \vec{\beta}_{20} \right] + \mathbf{T}_{1(1)} \cdot \left[ \vec{\alpha}_{13} + \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \vec{\alpha}_{23} \right] \cdot \mathbf{T}_{3(3)} \cdot \vec{\beta}_{30}. \\
\] (5.184)

Now we can write
\[
\begin{align*}
\mathbf{T}_{1(3)} \cdot \vec{\beta}_{10} &= \left[ \mathbf{I} - \mathbf{T}_{1(1)} \cdot \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \vec{\alpha}_{21} \right]^{-1} \cdot \mathbf{T}_{1(1)} \cdot \left[ \vec{\beta}_{10} + \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \vec{\beta}_{20} \right] \\
+ \left[ \mathbf{I} - \mathbf{T}_{1(1)} \cdot \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \vec{\alpha}_{21} \right]^{-1} \mathbf{T}_{1(1)} \cdot \left[ \vec{\alpha}_{13} + \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \vec{\alpha}_{23} \right] \cdot \mathbf{T}_{3(3)} \cdot \vec{\beta}_{30}.
\end{align*}
\] (5.185)

From the expression for \( \mathbf{T}_{1(2)} \), see Equation (5.175), we can recognize that the first term on the right-hand side is \( \mathbf{T}_{1(2)} \cdot \vec{\beta}_{10} \). For the last term of Equation (5.185), if we suppose that the third scatterer is outside of a sphere embracing the first two scatterers with the center at the origin of the global coordinate system, the following identities hold

\[
\begin{align*}
\vec{\alpha}_{13} &= \vec{\beta}_{10} \cdot \vec{\alpha}_{03}, \\
\vec{\alpha}_{23} &= \vec{\beta}_{20} \cdot \vec{\alpha}_{03}, \\
|\mathbf{r}_{3,0}| &= \max(|\mathbf{r}_{1,0}|, |\mathbf{r}_{2,0}|). \\
\end{align*}
\] (5.186) (5.187) (5.188)

So, now we can also state that
\[
\mathbf{r}_{3,0} \notin (S_{0,1} \cup S_{0,2}). \\
\] (5.189)

If we use the identities of Equations (5.186)-(5.187) in the second term of Equation (5.185). We denote this term as (II). This term may be written as
\[
\begin{align*}
(II) &= \left[ \mathbf{I} - \mathbf{T}_{1(1)} \cdot \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \vec{\alpha}_{21} \right]^{-1} \mathbf{T}_{1(1)} \cdot \left[ \vec{\alpha}_{13} + \vec{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \vec{\alpha}_{23} \right] \cdot \mathbf{T}_{3(3)} \cdot \vec{\beta}_{30} \\
&= \mathbf{T}_{1(2)} \cdot \vec{\beta}_{10} \cdot \vec{\alpha}_{03} \cdot \mathbf{T}_{3(3)} \cdot \vec{\beta}_{30}. \\
\end{align*}
\] (5.190)

where Equation (5.175) has been used. Using Equations (5.190) and (5.185) yields
\[
\mathbf{T}_{1(3)} \cdot \vec{\beta}_{10} = \mathbf{T}_{1(2)} \cdot \vec{\beta}_{10} \cdot \left[ \mathbf{I} + \vec{\alpha}_{03} \cdot \mathbf{T}_{3(3)} \cdot \vec{\beta}_{30} \right]. \\
\] (5.191)
5.4. **MULTIPLE SCATTERING**

Equation (5.191) represents the desired form for $\mathbf{T}_{1(3)}$. By the same token, we can find a similar expression for $\mathbf{T}_{3(3)}$ by substituting Equation (5.180) in Equation (5.181), to obtain

$$
\mathbf{T}_{2(3)} \cdot \bar{\beta}_{20} = \mathbf{T}_{2(2)} \cdot \bar{\beta}_{20} \cdot \left[ \mathbf{I} + \bar{\alpha}_{03} \cdot \mathbf{T}_{3(3)} \cdot \bar{\beta}_{30} \right].
$$

(5.192)

Substituting Equations (5.191) and (5.192) in the expression for $\mathbf{T}_{3(3)} \cdot \bar{\beta}_{30}$ in Equation (5.182) and solving for $\mathbf{T}_{3(3)} \cdot \bar{\beta}_{30}$, we obtain

$$
\mathbf{T}_{3(3)} \cdot \bar{\beta}_{30} = \left[ \mathbf{I} - \mathbf{T}_{3(1)} \cdot \sum_{i=1}^{2} \bar{\alpha}_{3,i} \cdot \mathbf{T}_{i(2)} \cdot \bar{\beta}_{i0} \cdot \alpha_{03} \right]^{-1} \mathbf{T}_{3(1)} \cdot \left[ \bar{\beta}_{3,0} + \sum_{i=1}^{2} \bar{\alpha}_{3,i} \cdot \mathbf{T}_{i(2)} \cdot \bar{\beta}_{i0} \right].
$$

(5.193)

Equations (5.191), (5.192) and (5.194) together constitute the recursive formulas yielding $\mathbf{T}_{i(3)} \bar{\beta}_{i0}$, $i = 1, 2, 3$, from $\mathbf{T}_{i(2)} \cdot \bar{\beta}_{i0}$, $i = 1, 2$. These results for $\mathbf{T}_{1(3)} \bar{\beta}_{10}$, $\mathbf{T}_{2(3)} \bar{\beta}_{20}$ and $\mathbf{T}_{3(3)} \bar{\beta}_{30}$ are used in Equation (5.178). This completes the computation of the scattering by three particles.

To discuss if the found restriction is stringent enough, we can also reconstruct the three-scatterer solution by directly using the two-scatterer solution. From the definition of the two-scatterer $\mathbf{T}$ matrices given in the last section, we have

$$
\mathbf{T}_{1(3)} \cdot \bar{\beta}_{10} = \mathbf{T}_{1(2)} \cdot \left[ \bar{\beta}_{10} + \bar{\alpha}_{13} \cdot \mathbf{T}_{3(3)} \cdot \bar{\beta}_{30} \right],
$$

(5.195)

$$
\mathbf{T}_{2(3)} \cdot \bar{\beta}_{20} = \mathbf{T}_{2(2)} \cdot \left[ \bar{\beta}_{20} + \bar{\alpha}_{23} \cdot \mathbf{T}_{3(3)} \cdot \bar{\beta}_{30} \right].
$$

(5.196)

Since Equations (5.185) and (5.195) both express $\mathbf{T}_{1(3)} \cdot \bar{\beta}_{10}$, the right-hand sides must be the same. In order to be equal, we require that

$$
(\text{II}) = \mathbf{T}_{1(2)} \cdot \left[ \bar{\alpha}_{13} \cdot \mathbf{T}_{3(3)} \cdot \bar{\beta}_{30} \right].
$$

(5.197)

Using the identity $\bar{\beta}_{ij} = \bar{\beta}_{i0} \cdot \bar{\beta}_{0j}$, $\mathbf{T}_{1(2)}$ becomes

$$
\mathbf{T}_{1(2)} = \left[ \mathbf{I} - \mathbf{T}_{1(1)} \cdot \bar{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \bar{\alpha}_{21} \right]^{-1} \cdot \mathbf{T}_{1(1)} \cdot \left[ \mathbf{I} + \bar{\alpha}_{12} \cdot \mathbf{T}_{2(1)} \cdot \bar{\beta}_{21} \right].
$$

(5.198)

From this equation and Equation (5.185), we can see that in order to satisfy Equation (5.197), the following identity has to hold

$$
\bar{\alpha}_{23} = \bar{\beta}_{21} \cdot \bar{\alpha}_{13},
$$

(5.199)

which is only valid when $d_{1,3} > d_{1,2}$, so scatterer 3 is located outside $S_{1,2}$. Using the same analysis to recover Equation (5.196) from Equations (5.180-5.181), the following identity is required:

$$
d_{2,3} > d_{1,2},
$$

(5.200)
which obviously means that scatterer 3 has to be outside $S_{2.1}$. Combined, these restraint conditions become

$$r_{3,0} \notin (S_{1,2} \cup S_{2,1}).$$  \hspace{1cm} (5.201)

Comparing condition (5.189) with condition (5.201) shows that the latter one is much stronger than (5.189).

### 5.4.5 T-Matrix for N-Scatterers – Recursive Solution

In this section we shall derive the recursive formulas which allow us to obtain the $(N+1)$-scatterer solution from the $N$-scatterer solution. For an $N$-scatterer problem, the total field exterior to the $N$ scatterers is of the form

$$\phi(r) = \mathbf{a}^t \cdot \mathbf{R} \mathbf{g} \psi(k_0, r_0) + \sum_{i=1}^{N} \left[ \mathbf{T}_{i(N)} \cdot \overline{\mathbf{\beta}}_{i0} \cdot \mathbf{a} \right]^t \cdot \psi(k_0, r_i).$$ \hspace{1cm} (5.202)

Suppose that the $N$-scatterer solution is known, that is, all of the $\mathbf{T}_{i(N)} \cdot \overline{\mathbf{\beta}}_{i0}, i = 1, 2, ..., N$, are known. Remember that each $\mathbf{T}_{i(N)} \cdot \overline{\mathbf{\beta}}_{i0}$ relates the scattered field from the $i$-th scatterer to the incident field expressed in terms of the global coordinate system. Similarly, the $(N+1)$-scatterer solution has the form

$$\phi(r) = \mathbf{a}^t \cdot \mathbf{R} \mathbf{g} \psi(k_0, r_0) + \sum_{i=1}^{N+1} \left[ \mathbf{T}_{i(N+1)} \cdot \overline{\mathbf{\beta}}_{i0} \cdot \mathbf{a} \right]^t \cdot \psi(k_0, r_i).$$ \hspace{1cm} (5.203)

The above can be rewritten as

$$\phi(r) = \mathbf{a}^t \cdot \mathbf{R} \mathbf{g} \psi(k_0, r_0) + \sum_{i=1}^{N} \left[ \mathbf{T}_{i(N+1)} \cdot \overline{\mathbf{\beta}}_{i0} \cdot \mathbf{a} \right]^t \cdot \psi(k_0, r_i) + \left[ \mathbf{T}_{N+1(N+1)} \cdot \overline{\mathbf{\beta}}_{N+1,0} \cdot \mathbf{a} \right]^t \cdot \psi(k_0, r_{N+1}).$$ \hspace{1cm} (5.204)

Again, the first and the last term in Equation (5.204) can be thought of as the total incident field impinging on the $i = 1, ..., N$ scatterers. Therefore,

$$\mathbf{T}_{i(N+1)} \cdot \overline{\mathbf{\beta}}_{i0} \cdot \mathbf{a} = \mathbf{T}_{i(N)} \cdot \overline{\mathbf{\beta}}_{i0} \cdot \left[ \mathbf{I} + \overline{\mathbf{\alpha}}_{0,N+1} \cdot \mathbf{T}_{N+1(N+1)} \cdot \overline{\mathbf{\beta}}_{N+1,0} \right] \cdot \mathbf{a},$$ \hspace{1cm} (5.205)

where we have applied the translation formula of Equation (5.165) to translate the last terms from the coordinate system of the $i$-th scatterer to the global coordinate system. Note that the total field for an $N$-scatterer problem can be expressed in terms of Equation (5.204), only when the source of the scattering problem is outside of the sphere embracing the $N$ scatterers, i.e. the source has to be located outside a domain $D_N$, where

$$D_N \equiv \bigcup_{i=1}^{N} S_{0,i}.$$

(5.206)

Therefore, the $(N+1)$-scatterer has to be outside $D_N$, thus the distances of the scatterers have to be ordered. The scattered field amplitude from the $(N+1)$-th scatterer is due to
the scattering of the incident field from the other $N$ scatterers via the isolated-scatterer $\mathbf{T}$ matrix. Hence, the scattered field amplitude due to the $(N+1)$-th scatterer is related to the other field amplitudes as

$$\mathbf{T}_{N+1(N+1)} \cdot \bar{\beta}_{N+1,0} \cdot \mathbf{a} = \mathbf{T}_{N+1(1)} \cdot \left[ \bar{\beta}_{N+1,0} + \sum_{i=1}^{N} \bar{\alpha}_{N+1,i} \cdot \mathbf{T}_{i(N+1)} \cdot \bar{\beta}_{i0} \right] \cdot \mathbf{a}. \quad (5.207)$$

If we now use Equation (5.205) in Equation (5.207), we get

$$\mathbf{T}_{N+1(N+1)} \cdot \bar{\beta}_{N+1,0} = \mathbf{T}_{N+1(1)} \cdot \left[ \bar{\beta}_{N+1,0} + \sum_{i=1}^{N} \bar{\alpha}_{N+1,i} \cdot \mathbf{T}_{i(N)} \cdot \bar{\beta}_{i0} + \sum_{i=1}^{N} \bar{\alpha}_{N+1,i} \cdot \mathbf{T}_{i(N)} \cdot \bar{\beta}_{i0} \cdot \bar{\alpha}_{0,N+1} \cdot \mathbf{T}_{N+1(N+1)} \cdot \bar{\beta}_{N+1,0} \right]. \quad (5.208)$$

Solving this equation for $\mathbf{T}_{N+1(N+1)} \cdot \bar{\beta}_{N+1,0}$, we obtain

$$\mathbf{T}_{N+1(N+1)} \cdot \bar{\beta}_{N+1,0} = \left[ I - \mathbf{T}_{N+1(1)} \cdot \sum_{i=1}^{N} \bar{\alpha}_{N+1,i} \cdot \mathbf{T}_{i(N)} \cdot \bar{\beta}_{i0} \cdot \bar{\alpha}_{0,N+1} \right]^{-1} \cdot \mathbf{T}_{N+1(1)} \cdot \left[ \bar{\beta}_{N+1,0} + \sum_{i=1}^{N} \bar{\alpha}_{N+1,i} \cdot \mathbf{T}_{i(N)} \cdot \bar{\beta}_{i0} \right]. \quad (5.209)$$

This equation together with Equation (5.205) enable us to calculate the $\mathbf{T}_{i(N+1)} \cdot \bar{\beta}_{i0}$ matrices, $i = 1, ..., N$. Hence, given the knowledge of the isolated $\mathbf{T}$ matrices, the $N$-scatterer solution is constructed recursively, starting from the one-scatterer solution. Once $\mathbf{T}_{i(N)} \cdot \bar{\beta}_{i0}$, $i = 1,2,...,N$, are derived by using the recursive relations in Equations (5.205) and (5.209), these matrices are used in Equation (5.202) and this completes the computation of the scattering of $N$ particles.

However, these equations are only valid if they are restricted by the fact that the $(N+1)$-scatterer has to be located outside $D_N$. So we need to choose a proper global coordinate system and to sort the $N$ scatterers in this global coordinate system such that this is always true in every recursive step. This could be achieved by reordering the scatterers in the global coordinate system as

$$|r_{1,0}| < |r_{2,0}| < |r_{N,0}|. \quad (5.210)$$

The global coordinate system could be chosen in the following way. We view every scatterer as a unit mass point and choose the weight center of the $N$-mass point system as the origin of the global coordinate system. After ordering the scatterers according to the condition of Equation (5.210) in the global coordinate system, the recursive relations will be eligible. Fortunately, this condition, see Equation (5.210), is easily satisfied for most applications. When we put the particles in a lattice with the global coordinate system at its center, it seems that we have a problem, since when we put a particle at
the origin of the global coordinate system and by using a certain lattice constant, there are more than two scatterers located within the sphere $S_{01}$. By simply moving the entire structure a small distance $\delta$ from the global coordinate system (shown in Figure 5.13) the recursive relations can be applied for the solution of the multiple scattering problem.

**Implementation**

Theoretically, the recursive relations give an exact solution of the scattering problem if the dimensions of the matrices are infinite. In order to implement the algorithm numerically, the matrices have to be truncated to finite dimensions. For the $N$-scatterer problem, if the field around each scatterer is approximated by $M$ harmonics, where $M$ is the finite dimension of the vectors defined in Equations (5.154) and (5.155). The total number of unknowns of the problem will be $NM$. In this case, $\vec{T}_{i(N)} \cdot \vec{\beta}_{i0} \cdot \vec{a}$ in Equation (5.202) is a column vector with $M$ elements. When the scatterers are small, $M$ can be kept small. On the other hand, the number of terms in the translation formulas should be large enough to maintain their accuracy, i.e. $\vec{T}_{i(N)} \cdot \vec{\beta}_{i0}$ is a $M \times P$ matrix where $P$ is large enough to keep the translation accurate. Obviously, $P$ is the number of harmonics needed to expand the field around the aggregated scatterers. In order to explicitly show the dimensions of the matrices involved, we rewrite Equations (5.209) and (5.205) with their dimensions as

\[
\begin{align*}
\overline{T}_{N+1(N+1)} & \cdot \overline{\beta}_{N+1,0} = \left[ I - \overline{T}_{N+1(1)} \cdot \sum_{i=1}^{N} \overline{\alpha}_{N+1,i} \cdot \overline{T}_{i(N)} \cdot \overline{\beta}_{i0} \cdot \overline{\alpha}_{0,N+1} \right]^{-1} \cdot \\
\overline{\beta}_{N+1,0} & + \sum_{i=1}^{N} \overline{\alpha}_{N+1,i} \cdot \overline{T}_{i(N)} \cdot \overline{\beta}_{i0},
\end{align*}
\]

(5.211)
\[
\frac{T_{i(N+1)} \cdot \vec{\beta}_{0,i}}{M \times P} = \frac{T_{i(N)} \cdot \vec{\beta}_{0,i}}{M \times P} + \left( \frac{T_{i(N)} \cdot \vec{\beta}_{0,i} \cdot \vec{\alpha}_{0,N+1}}{M \times P} \right) \cdot \frac{T_{N+1(N+1)} \cdot \vec{\beta}_{N+1,0}}{P \times M}. \tag{5.212}
\]

from which it is easy to deduce the number of computations to be carried out. In this algorithm \( T_{i(N+1)} \cdot \vec{\beta}_{0,i} \) is the unknown function to be solved recursively.

**Recursive Algorithm**

In order to make the floating-point operations at each recursion independent of the number of the scatterers involved, we need to find a way to remove the summations in the recursive relation, see Equation (5.209). Actually the two summations in Equation (5.209) are the same, because \( \vec{\alpha}_{0,N+1} \) in the first summation term can be taken out of the summation. The two equivalent summations left are of the type \( \sum_{i=1}^{N} \vec{\alpha}_{N+1,i} \cdot T_{i(N)} \cdot \vec{\beta}_{i,N+1} \), which can be physically interpreted as the outgoing harmonics expressed in the local coordinate systems of the corresponding scatterers, from scatterers \( i, i = 1, 2, \ldots, N \), have been translated to the harmonics in the local coordinate system of scatterer \( N+1 \). These translations have to be repeated in every recursion step. The recursive relations can be further manipulated to a different form by writing

\[
\vec{\alpha}_{N+1,i} = \vec{\alpha}_{N+1,0} \cdot \vec{\beta}_{0,i}, \quad \forall i < N + 1. \tag{5.213}
\]

Since the scatterers of the problem have been ordered according to Equation (5.210), this identity is always valid. Then Equation (5.209) becomes

\[
T_{N+1(N+1)} \cdot \vec{\beta}_{N+1,0} = \left[ I - T_{N+1(1)} \cdot \vec{\alpha}_{N+1,0} \cdot \left( \sum_{i=1}^{N} \vec{\beta}_{0i} \cdot T_{i(N)} \cdot \vec{\beta}_{0i} \right) \cdot \vec{\alpha}_{0,N+1} \right]^{-1} \cdot
\]

\[
T_{N+1(1)} \cdot \left[ \vec{\beta}_{N+1,0} + \vec{\alpha}_{N+1,0} \cdot \left( \sum_{i=1}^{N} \vec{\beta}_{0i} \cdot T_{i(N)} \cdot \vec{\beta}_{0i} \right) \right]. \tag{5.214}
\]

Then an aggregate \( T \) matrix for \( N \) scatterers can be defined such that

\[
\tau(N) = \sum_{i=1}^{N} \vec{\beta}_{0i} \cdot T_{i(N)} \cdot \vec{\beta}_{0i}. \tag{5.215}
\]

Now we can write for Equation (5.214)

\[
T_{N+1(N+1)} \cdot \vec{\beta}_{N+1,0} = \left[ I - T_{N+1(1)} \cdot \vec{\alpha}_{N+1,0} \cdot \tau(N) \cdot \vec{\alpha}_{0,N+1} \right]^{-1} \cdot
\]

\[
T_{N+1(1)} \cdot \left[ \vec{\beta}_{N+1,0} + \vec{\alpha}_{N+1,0} \cdot \tau(N) \right]. \tag{5.216}
\]

Multiplying Equation (5.216) from the left by \( \vec{\beta}_{0i} \), summing over \( i \) from 1 to \( N \), and adding \( \vec{\beta}_{0,N+1} \cdot T_{N+1(N+1)} \cdot \vec{\beta}_{N+1,0} \) to both sides of the equation, we obtain

\[
\tau_{N+1} = \tau(N) + \left[ \vec{\beta}_{0,N+1} \cdot \tau(N) \cdot \vec{\alpha}_{0,N+1} \right] \cdot T_{N+1(N+1)} \cdot \vec{\beta}_{N+1,0}. \tag{5.217}
\]
Now, Equations (5.216)-(5.217) constitute the recursive formulas for $\varphi$ expressing $\varphi_{(N+1)}$ in terms of $\varphi_{(N)}$. With the aggregate $\varphi$-matrix expression, Equation (5.202) becomes

$$\phi(r) = a^i \cdot Rg\psi(k_0, r_0) + [\varphi_{(N)} \cdot a]^i \cdot \psi(k_0, r_0).$$

(5.218)

Here has been used that

$$\psi(k_0, r_i) = \beta_{0i}^j \cdot \psi(k_0, r_0), \quad |r_0| > d_0i.$$  

(5.219)

The aggregate $\varphi$-matrix defined in Equation (5.215) is a global representation of the transition matrices by translating every $\varphi_{(N)}$-matrix from its own local coordinate system related to the $i$-th scatterer to the origin of a global coordinate system. With Equation (5.218) together with Equations (5.216)-(5.217) we have achieved our objectives that the scattered field can be computed outside a configuration of $N$ scatterers and where the number of matrix multiplications in the recursive Equations (5.216) and (5.217) is independent of $N$.

The physical explanation follows directly from Equation (5.216). This equation describes the recursion from a scattering configuration with $N$ scatterers to a scattering configuration with $N+1$ scatterers. The first scattering configuration is characterized by the $N$-th aggregate $\varphi_{(N)}$-matrix located at the origin of the global coordinate system. The second is the configuration of the $(N+1)$-scatterer characterized by an isolated single $\varphi_{N+1(1)}$ matrix located at a local origin, which is described by $r_{N+1,0}$. This will become more obvious when we compare Equation (5.216) with Equation (5.209). Let $N$ equal 1 in Equation (5.209) and suppose that scatterer 1 is located at the origin of the global coordinate system, then, these two equations will be exactly the same if we replace $\varphi_{(N)}$ in Equation (5.216) with $\varphi_{1(1)}$.

For the convenience of discussion of the computational complexity of the algorithm, let us rewrite Equations (5.216) and (5.217) with the dimension indices included:

$$\frac{M \times P}{T_{N+1(1)} \cdot \beta_{N+1,0}} = \left[ \frac{M \times M}{I} - \frac{M \times M}{T_{N+1(1)} \cdot \alpha_{N+1,0} \cdot \varphi_{(N)} \cdot \alpha_{0, N+1}} \right]^{-1} \cdot \frac{P \times P}{T_{N+1(1)} \cdot \beta_{N+1,0} + \alpha_{N+1,0} \cdot \varphi_{(N)}}. \quad (5.220)$$

$$\frac{P \times P}{\varphi_{(N+1)}} = \frac{P \times P}{\varphi_{0, N+1}} \cdot \frac{P \times P}{T_{N+1(1)} \cdot \beta_{N+1,0}} + \frac{P \times M}{\varphi_{(N)} \cdot \alpha_{0, N+1} \cdot T_{N+1(1)} \cdot \beta_{N+1,0}} \quad (5.221)$$

Because Equation (5.220) always involves a relation between two scattering configurations, the number of matrix multiplications will be a constant. In Equation (5.220), indices $P$ and $M$ represent the number of harmonics in the translation formulas and the number of harmonics in the isolated scatterer $\varphi$-matrix, respectively.
5.4.6 Results

For the multiple scattering two configurations have been tested. The first simulation will handle 27 particles in a cube structure as shown in Figure 5.14. The origin of the global coordinates is centered in the middle of this cube. The first particle is located nearest to this global origin. That is the main reason for expanding it to 27 particles: you can look at it as 8 cubes, configured in that way that the first particle is in the centre of this geometry (3 layers of 9 particles each). Also, a similar simulation consisting out of 125 particles has been tested. The wavelength used here is 10.59 $\mu$m, which is the wavelength of the electromagnetic wavefield from a carbon dioxide laser. That means that we are dealing with a very high frequency. Furthermore, the wavelength is less than or in the same order of the particle-size. When the wavelength is in the same order or several orders smaller than the size of a single sphere, many spherical harmonics have to be taken; from a computational point of view this is very expensive. Here, we have taken a sphere radius of 10 $\mu$m. Remember that $k_0a = \frac{2\pi}{\lambda}a$, where $a$ is the radius. The smallest interparticle distance is approximately 4, in which the interparticle distance is defined by the ratio of the diameter of the particle and the distance between both local origins (dimensionless quantity). Here, the interparticle distance varies from 4 to 7, since we also have cross-distances in the cube structure. The main problem is the memory management during execution of a simulation. $M$ is the number of harmonics needed to expand the field around a single scatterer, and $P$ is the number of harmonics to expand the field around the aggregated scatterers. In practice, $M$ is proportional to $(k_0a)^2$, where $a$ is the radius of the scatterer, and $P$ is proportional to $(k_0L)^2$, where $L$ is the 'radius' of the region occupied by the scatterers. In both configurations the radar cross section is calculated. This is the intensity of the scattered field as a function of the angle between the incident and scattered waves. The usual convention with 3-D particles is that the incident wave propagates in the $\theta = 0^\circ$ direction. The relative permittivity in both cases has been taken $\varepsilon_r = 2$. 
Figure 5.15: Angular scattered intensity for 27 spheres with \( ka \approx 6 \) and \( \varepsilon_r = 2; \)
\( P = 144 \), dashed line: \( M = 36 \), solid line: \( M = 49 \).

27-Particles Configuration

The 27-particle configuration is approximately 24 wavelengths long from side to side of
the hypothetical cube. The radius of a single sphere has been taken one wavelength, so
we are dealing with large spheres. Large means here that the particle-size is in the same
order or greater than the wavelength. From this point of view, we can make a guess how
many \( P \) and \( M \) harmonics are needed to reach convergence. In Figure 5.15, the result
is shown for 27 particles when the \( M \) harmonics are varied from 36 to 49. The same
has been done in Figure 5.16 where \( M \) has been changed from 49 to 64. It can be seen
that after taking into account 49 harmonics the result has almost converged. This is in
agreement with our rule of thumb in terms of the \( ka \) value. One could also say the result
has converged after \( n(n+1) \) harmonics have been taken into account (where \( n = ka \)).
The same analysis can be made for the \( P \) harmonics. During simulations the \( P \) value has
been changed from 100 to 144. After 144 steps, no more steps could be made since the
memory of the computer was used at its limits. In all simulations \( M = 49 \). In Figure
5.17, \( P \) is varied from 100 to 121 harmonics; the difference between both simulation is
large. In Figure 5.18, \( P \) has been taken 121 and 144, respectively. The differences between
both solutions become smaller, but this is no direct indication for convergence. It seems
that the result will shift more to smaller scattering angles when more harmonics are being
used. This could not be seen when \( M \) was varied. These results do not show that the
scattering solution has converged and we probably need a lot more \( P \) harmonics for this
configuration to converge. This is not very surprising when we observe that the scatterers
Figure 5.16: Angular scattered intensity for 27 spheres with $ka \approx 6$ and $\varepsilon_r = 2$; $P = 144$, dashed line: $M = 64$, solid line: $M = 49$.

are distributed over a three-dimensional domain with size of 24 wavelengths!
Figure 5.17: Angular scattered intensity for 27 spheres with $ka \approx 6$ and $\varepsilon_r = 2$; $M = 49$, dashed line $P = 121$, solid line $P = 100$.

Figure 5.18: Angular scattered intensity for 27 spheres with $ka \approx 6$ and $\varepsilon_r = 2$; $M = 49$, dashed line $P = 121$, solid line $P = 144$. 
5.4. **MULTIPLE SCATTERING**

![Graph showing scattered intensity](image)

**Figure 5.19:** Angular scattered intensity for 27 spheres with $ka \approx 0.6$ and $\varepsilon_r = 2$; $M = 9$, solid line: $P = 64$, dashed line: $P = 81$, dashdotted line: $P = 100$.

**Larger Wavelength**

To investigate the rate of convergence, the same configuration has been tested with a ten times larger wavelength. First, we would expect the needed harmonics to build the field around a single scatterer to be smaller than in the previous case. After $M = 9$ no differences could be noticed. In all these simulations $M = 9$ has been used. We start our analysis of the $P$ harmonics with Figure 5.19. Here the simulation used $P = 64, 81, 100$, respectively. In Figure 5.20 the results have been plotted for $P = 100$ and $P = 121$. Here can be noticed that especially the sharp dips seem to need more harmonics. This is even better illustrated in Figure 5.21, where the differences between the $P = 121$ and $P = 144$ solution is smaller. Except for the amplitudes of the dips, the general behaviour at an angle coincides. Especially the sharp dips need more harmonics.

**125-Particles Configuration**

Also, a configuration with 125 particles has been tested. This configuration uses a wavelength of 10.59 μm and the domain size (from side to side) is approximately 32 wavelengths. The $5 \times 5 \times 5$-simulation could be done, but the amount of harmonics used was unfortunately very limited. From the previous discussion $M$ could be set on 49. For this process to converge, a lot more $P$-harmonics are needed. This could not be reached by far. Results are shown in Figure 5.22.
**Figure 5.20:** Angular scattered intensity for 27 spheres with $ka \approx 0.6$ and $\varepsilon_r = 2$; $M = 9$, solid line: $P = 100$, dashed line: $P = 121$.

**Figure 5.21:** Angular scattered intensity for 27 spheres with $ka \approx 0.6$ and $\varepsilon_r = 2$; $M = 9$, solid line: $P = 121$, dashed line: $P = 144$. 
Figure 5.22: Angular scattered intensity for 125 spheres with $k\alpha \approx 6$ and $\varepsilon_r = 2$; $M = 49$, solid line: $P = 64$, dashed line: $P = 49$.

5.5 Field inside the Scatterers

Unfortunately, the $N$-scatterer solution is only valid outside of a sphere which closely embraces all of the subobjects. So, when the field inside the scatterers has to be calculated, which is evident for the case of absorption, another algorithm is needed. Again, we start off with

$$
\phi(r) = \Re \psi^i(k_0, r_0) \cdot \alpha + \sum_{i=1}^{n} \psi^i(k_0, r_i) \overline{T}_{i(n)} \cdot \overline{\beta}_{j0} \cdot \alpha,
$$

(5.222)

which is the total field exterior to the $n$ scatterers. If the internal field of the $j$-th scatterer is of interest, the fields of the other scatterers can be expressed in terms of the $j$-th coordinate system as

$$
\phi(r) = \Re \psi^i(k_0, r_j) \cdot \overline{\beta}_{j0} \cdot \alpha + \sum_{i \neq j} \Re \psi^i(k_0, r_j) \cdot \overline{\alpha}_{j0} \cdot \overline{T}_{i(n)} \cdot \overline{\beta}_{j0} \cdot \alpha + \psi^i(k_0, r_j) \overline{T}_{i(n)} \cdot \overline{\beta}_{j0} \cdot \alpha,
$$

(5.223)

where Equation (5.165) from the translational formulas has been used. The first two terms can be treated as the total incident field impinging upon scatterer $j$. Therefore, in order to calculate the field inside the object, the $T_{i(N)}$ matrices, $i = 1, ..., N$, have to be found. Since we already have the recursion relations for the $T_{i(i)}$ matrices, this can be achieved by a backward recursion scheme, obviously starting with $T_{N(N)}$. To find the $T_{i(N-1)}$ matrix, we consider the incident field consisting out of the original incident field and the scattered field from the $N$-th scatterer, which is represented by the known
quantity $\mathbf{T}_{N(N)} \cdot \mathbf{\bar{\beta}}_{N,0}$. With $\mathbf{T}_{N-1(N-1)} \cdot \mathbf{\bar{\beta}}_{N-1,0}$, this reads as

$$
\mathbf{T}_{N-1(N)} \cdot \mathbf{\bar{\beta}}_{N-1,0} = \mathbf{T}_{N-1(N-1)} \cdot \mathbf{\bar{\beta}}_{N-1,0} \cdot \left[ \mathbf{I} + \mathbf{\bar{\alpha}}_{0,N} \cdot \mathbf{T}_{N(N)} \cdot \mathbf{\bar{\beta}}_{N,0} \right].
$$

(5.224)

Similarly, for the $(N-2)$-th scatterer, we can write

$$
\mathbf{T}_{N-2(N)} \cdot \mathbf{\bar{\beta}}_{N-2,0} = \mathbf{T}_{N-2(N-2)} \cdot \mathbf{\bar{\beta}}_{N-2,0} \cdot \left[ \mathbf{I} + \mathbf{\bar{\alpha}}_{0,N} \cdot \mathbf{T}_{N(N)} \cdot \mathbf{\bar{\beta}}_{N,0} + \mathbf{\bar{\alpha}}_{0,N-1} \cdot \mathbf{T}_{N-1(N-1)} \cdot \mathbf{\bar{\beta}}_{N-1,0} \right].
$$

(5.225)

Generally, the recursive equation can be written as

$$
\mathbf{T}_{N-i(N)} \cdot \mathbf{\bar{\beta}}_{N-i,0} = \mathbf{T}_{N-i(N-i)} \cdot \mathbf{\bar{\beta}}_{N-i,0} \cdot \left[ \mathbf{I} + \sum_{j=0}^{i-1} \mathbf{\bar{\alpha}}_{0,N-j} \cdot \mathbf{T}_{N-j(N)} \cdot \mathbf{\bar{\beta}}_{N-j,0} \right].
$$

(5.226)

Now we define a complementary partial $N$-th aggregate $\mathbf{\bar{\tau}}_{i(N)}$ as

$$
\mathbf{\bar{\tau}}_{i(N)} = \sum_{j=0}^{i-1} \mathbf{\bar{\alpha}}_{0,N-j} \cdot \mathbf{T}_{N-j(N)} \cdot \mathbf{\bar{\beta}}_{N-j,0}.
$$

(5.227)

Using Equation (5.227) in Equation (5.226), we get

$$
\mathbf{T}_{N-i(N)} \cdot \mathbf{\bar{\beta}}_{N-i,0} = \mathbf{T}_{N-i(N-i)} \cdot \mathbf{\bar{\beta}}_{N-i,0} \cdot \left[ \mathbf{I} + \mathbf{\bar{\tau}}_{i(N)} \right].
$$

(5.228)

From Equation (5.227), the next complementary partial aggregate matrix $\mathbf{\bar{\tau}}$ can be obtained from

$$
\mathbf{\bar{\tau}}_{i+1(N)} = \mathbf{\bar{\tau}}_{i(N)} + \mathbf{\bar{\alpha}}_{0,N-i} \cdot \mathbf{T}_{N-i(N)} \cdot \mathbf{\bar{\beta}}_{N-i,0}.
$$

(5.229)

Equations (5.228)-(5.229) constitute the backward recursion scheme for $\mathbf{T}_{N-i(N)} \cdot \mathbf{\bar{\beta}}_{N-i,0}$, $i = 1, 2, ..., N-1$. Since the first two terms of Equation (5.223) can be treated as the total incident field impinging upon scatterer $j$, the scattered amplitude $\mathbf{T}_{j(N)} \cdot \mathbf{\bar{\beta}}_{j0}$ can be related to the isolated transition matrix of the scatterer $j$, $\mathbf{T}_{j(1)}$, and the total incident field according to

$$
\mathbf{T}_{j(1)} \cdot \left[ \mathbf{\bar{\beta}}_{j0} + \sum_{i \neq j} \mathbf{\bar{\alpha}}_{ji} \cdot \mathbf{T}_{i(N)} \cdot \mathbf{\bar{\beta}}_{i0} \right] \cdot \mathbf{a} = \mathbf{T}_{j(N)} \cdot \mathbf{\bar{\beta}}_{j0} \cdot \mathbf{a}
$$

(5.230)

Rewritten as

$$
\left[ \mathbf{\bar{\beta}}_{j0} + \sum_{i \neq j} \mathbf{\bar{\alpha}}_{ji} \cdot \mathbf{T}_{i(N)} \cdot \mathbf{\bar{\beta}}_{i0} \right] \cdot \mathbf{a} = \mathbf{T}^{-1}_{j(1)} \cdot \mathbf{T}_{j(N)} \cdot \mathbf{\bar{\beta}}_{j0} \cdot \mathbf{a},
$$

(5.231)

it is clear that the left-hand side is the total incident-field amplitude, but also that the right-hand side provides a simple way to calculate the incident-field amplitude. Once the total incident-field amplitude of scatterer $j$ has been found, the internal field of scatterer $j$ can be found using the isolated transmission matrix $\mathbf{\bar{W}}_{j(1)}$ as

$$
\phi(r) = \Re g \psi'(k_j, r_j) \cdot \mathbf{\bar{W}}_{j(1)} \cdot \mathbf{T}^{-1}_{j(1)} \cdot \mathbf{T}_{j(N)} \cdot \mathbf{\bar{\beta}}_{j0} \cdot \mathbf{a}, \quad r \in \Omega_j,
$$

(5.232)
where
\[ \Omega_j \equiv \{ \mathbf{r} | \mathbf{r} \text{ inside the scatterer } j \}, \quad k_j = k_0 \sqrt{\varepsilon_j}. \] (5.233)

At this point we have arrived at the representation for the internal field in the j-th spherical scatterer. In this representation we need the transmission matrices \( \mathbf{W}_{j(1)} \). For a single sphere the transmission matrix is diagonal and consisting only out of the transmission coefficients. This matrix is given as,
\[
\mathbf{W}_{j(1)} = \begin{bmatrix} W_n^m & 0 \\ 0 & W_n^e \end{bmatrix},
\] (5.234)

where \( \mathbf{W}_{j(1)} \) indicates that this is the isolated matrix of the first scatterer. For example, \( \mathbf{W}_{2(1)}, \mathbf{W}_{i(1)} \) would be the isolated transmission matrix of the second scatterer and i-th scatterer, respectively. From Section 5.3 we know that these transmission coefficients are given as, see Equations (5.58) and (5.60),
\[
W_n^e = \frac{i \varepsilon_1 \sqrt{\mu} \hat{J}_n(k_1 r_s) \hat{H}_n^{(1)}(k_0 r_s) - \sqrt{\varepsilon_0 \mu_1} \hat{H}_n^{(1)}(k_0 r_s) \hat{J}_n(k_1 r_s)}{\sqrt{\varepsilon_0 \mu_1} \hat{J}_n(k_1 r_s) \hat{H}_n^{(1)}(k_0 r_s) - \sqrt{\varepsilon_1 \mu} \hat{H}_n^{(1)}(k_0 r_s) \hat{J}_n(k_1 r_s)},
\] (5.235)
\[
W_n^m = \frac{i \mu_1 \sqrt{\varepsilon} \hat{J}_n(k_1 r_s) \hat{H}_n^{(1)}(k_0 r_s) - \sqrt{\varepsilon_0 \mu_1} \hat{H}_n^{(1)}(k_0 r_s) \hat{J}_n(k_1 r_s)}{\sqrt{\varepsilon_0 \mu_1} \hat{J}_n(k_1 r_s) \hat{H}_n^{(1)}(k_0 r_s) - \sqrt{\varepsilon_1 \mu} \hat{H}_n^{(1)}(k_0 r_s) \hat{J}_n(k_1 r_s)}.
\] (5.236)

With this result the discussion for computing the internal fields in the spherical scatterers is completed.

### 5.6 Conclusions and Recommendations

#### 5.6.1 Conclusions

In this chapter the scattering problem by a single sphere as well as the scattering by multiple spherical particles is discussed. The internal field for a single sphere and an algorithm for the computation of the internal field of a single sphere in a configuration of particles is explicitly given.

Numerical computation pertaining the single sphere has been carried out and excellent agreement with results in the literature is obtained. The multiple scattering analysis caused computational problems. For our configurations many harmonics are needed. Especially the number of harmonics to expand the field around the scattering configuration \((P)\), is necessarily large which was not feasible since the \(\tau\)-matrix could not be stored in the computer memory (Fortran programs use static memory). Albeit a solution for this is available, it should be noted that only a small part of the project is solved herewith, as will become clear in the recommendations. The more harmonics we take into account, the more accurate the spherical solution will be. This is due to the fact that this method is exact (if we have infinite computer power). For a cubic domain it is anticipated that many
(P) harmonics are needed. It is expected that the scattering problem of many spherical scatterers located in a spherical domain needs less spherical harmonics. This will reduce the number P. Furthermore, it is expected that the harmonics for the internal field need not be very large.

5.6.2 Recommendations

It should be stressed that the T-matrix analysis presented so far only takes spherical particles of one fixed size into consideration. In the end, instead of a mono-disperse particulate system, a system with a particle size distribution is required, non-spherical particles and non-planar incident waves need to be implemented, the internal field algorithms (absorption) need to be expanded and coupled with heat transfer equations, and several other facets need to be addressed. Although ambitious, it is more than worthwhile to pursue this route. The application range of such a software tool is enormous, ranging from the field of optics, astrophysics, medicine, climatology to remote sensing as well in engineering disciplines like mechanical engineering (e.g. automobile industry), chemical engineering (e.g. laser curing, aerosol technology), electrical engineering and so on.
Chapter 6

Discussion of the laser ignition experiments

The experimental results obtained with the laser ignition facility and the two dimensional levitator are presented and linked with macroscopic parameters. The applicability of the technique used and the experimental data are discussed.

6.1 Introduction

In this chapter the laser ignition experiments are described and discussed. Firstly, the experiments with the single particle levitator are described and explained, then the experiments with the two-dimensional levitator. The section following the experimental results compares the standardized techniques (furnace and spark) with the laser ignition technique. The chapter closes with a section on the relevance of the concept of pyrophoricity in relation to the laser ignition experiments.

6.2 Single particle ignition

6.2.1 Experimental Methodology

Metal particles were ignited with the single particle laser ignition facility described in Chapter 4. Magnesium particles ignited with a bright white flash, as can be seen on the cover of this dissertation, making the ignition visually traceable. Spherical and nearly spherical particles in the size range of 150 to 750 μm were used. The size of individual particles was measured using a microscope. The measured particles were inserted in the most stable pressure well of the levitator by means of a pair of tweezers. The beams of the carbon dioxide laser were aligned using a Helium neon laser that was placed in the pathway of the laser beam of the carbon dioxide laser. To simplify the alignment, the position of the beam splitter and mirrors were fixed first, after which the focusing lenses
were the only degree of freedom to align the laser beams. After fixing the position of the focusing lenses, the alignment was checked by igniting particles with each of the two infrared beams individually.

The sapphire rod of the optical fiber thermometer was placed in close proximity of the particles (in the order of a few millimeters) to ensure that enough radiation would be collected to exceed the threshold value of the thermometer, but not that close that a combusting particle could damage the rod. The emissivity of the particle material in question as function of wavelength and temperature, the latter whenever available, was given as input to the thermometer.

The experiments with the heating wire, see Section 4.3, had shown that the thin oxide layer on the heating wire had a negligible effect on the temperature readings, and only the emissivity of the pure metal needed to be considered.

The laser was employed in the continuous mode until ignition was achieved. The pulse mode of the laser did not make any significant contribution to the ignition process. In case the pulse duration was too short, the particles did not ignite, and as such a kind of 'residence time' effect would be introduced, which was previously argued to be unintended.

6.2.2 Results

Magnesium

A typical ignition curve is depicted in Figure 6.1. At low temperatures, the radiance of the particle is seen to be insufficient to reach the threshold value of the thermometer. Reaching the threshold value, the temperature is seen to increase nearly linearly but relatively slowly (ca. 8000 K/s) with time to its ignition point. Upon ignition, a discontinuity appears: the temperature rises very rapidly to its combustion temperature, which exceeds the upper temperature limit of the thermometer. The particle combuts for a certain period, after which the temperature rapidly decreases. The period of high temperature is not equal to the combustion duration of the particle. While combusting, the stability of the particle in the pressure well decreases, and at a certain moment it is propelled from its position in the pressure well of the levitator and thereby moves out of focus of the thermometer. The temperature transient in Figure 6.1 is that for a 720 µm magnesium particle for which the heating time from the temperature threshold of the thermometer to the ignition point is relatively long and hence more clearly visible.

With the model (Equations 3.37 and 3.38) for heating a single particle, including the Poynting vector (Appendix B), the temperature increase was calculated. In Table 6.1 the model parameters are presented. The modeled temperature increase due to laser heating and the measured temperature increase are presented in Figure 6.2. Agreement between measured and calculated temperature increase due to laser heating is seen to be good. For convenience the high combustion temperature is artificially truncated at 850 K. The temperature transient at lower temperatures was filtered to reduce noise. As can be seen from the figure, the heating time of the particle (55 ms) is much longer than the characteristic time for heat conduction (in the order of 1 ms). The existence of temperature gradients within the particle can therefore be expected to be negligible.
6.2. SINGLE PARTICLE IGNITION

![Graph showing temperature transient](image)

**Figure 6.1:** Typical temperature transient of an igniting and combusting 720 micron magnesium particle.

This was checked with the numerical results, and the maximum temperature difference between the center of the particle and the outside surface for this particle was calculated to be 3 K.

The point at which the measured temperature values deviate from the model values, i.e. the temperature-time discontinuity, is designated the ignition point, as at this point the initiated combustion process leads to a huge increase in heat production, causing the temperature to jump. In the beginning of the curve the deviation from the modeled temperatures is slightly larger than at higher temperatures. This is probably caused by the lower sensitivity of the detectors at lower temperatures. The ignition point, as determined from Figure 6.1, corresponds with a measured ignition temperature of 720 K. As discussed in Chapter 3, the radiative heat loss term can be neglected in the temperature interval from room temperature to the ignition temperature. From Figure 6.2 it can be seen that the convective heat loss term is also significantly smaller than the laser heat input term, despite the acoustic streaming effect. This does not imply that the convective heat losses are negligible in absolute terms, but that compared to the heat input term, its influence on the heat balance is limited. Reducing the laser power resulted in a longer heating time, but did not affect the position of the ignition point in terms of absolute temperature.

The ignition temperature of magnesium particles of different particle size is presented in Figure 6.3. The minimum ignition temperature is found to be particle size invariant over the particle size range studied (ca. 175 - 775 \(\mu m\)) and equals 725 ± 2 K. This temperature corresponds to what is known in materials science as the transition temper-
Table 6.1: Thermophysical properties and optical constants of magnesium.

<table>
<thead>
<tr>
<th>Property</th>
<th>value</th>
<th>unit</th>
<th>range</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_m$</td>
<td>$0.270 \left( \lambda = 0.7\mu m \right) - 0.233 \left( \lambda = 1.8\mu m \right)$</td>
<td>-</td>
<td>n.a.</td>
<td>[133]</td>
</tr>
<tr>
<td>$C_{p,s}$</td>
<td>$20.44 + 0.071T - 7.24 \cdot 10^6 T^{-2}$</td>
<td>J/mole/K</td>
<td>295 - 543 K</td>
<td>[134]</td>
</tr>
<tr>
<td>$\bar{n}_i$</td>
<td>22.13 - 44.29i</td>
<td>-</td>
<td>n.a.</td>
<td>[46]</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>1740</td>
<td>kg/m³</td>
<td>250 - 750 K</td>
<td>[135]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$165.81 \cdot 3.77 \cdot 10^{-2} T + 1.61 \cdot 10^{-5} T^2$</td>
<td>W/m/K</td>
<td>200 - 900 K</td>
<td>[134]</td>
</tr>
</tbody>
</table>

Figure 6.2: Comparison of modeled and measured temperature for a 720 \mu m magnesium particle.

...ture' of magnesium, 723 - 733 K [136, 137], defined as that temperature at which the oxide layer has either become porous or cracked and hence offers no protection to further oxidation of the metal surface by the surrounding oxidising environment [136]. With the laser heating technique the cracking of the oxide layer is further aided due to the high heating rates achieved. The possibility of oxygen depletion in the vicinity of the particle surface is negligible, due to the enhanced mass transfer caused by the acoustic streaming effect in the ultrasonic levitator. The measured minimum ignition temperature is below the melting temperature of magnesium (923 K). In the temperature trace, a transition to melting is not visible. The optical fiber thermometer measures the temperature of the particle. Upon ignition a cloud of magnesium oxide is formed around the particle that...
is significantly larger than the initial diameter of the magnesium particle (see cover), a process aided by the acoustic streaming effect. As such the thermometer measures the temperature of the hot oxide in the direct vicinity of the particle instead of the particle surface temperature.

![Graph showing minimum ignition temperature vs. particle diameter](image)

**Figure 6.3:** Minimum ignition temperature of magnesium particles as function of particle size.

As very important advantage of the laser ignition method is that integration of the modeled energy balance over the duration of the heating period until ignition yields the amount of energy absorbed by the particles, causing ignition and hence gives the minimum ignition energy of the particle in question. As such the method links the concept of the minimum ignition energy (MIE) with that of the minimum ignition temperature (MIT). Directly linking these two concepts experimentally is probably the greatest advantage of the laser ignition method compared to the conventional means, the furnace (MIT) and spark method (MIE).

Because the particle heating time is significantly longer (several tens of milliseconds, depending on particle size) than the heat conduction within the particle (less than one millisecond), the entire particle volume can be assumed to have the same temperature. The point in time, where ignition takes place, is well defined. Integration over the entire particle volume from the moment of switching on the laser up to the moment the particle ignites, represents the amount of energy accumulated by the particle, and hence the minimum amount of energy needed to ignite the particle. Note that this is not the minimum laser energy, since only part of the electromagnetic radiation is absorbed, while the rest is being scattered.
Taking the parameters of the model into consideration, the particle size is the only variable in the equations presented. The volume of a particle scales with the third order in particle size, and hence the minimum ignition energy also scales with the third order in particle diameter. Since the temperature distribution within the particle is homogeneous, the volume normalised minimum ignition energy is particle size invariant, see Figure 6.4 and equal to $7.60 \times 10^8 \text{ J/m}^3$. Note that the modeled curve was integrated and not the actual curve, since the latter curve could not be measured for the entire temperature trajectory, due to the temperature threshold value of the optical fiber thermometer. Hence the integrated curves yield nearly identical values for the volume normalized ignition energy. This also shows that the heat loss terms are negligible compared to the absorption term.

![Graph showing volume normalized minimum ignition energy of magnesium particles as function of particle size](image)

**Figure 6.4**: Volume normalized minimum ignition energy of magnesium particles as function of particle size in the size range studied.

**Zirconium**

Zirconium ignited at a temperature below the threshold value of the optical fiber thermometer, as can be seen in Figure 6.5. Despite the fact that no clear transition point between the heating process and the sustained combustion process can be observed, a reasonably accurate estimation of the minimum ignition temperature can be derived from this graph. As observed with the ignition of magnesium particles, the temperature increase after reaching the ignition point is steep, see Figure 6.1. Accordingly, assuming the same behavior for zirconium, the ignition point and thus ignition temperature can be found by
taking the intersection of the modeled temperature rise due to laser heating (see Table 6.2 for the properties of zirconium) and the vertical of the initial temperature reading of the optical fiber thermometer, see Figure 6.6. Using this approach, the minimum ignition temperature of zirconium was found to be $501 \pm 4$ K, irrespective of particle size. This corresponds with the data of Karpova et al [137] who measured a value of 498 K using a thermogravimetric analyzer. The absorption efficiency of zirconium is about a factor 15 higher than that of magnesium, depending on particle size. As such the time required to reach the ignition point is considerably smaller than that of magnesium.

![Temperature vs Time](image)

**Figure 6.5:** Ignition behaviour of a 510 µm zirconium particle.

**Table 6.2:** Thermophysical properties and optical constants of zirconium.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
<th>Range</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_m$</td>
<td>0.32 ($\lambda = 0.7\mu m$)</td>
<td>-</td>
<td>n.a.</td>
<td>[133]</td>
</tr>
<tr>
<td>$C_{p,s}$</td>
<td>$27.65 - 5.88 \cdot 10^{-3} T + 9.31 \cdot 10^{-6} T^2$</td>
<td>J/mole/K</td>
<td>333 - 1013 K</td>
<td>[134]</td>
</tr>
<tr>
<td>$\tilde{n}$</td>
<td>5.01 - 1.58i</td>
<td>-</td>
<td>n.a.</td>
<td>[46]</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>6500</td>
<td>kg/m$^3$</td>
<td>n.a.</td>
<td>[135]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$27.4961 - 2.08 \cdot 10^{-2} T + 1.66 \cdot 10^{-5} T^2$</td>
<td>W/m/K</td>
<td>250 - 1200 K</td>
<td>[134]</td>
</tr>
</tbody>
</table>
Figure 6.6: determination of the minimum ignition temperature of a 510 μm zirconium particle.

Other metals: Titanium, Nickel, Aluminum and Iron

Several titanium particle batches were found to contain highly irregular particles with particles sizes above 75 μm, making levitation difficult. Most batches were not comprised of particles larger than 125 μm. The experimental ignition temperature was found to vary between the batches for a certain fixed value of the emissivity by as much as 80 K. This is contrary to the experiments with magnesium, zirconium, and aluminum. It is suspected that some of the batches did not contain pure titanium, but alloys mainly consisting of titanium.

Experiments with nickel showed an important feature of the laser ignition technique. If a particle does not absorb the radiation its temperature will not increase, and therefore it will not ignite. Upon irradiation, the nickel surface changes color from shiny metallic to greenish, the nickel oxide. Despite the lack of data on optical constants for nickel oxide, the apparent penetration depth of the oxide layer as well as the absorption efficiency is so low that the temperature of the particles does not increase further. It should be mentioned that nickel is known to be hardly ignitable with the conventional techniques. Furthermore, when it is ignited, propagation of the flame is difficult.

Experiments with aluminum and iron did not result in ignition. The absorption efficiency of aluminum is, for comparable particle sizes, a factor 3 lower than that of magnesium. The particles were seen to glow to a certain degree (± 500 °C ), but failed to ignite, see Figure 6.7. Iron exhibited the same features.
Figure 6.7: Irradiated aluminum particle failing to ignite.

Non-metals: Coal and Polyethylene

Some experiments were carried out with coal (lignite) and polyethylene particles to confirm the hypothesis that these particles would not ignite in the present configuration. Upon irradiation, the polyethylene particles were seen to crack and evaporate quickly, the latter as seen from the white ethylene vapors emitted from the particles. The acoustic streaming effect was seen to create a rather large horizontal plane of (poly)ethylene vapor, approximately 30 to 40 centimeters in diameter, with two clear jets of polyethylene vapor along the axis of the laser beams. Neither the vapor nor the particles were seen to ignite. With increasing distance from the particle surface, the temperature of the cloud decreases and the oxygen concentration increases. These two effects minimize the possibilities for a homogeneous ignition. The coal particles did not ignite either. The visual effects, i.e. cloud formation, were less pronounced than with the polyethylene particles.

The hypothesis that homogeneously igniting particles would not be ignitable in the current set-up, was based on observations made by other researchers, as previously mentioned in Chapter 3. Upon irradiation, volatile (organic) particles will tend to produce flammable vapors due to devolatilization and pyrolysis. The evolved vapors will form an envelop around the heated particle, lowering the oxygen concentration, close to the particle surface, and hence lowering the ignition probability. One may argue that coal, after depletion of the volatile vapors, will ignite because the oxygen concentration around the particle will increase to the atmospheric value again. However, as pointed out in Chapter 3, carbonaceous particles are difficult to ignite in atmospheric air. Usually, oxygen enriched atmospheres are required to ignite these particles. Even if the particles will ignite
in atmospheric air, all relevant parameters like optical constants, emissivity, conductivity need to be known in order to model the heating transient of the particles in question.

6.3 Two dimensional cloud ignition

6.3.1 Introduction

Using the knowledge from the previous section, i.e. the minimum ignition temperature and the volume normalized minimum ignition energy are constant, research on (metal) particle cloud ignition can now be simplified. It is hypothesized that, in order to ignite a cloud of particles, the particles in the cloud will need to attain the same temperature as that required to ignite single particles. To determine the minimum ignition energy, only the initial number of particles that are required to ignite the entire cloud needs to be clarified. This will result in the minimum ignition energy of the cloud with that specific interparticle distance and particle size (distribution), with aid of the following simple relation:

\[ MIE_{\text{cloud}} = \left( \frac{MIE}{V_p} \right)_{\text{single}} \times \sum V_{p,i} \]  \hspace{1cm} (6.1)

6.3.2 Experimental Methodology

The system of Apfel [94] was designed to levitate up to 20 water droplets. From initial tests [95] it became apparent that (nearly) spherical magnesium particles up to 300 \( \mu \text{m} \) could be stably levitated. In the size range of 240 to 300 \( \mu \text{m} \) about 15 particles could be stably levitated. In the size range of 106 to 150 \( \mu \text{m} \) up to 70 particles could be levitated, as shown in Figure 6.8b. A stable levitation is defined here as an array of particles that remains in suspension for a period of at least several minutes, even though the array would rotate and slightly vibrate along its vertical axis. Most experiments were performed with particles in this size range, i.e. from 106 to 150 \( \mu \text{m} \) in diameter. At these high number densities the formation of clusters of particles was unavoidable. Particles smaller than 106 \( \mu \text{m} \) were difficult to levitate due to the formation of clusters of particles. This problem can be solved by increasing the frequency of the piezo-electric crystal, although this is not a straightforward step. The quality of the higher frequency wave as well as the levitation force need to be at least equal to that of the lower frequency crystal currently employed. Levitation of multiple non-spherical particles was hardly ever accomplished for a period longer than several seconds. To accomplish a stably levitated particle cloud containing more than 20 particles, an electric field of 2800 V across the levitator was required. Due to the high voltage applied, particle clouds containing more than 30 particles would become pseudo-three-dimensional, due to repulsion forces between the particles. The stability of this cloud was low, since the levitator can not create multiple pressure wells (see Section 4.1) strong enough to levitate particles three dimensionally.

The interparticle distance was dependent on the electric field and the position of the reflector. The position of the reflector determines the position of the optimum pres-
sure well and also influences the interparticle distance. The electric field determines the inter-particle repulsion forces as well as contributing to the levitation capabilities of the particles. An oscilloscope was used to determine the optimum stability of the cloud. The interparticle distance varied between 5 to 15 particle diameters. This is comparable to a 11.31 to 0.419 kg/m³ dust loading. Therefore experiments with interparticle distances of 10 to 15 (1.415 to 0.419 kg/m³) gave the best resemblance to practical situations. As soon as a stably levitated particle array was formed, the interparticle distance could only be varied with a factor 1.1 without disturbing the field. This can be explained as follows. As the levitation of the particle array is accomplished, the system is in an energetic equilibrium. Changing the array to another equilibrium can only be achieved with loss of particles from the first equilibrium.

The optical fiber thermometer could not be used to measure the particle surface temperatures. The thermometer needs to be placed in close proximity of the particles to be heated to collect sufficient radiation for measurement. Inserting the sapphire rod in the levitator destroyed the stability of the particle array.

![Figure 6.8: Stable levitation of 8 (a) and 70 (b) magnesium particles in the size range 106 to 150 μm.](image)

### 6.3.3 Results

When the laser was employed, the levitated field lost stability, due to the interference of the electromagnetic field of the laser beam with the electric field of the levitator. This disturbance caused the particles to migrate to the laser beam, hereby reducing the interparticle distance. To show this effect more clearly a cloud of around 70 particles was suspended, see Figure 6.9. In one of the pictures a particle is seen to ignite that subsequently dropped out of the levitator or extinguished or burnt while in suspension. In any case, a sustained combustion process was not achieved in the levitator. After some time a
larger flash is observed associated with the ignition of multiple particles and subsequent destabilisation of the particle array, although a sustained combustion process was not possible. With a CCD framing speed of 30 pictures per second and the knowledge that the frame actually represents an area of 7 by 5 mm, the velocity with which the particles traveled in the direction of the laser beam was calculated to be in the order of 15 mm/s.

Figure 6.9: Interaction of the electromagnetic field of the laser beam with the electric field of the laser facilitating migration of the particles in the direction of the laser beam and subsequent, non-sustaining ignition.

A few experiments resulted in what is believed to be sustained ignition, see Figure 6.10. In this figure two particles almost immediately ignited after employing the laser and resulted in large flash, believed to be multiple combusting particles. As can be observed, the flash gradually expanded over the entire view of the CCD camera, after which the flash diminished. No particles were found to be levitated after this experiment and white powder was found in the levitator, indicating oxidized magnesium. A few magnesium particles were found in the direct vicinity of the levitator after this experiment, but it
could not be judged if they originated from the levitated particles during this experiment or from other experiments. To elucidate the ignition sequence, a filter is required to remove the radiation from the combusting particles so as to follow the movement of the other, non-ignited particles in the levitator. The filter, however, also diminishes the contrast of the levitated particles, reducing their visibility to the CCD camera.

Figure 6.10: Ignition of two particles heated by the laser beam resulting in what is believed sustained combustion of several particles.

6.4 Discussion

6.4.1 Single Particle Ignition

General Considerations

Although the absolute value of the minimum ignition temperature for the metals tested may vary somewhat due to the uncertainties in the value of the emissivity, the fact that the ignition temperature is particle size invariant will always be observed experimentally. This can be explained as follows. The effect of the emissivity on the measured ignition temperature of magnesium was experimentally determined [25]. Assuming a step of 20 percent in the emissivity, the deviation compared with the original temperature value equaled 11 °C. The invariance applies for all particle sizes, including the extremes of very small (nanoparticles and smaller) and very large particles (particles having diameters of several millimeters and larger).
From the observed temperature-time curves, the following observations can be made. Both the experimental curve and theoretical line up to the ignition point are linear. This means that neither the heat losses, nor chemical oxidation reactions play a significant role in the heating process of the particles. If heat losses would be significant, as can be seen from Equations 3.37 and 3.38, the heat loss effect would cause the curve to deflect downwards. As mentioned before, the emissivity based radiation term in the heat balance can be neglected for temperatures below 1000 K. The heat loss through conduction term in the heat balance can be calculated to be at least one order of magnitude lower than the laser heat input term, depending on the ignition temperature.

In case chemical oxidation reactions would play a significant role, the temperature-time curve up to the point of ignition would tend to be more exponential in nature. This can be explained as follows. The heat production caused by oxidation reactions is exponential in time, while the laser radiation absorption term is linear to time.

If the metal particles in question do ignite, it can be seen from the obtained temperature-time curves that the ignition energy and ignition temperature are directly coupled. The ignition temperature can be identified as that point where a clear discontinuity in the temperature-time curve can be observed. With the time required to achieve ignition now known, the surface area underneath the curve up to the ignition temperature will represent the amount of energy absorbed by the particle and hence the energy required to achieve ignition. The standard techniques (furnace and spark) do not consider this feature, although obvious from an energy balance point of view. In this specific case the minimum ignition energy can also be calculated, without integration of the energy balance. Since metals have a high thermal conductivity, the thermal gradient in the particle is negligible and the entire particle volume can be assumed to have the same temperature, namely \( T = MIT \). Hence the calculation of the minimum energy is time invariant and can be determined as follows:

\[
MIE = V_p \rho C_{P, s} (MIT - T_0)
\]  

The ignition temperature of metal particles is seen to be particle size invariant. This is contrary to the commonly accepted perception that the ignition temperature is particle size invariant. However, this perception is based on experimental observations and in this respect logical. The apparent particle size dependence is caused by the characteristics of the furnaces used. The shorter the residence times of the particles in the furnace, the higher the temperature needs to be to heat the particles to their ignition point. Conversely, the larger the particle, the shorter the residence time. From this one might conclude that, for instance, constructing a significant longer Godbert-Greenwald furnace, would solve all these deficits. Although a straightforward solution, the homogeneity of the cloud dispersion in the longer tube will pose a new problem.

The volume normalized ignition energy for metals is constant. This was indirectly already hypothesized by Bartknecht [138], who reported measurements of, for instance aluminum, in which the minimum ignition energy of a number of substances increased with the third power of particle diameter, and thus volume.

The volume normalized ignition energy is seen to be particle size invariant in the
particle size range studied in this investigation. However, for the extreme particle sizes, this relation will not hold. As the particle size decreases, the pyrophoricity phenomenon will increase in significance, and below a certain particle size, the input of energy from the laser beam will not be necessary to achieve ignition. When the heat balance is expanded to include heat generated by surface oxidation, the relation will still hold, although it no longer satisfies the definition of the minimum ignition energy as normally applicable in dust explosion science. This definition states that the minimum ignition energy is the minimum amount of energy required from an external stimulus (spark) to achieve sustained combustion. As such, for sufficiently small particles, the volume normalized minimum ignition energy will decrease to zero. For large particle diameters, the volume normalized ignition energy will also deviate from the horizontal line. With increasing particle size, the probability of temperature gradients increases and the volume normalized ignition energy will decline, since only the surface layer will be heated.

For the case of a cloud of metal particles, the lowest temperature at which these particles ignite (in the heterogeneous mode) is hypothesized to be the same as for an individual, isolated metal particle. The collective effect of the heterogeneously igniting particles in the cloud will not influence the ignition temperature, but only the route to that temperature (heating time).

The hypothesis is based on the following reasoning, starting with the single particle experiments. Assume an atom of a certain metal on the surface of the particle. For the sake of convenience, consider magnesium to be the metal. This specific magnesium atom is influenced by its neighboring magnesium atoms only and not by the diameter of the particle. At a certain temperature, the ignition temperature, a successful collision with an oxygen atom (oxygen will adsorb and dissociate on the particle surface) is achieved. This process is, considering the results, independent of the particle size. Hence, this atom could be located on any of the arbitrarily sized and ignited magnesium particles. In other words, only the temperature (atom vibration level) is of importance to achieve a successful collision rate, thus ignition, and not particle size. In case of a cloud, the same reasoning can be applied, since the atom on one of the particles is not aware of the presence of magnesium atoms on the particles in the direct vicinity of this particle and thus atom. Hence, it is postulated that the ignition temperature of metal particles in a cloud is identical to the ignition temperature of a single particle of the same material.

**Ignition Modes of Different Metals**

The ignition of metals can be classified according to the rate controlling steps as pointed out by Brzustowski and Glassman [139, 140], see Table 6.3.

The classification of the different ignition modes mentioned in Table 6.3 will be discussed in more detail in the following paragraphs [140, 139, 141].

Mode 1: Non-protective ignition mode. In this mode the oxide film that covers the particle is non-protective. The oxide layer is porous and does not prevent oxygen diffusion. In other words, continuous oxidation takes place at relatively low temperatures. The oxidation rate is linear. With time, ignition will take place below the melting point of
Table 6.3: Characteristics of heterogeneous metal ignition modes according to Brzustowski and Glassman [139, 140].

<table>
<thead>
<tr>
<th>Mode</th>
<th>Oxide property</th>
<th>Metal property</th>
<th>Controlling process</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Non-protective</td>
<td>-</td>
<td>Oxidation of metal</td>
<td>Mg, Ca, Ba</td>
</tr>
<tr>
<td>2</td>
<td>Protective,</td>
<td>-</td>
<td>Melting and</td>
<td>Zr, Ti</td>
</tr>
<tr>
<td></td>
<td>metal dissoluble</td>
<td></td>
<td>dissolution of oxide</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>Protective,</td>
<td>Volatile</td>
<td>Melting and</td>
<td>Zn</td>
</tr>
<tr>
<td></td>
<td>undissoluble,</td>
<td></td>
<td>metal oxidation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>non-volatile</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>Protective,</td>
<td>Non-volatile</td>
<td>Melting of oxide</td>
<td>Al, Ni, Fe</td>
</tr>
<tr>
<td></td>
<td>undissoluble,</td>
<td>$T_b^m &gt; T_b^{ox}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>non-volatile</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>Protective,</td>
<td>Non-volatile</td>
<td>Boiling of metal</td>
<td>Be</td>
</tr>
<tr>
<td></td>
<td>undissoluble,</td>
<td>$T_b^m &lt; T_b^{ox}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>non-volatile</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Protective,</td>
<td>-</td>
<td>Oxidation of metal</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>volatile</td>
<td></td>
<td>Boiling of oxide</td>
<td></td>
</tr>
</tbody>
</table>

the metal and hence also below that of the metal oxide. Magnesium, calcium and barium ignite according to this mode.

Mode 2: Ignition mode associated with metal oxide solubility. In this mode the oxide layers covering the particles protect the underlying metal mass. The corresponding metal oxides are soluble in the metals upon melting. Cracks in the oxide layer will enable oxygen diffusion. Ignition will take place below the melting point of the metal. Zirconium and titanium ignite according to this mode.

Mode 3a: Ignition mode associated with melting of the metal. The metal oxide layer is oxygen impermeable and the metal has a high vapor pressure. Upon melting of the metal, the vapor pressure behind the protective oxide layer increases significantly. Eventually the force exerted by both the vapor pressure and the expansion of the now liquid metal will destroy the oxide film. Ignition of the particles can take place at temperatures equal or higher than the melting point temperature, depending on the violence of the destruction of the oxide layer. Zinc is known to ignite in this mode.

Mode 3b: Ignition mode associated with melting of the oxide film. The metal oxide layer is oxygen impermeable, but, contrary to mode 3a, the vapor pressure of the liquid metal is low. Depending on the particle size, the ignition temperature will be lower or higher than the melting point temperature of the metal. As the particle size decreases, the heat loss rate increases and the strength of the oxide layer increases. Examples of metals are aluminum, iron, nickel, and copper.

Mode 3c: Ignition mode associated with boiling of the metal. The oxide layer is oxygen impermeable, the vapor pressure of the liquid metal is low, but the boiling point temperature of the metal is lower than the melting point temperature of the metal oxide. At a certain vapor pressure (temperature) the vapor pressure is sufficiently high to destroy
the oxide layer. The ignition temperature will be equal or lower than the boiling point temperature of the metal. Beryllium ignites in this mode.

Mode 4: Ignition mode associated with vaporization of oxide film. The melting point temperature of the metal oxide is, contrary to the metals in all other modes, lower than the melting point temperature of the metal. As the metal oxide layer melts, the metal underneath is exposed to the oxidising environment and ignites. Ignition temperatures are therefore equal to or larger than the melting point temperature of the metal oxide. Boron ignites in this mode.

It should be stressed that the characteristics mentioned in Table 6.3 do not consider all possible processes that take place during ignition, like for instance the forced destruction of the oxide layer due to high heating rates. However, as a general observation, it can be stated that for metals with a non-protective oxide layer, like magnesium, the oxidation process is only dependent on the heat and mass transfer processes with the surrounding medium, whereas for metals possessing protective oxide layers (e.g. aluminum) the oxidation is dependent on the rate of temperature increase of the particle surface. Hence, in the case of magnesium, the oxide is not able to form a coherent surface, and metallic magnesium is continuously exposed to oxygen. This observation is confirmed by the laser ignition results.

The metal ignition modes can occur either in the diffusion (physical) or kinetic (chemical) regime [139, 140, 141], depending on the significance of the heat loss term. As the heat loss term becomes more important (substantial forced convective transport), the diffusion ignition regime dominates. Ignition is under these circumstances is only possible if the diffusion resistance changes considerably, associated with a phase change of the metal or the metal oxide. The diffusion rate will sharply increase, and the process returns to the kinetic regime. The laser induced ignition processes are dominated by the kinetic regime. This means that the so-called thermal auto-ignition condition needs to be satisfied, i.e., ignition takes place at the temperature at which the heat production equals or exceeds the heat losses, also better known as Semenov’s Theory.

**Observed Ignition Mode Characteristics**

Considering the different ignition modes of the different metals used in this work, the experimental results obtained coincide with the classification mentioned above. Magnesium is a good example in this respect. The larger the particle size, the lower the probability of an explosion, due to the reduced surface area to volume ratio. However, this does not mean that oxidation processes may not occur for large particles. Although large magnesium particles will not spontaneously ignite to cause an explosion, whenever the temperature of a large block of magnesium is raised to the transition temperature in an adiabatic confinement and given enough time and oxygen, it is argued that the entire piece will eventually be completely oxidised, since at temperatures equal or above the transition temperature the oxygen can penetrate the oxide layer to any depth.

While the zirconium particles combust, the oxide layer formed is seen to influence the
temperature reading, in accordance with the behaviour of the oxide as mentioned in Table 6.3. The melting point of zirconium oxide is 2950 K. The optical fiber thermometer is focused on the particle surface. With zirconium it will register the temperature of the surface area during the heating process. In the period during which the ignition point is being reached and during the subsequent combustion, the clouds of cooling zirconium and zirconium oxide surrounding the particle will influence the temperature readings of the thermometer. One hypothesis is that while pure zirconium ignites and combusts, cracks appear in the protective oxide layer, and periodic eruptions of a mixture of the oxidized zirconium and pure zirconium take place, creating the oscillations in the temperature readings.

Aluminum and iron, like nickel ignite in mode 3b according to Table 6.3. The oxide layers initially present neither inhibit nor contribute to the heating process of the particle. Both iron oxide and aluminum oxide have high penetration depths and have strong absorption characteristics for the wavelength emitted by the carbon dioxide laser (10.59 μm). Despite the strong absorbing characteristics of the oxide layers, the small thickness and high penetration depth minimize the influence of the oxide layer on the heating process. With a more powerful laser or with smaller particle sizes, both iron and aluminum will ignite, the latter being confirmed by Marion et al [78] with particle sizes smaller than 70 μm, see Chapter 3. These researchers were able to ignite particles, but unable to see the ignition point in the measurements with their photomultiplier tubes. This is again related to the particle size used, which is too small to exceed the measurement threshold of the photomultiplier tubes.

Relation of Ignition and Kinetic Characteristics

The particle ignition process can be modeled to obtain the kinetic parameters from the measurements. For this purpose the equations for energy conservation and the kinetics of oxide film growth need to be solved simultaneously. Based on Semenov's approach (ignition occurs when heat production is equal or larger than heat loss), from the thermal history of the particle, the activation energy for oxidation can be determined. The equations that need to be solved are thus [140, 142, 143, 144]:

\[ V \rho C_{p,s} \frac{dT}{dt} = \left[ \frac{Q_s I_0}{4} + Q_d \frac{d\delta}{dt} - h(T - T_0) - \epsilon \sigma (T^4 - T_0^4) \right] \pi d^2 \quad (6.3) \]

with

\[ \frac{d\delta}{dt} = \frac{k_0}{\delta^n} \exp \left( \frac{-E_a}{RT} \right) \quad (6.4) \]

The \( n \) is the oxidation law index and has the value of 0, 1 and 2 when the oxidation law is linear, parabolic, or cubic, respectively.

In order to solve this set of equations, the above mentioned equations are put in non-dimensionless form and given the following dimensionless variables for temperature, time and oxide film thickness, respectively [140].

\[ \theta = \frac{E_a}{RT_*} (T - T_*) \quad (6.5) \]
6.4. DISCUSSION

\[
\tau = \left[ \frac{4QE_a}{C_{p,s} \rho RT^2_s d} \right]^{n+1} k_0 \exp \left[ -\frac{E_a}{RT_s} \right] t \\
\tau = \frac{4QE_a}{C_{p,s} \rho RT^2_s d} \frac{\delta}{d}
\]

(6.6)

Furthermore, the following variables are found:

\[
\beta = \frac{RT_s}{E_a}
\]

(6.8)

\[
\kappa = \frac{k_0 d}{\lambda_0} \left[ \frac{4}{C_{p,s} \rho d} \right]^n \left[ \frac{Q E_a}{RT^2_s} \right]^{n+1} \exp \left[ -\frac{E_a}{RT_s} \right]
\]

(6.9)

\[
\epsilon_c = \frac{c_0 T^4 (C_{p,s} \rho RT^2_s d)^n}{Qn_0 (4QE_a)^n} \cdot \exp \left( \frac{E}{RT_s} \right)
\]

(6.10)

By introducing \( T_s \) it is possible to avoid an explicit dependence of the particle heating on the value of the laser power. The critical conditions will be found for \( \kappa = \kappa_c \) as follows:

\[
\kappa_c = a_n f_1(\theta, Nu) \cdot f_2(\beta) \cdot f_3(\epsilon_c) \cdot (z_0)
\]

(6.11)

with

\[
a_n = \frac{Nu_0}{\kappa_c} \left( \frac{2 + \beta \theta_0}{2(1 + \beta \theta_0)} \right)^s
\]

(6.12)

To find the kinetic parameters, the order of the oxidation law needs to be known. Magnesium obeys the parabolic oxidation law, while zirconium obeys the cubic law at moderate temperatures. With this information and taking the logarithm of Equation 6.11, the following relation is obtained

\[
\ln(T_{s,cr}^{2n+2}Nu \cdot d^n) + \ln f_2(\beta) + \ln f_3(\epsilon_c) + \ln f_4(z_0) = \ln \frac{Qn_0 (4QE_a)^n E_a}{a_n c_0 (C_{p,s} \rho)^n R^{n+1}} - \frac{E_a}{R} \frac{1}{T_{s,cr}}
\]

(6.13)

Approximation of the initial parameters and using the output values of these approximations such as the initial input data for the next approximation, will reveal the kinetic data.

Using the experimentally determined minimum ignition temperature of magnesium and zirconium and the above mentioned equations, the activation energy for the oxidation reactions of these metals to the corresponding oxides are determined to be 105 ± 4 kJ/mole for magnesium and 94 ± 3 kJ/mole for zirconium.

The obtained results correspond with data found in literature. For magnesium Elkoth et al [145] found 100 kJ/mole, Rosenband et al [144] 105 kJ/mole and Hauffe [146] 106 kJ/mole. For zirconium Karpova et al [137] found 92 kJ/mole. Conversely, knowing the activation energy for the oxidation reaction of a metal, the particle size invariant minimum ignition temperature can be determined, as well as the minimum ignition energy of a particle or particle cloud.
6.4.2 Multiple Particle Ignition

Despite the fact that the levitator used was two-dimensional, valuable information was obtained. With the experience of the single particle, ultrasonic levitator, the scaling up to a two-dimensional, electro-acoustico levitator gives insight in the feasibility of developing a three-dimensional ultrasonic levitator and its use. As could be seen, a levitator employing some kind of electric field will not facilitate the stability of the levitated particle array. The electromagnetic beam interacts with the electric field and induces migration of the particles towards the laser beam, thus obstructing the effect of a fixed interparticle distance. Interparticle distance is important in determining the minimum number of particles required for ignition.

It should be noted that Equation 6.1 considers that all the particles subject to electromagnetic radiation, and present in the ignition kernel, are being heated by absorption of laser radiation only. We explain this in more detail. Suppose the ignition kernel consists of three particles, all three absorbing laser radiation. One particle can reach its ignition point, while the other two particles are still being heated to this point. As the ignited particle starts combusting, the other two particles are no longer exclusively heated by laser radiation. The heat of combustion of the one particle will contribute in raising the temperature of the other two particles. On the other hand it is required to heat at least three particles by the laser in order to get a self-sustaining combustion process throughout the cloud. Returning to the initial kernel of three particles: suppose only one of those three particles is heated, then, due to the interparticle distance and size of the heated particle, the produced energy upon ignition is not sufficient to facilitate a sustained combustion. In other words, in this example, a minimum of three particles is required to ignite the rest of the cloud. The aforementioned equation gives the maximum amount of energy required to heat these three particles to their ignition point by absorption of laser light. Therefore, it represents the maximum absorbed laser energy required to ignite the entire cloud, by heating these three particles. The collective effect of the three particles will lower this energy. How much this collective effect will contribute can, however, be quantified only when a fully developed, heat balance coupled, T-matrix model is operational.

To take the previous example one step further. For ignition it is not required to heat the entire particle to the ignition temperature. It suffices to heat a critical layer of the particle, that subsequently ignites the rest of the particle and possibly some of its neighbors. Due to the high conductivity of the metal particles, however, the entire particle, prior to ignition, will have the same temperature, hereby simplifying the relation for the ignition energy of the cloud to Equation 6.1. Palmer [16] gives for the minimum ignition energy, determined with a conventional spark, for magnesium cloud with a median particle size of 28 µm a value of 40 mJ. Assuming that these particles could have been levitated in the two-dimensional levitator, the interparticle distance being appropriate for those conditions and that, conservatively speaking, a cubic formation of 8 particles was required to ignite the cloud. With the results of Section 6.2 it can be determined that the minimum ignition energy of the cloud with a laser would be 69.9 µJ. This is a significant difference, indicating the poor efficiency of the spark ignition method. However, it should be stressed, that a considerable amount of spark energy is used for purposes other than
heating (e.g. forming a shock wave). Such an argument can also be formulated for a laser beam, since only a fraction of the energy is used for absorption and the energy of the initial laser beam incident on the particle is not considered. However, with the laser method the actual absorption of energy by the particles can be accurately determined, a principle that is much less straightforward for the other two techniques, i.e., spark and furnace.

To create a three dimensional cloud the combination of the electric field and the single piezoelectric crystal to create the sound wave is impractical. Especially the latter aspect is important. In the two dimensional levitator the crystal is used to create one large stable pressure well. Multiple stable pressure wells along the vertical axis would require powers that go beyond the current capabilities of the crystals. Therefore using multiple crystals, each generating confined multiple pressure wells, placed in close proximity of each other, would create a stable three dimensional levitation field, making the electric field redundant for particle separation. The, in this case redundant electric field will also not interfere with the laser beam. As is known from Section 4.1, such a system is currently not feasible. Given the fact that both the minimum ignition temperature as well as the volume normalized minimum ignition energy are constant, the need for such a device is also significantly reduced, and the equipment proposed by Colver [96] (Section 4.1) can be an alternative. The optical fiber thermometer can be employed under the condition that impact of the particles will not destroy the sapphire rod as well as that the particles that are being heated by the laser will remain in focus for a sufficient amount of time. The latter property might pose a problem. Particles were quoted by Colver to have speeds in the order of 1 m/s, so very small particles need to be used to fulfill this requirement. However, the smaller the particle, the lower the chance of detection as well as the lower the absorption efficiency. The measurement of the temperature is only required to confirm the hypothesis that the ignition temperature of the particles in cloud formation is equal to that of a single particle. As soon as this hypothesis is confirmed, the minimum number of particles required to obtain sustained combustion of the particle cloud as function of inter particle size needs to be determined with some visual technique. The levitator of Colver, however, employs an electric field to suspend the particles. The laser will need to operate with a fixed laser pulse of sufficient duration to avoid disturbance of the levitated particle array.

6.4.3 The Concept of Pyrophoricity

As explained in the first paragraph of this section (6.4.1), as the metal particle size becomes small, i.e. smaller than about one micron, the volume normalized minimum ignition energy decreases to zero, due to a phenomenon known as pyrophoricity. It should be noted that this reduction is partly due to the definition of minimum ignition energy that is used, i.e. stating that the minimum ignition energy is the minimum amount of energy required from an external stimulus (spark) to achieve sustained combustion. Also the ignition temperature will apparently deviate from its constant value to lower temperatures.
Pyrophoricity refers to the property of a substance to spontaneously combust in air at ambient temperature [147, 148, 149]. The tendency toward pyrophoric behaviour depends primarily on three factors. Firstly, the specific surface area of the particles, i.e., the smaller the particle the larger the ratio of surface area to volume. The area exposed to an oxidising agent will reach a maximum when all the particles are suspended in an oxidising gas. However, some metals can even exhibit pyrophoric behaviour in the bulk state. Secondly the chemical reactivity, given by the electronegativity of the substance. The lower the electronegativity of the substance compared to that of oxygen, the greater the chemical reactivity and the higher the probability of pyrophoric behaviour. Thirdly, the degree to which the metal particles are covered by a layer of oxide; i.e. the chemical composition, especially at the surface. Metal particles will be most reactive when they are entirely pure, i.e. have no oxide film. Returning to the ignition temperature of zirconium, it is known that a cloud of zirconium with a particle size smaller than roughly 3 micron will certainly spontaneously ignite when dispersed in ambient air and possibly even without dispersion [149]. The hypothesis of a particle size invariant minimum ignition temperature seems not to hold, since ignition takes place at room temperature. However, in the latter case the reference point for measuring the temperature is that of the ambient air in which the zirconium cloud is dispersed.

Assume monosized, 1 micron diameter zirconium particles and expose them in particle cloud form to air. Oxygen molecules will adsorb on the zirconium surface and, due to the electronegativity of the zirconium, recombine to zirconium oxide. The first atom layer will immediately oxidise (in practice the first three atom layers will do so, the first layer having the highest oxidation rate). Assuming that the particle behaves adiabatically (no heat loss to the surrounding medium), the temperature of the next atom layer, which is oxidising already to a certain degree due to oxygen penetration, will increase further, and a sustained combustion mode is achieved as the oxide coating fails to offer protection for oxygen diffusion due to the increased temperature. It is argued here that the measured runaway temperature of the particle (ignition temperature) will be equal to the minimum ignition temperature as determined with the laser ignition technique. As the heat of combustion of the substance increases, this effect will have a more pronounced effect as well in that it will manifest itself at even larger particle diameters. Especially group 3 metals of the periodic table are known to exhibit these features. Hence, there is no deviation from the particle size invariant ignition temperature as measured with the laser, but merely a difference in choosing the reference point for measuring the temperature, which should be the particle temperature.

As is known from zirconium, dispersion of submicron particles is not required to achieve a sustained combustion mode. As such the levitator is not necessary, aside from the fact that it will not levitate such small particles. The laser is obviously not relevant to these experiments. Measurement of the temperature with the optical fiber might be possible, as long as the incident radiation is high enough to reach the threshold value for measurement of the thermometer. A simple hand held IR detector or thermocouple with small diameter will also suffice.
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_n$</td>
<td>Function</td>
<td></td>
</tr>
<tr>
<td>$C_{p,s}$</td>
<td>Heat capacity of particle</td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>Particle size</td>
<td></td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
<td></td>
</tr>
<tr>
<td>$h$</td>
<td>Heat transfer coefficient</td>
<td></td>
</tr>
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<td>$I_0$</td>
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### Greek symbols

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Chapter 7

Conclusions and perspectives

7.1 Conclusions

The new laser ignition technique for single particle studies is a much improved method to accurately and precisely determine the real minimum ignition temperature of metallic particles. The applicability of the technique is currently limited to predominantly metal particles. More precisely stated, the ignition characteristics of purely heterogeneously igniting particles can be determined, as long as the absorption characteristics are such that heat absorbed from the laser is larger than heat losses. Taking into consideration that this technique is in its infancy, significant progress can be expected in the years to come.

The minimum ignition temperature of a single particle is particle size invariant and equal to the minimum ignition temperature of a cloud comprising the same particles. This conclusion is contrary to common perception, that the minimum ignition temperature is indeed depends on particle size, as determined with the furnaces. That the laser ignition technique shows the particle size invariance of the minimum ignition temperature is directly related to the fact that with this technique the particles are heated until they ignited; i.e. (heating) time is not a constraint to reach ignition. With the furnace techniques, time is a variable. This occurs because the determination of the minimum ignition temperature by the furnace method is strongly influenced by the dimensions of the furnaces, as these influence a critically important parameter: particle residence time. For practical situations, residence times of particles in hot areas of an industrial plant need to be considered and compared with those of the standard furnaces. When the residence time in an industrial unit is smaller than that of the particles in the standardized technique, the determined values will provide useful information, under the condition that the concentrations (interparticle distance) is the same for both situations. In case the residence time in the practical situation is longer, however, the furnace technique will underestimate the potential hazard of the practical situation. Increasing the length of the furnace needs to be carefully evaluated to ensure that large concentration gradients are absent.

The minimum ignition energy is a useful quantity in a limited particle size interval
for heterogeneously igniting particles. The magnitude of the interval is predominantly determined by size, shape and thermal conductivity of the substance. For instance, for very small, submicron metallic particles, ignition can take place without the aid of external stimuli, due to pyrophoric behavior of the material in question.

The minimum ignition temperature is, more than the minimum ignition energy, a strictly material characteristic. The minimum ignition energy depends on particle shape and particle size, whereas the ignition temperature is independent of these parameters. Minimum ignition energy and minimum ignition temperature are linked: the integral of the temperature-time curve for a heated particle up to its ignition temperature, combined with particle volume and temperature corrected specific heat capacity, is equal to the minimum ignition energy. This obvious link has apparently been overlooked for decades by practical dust explosion researchers and, indeed, using the current measuring techniques (furnace and spark method) it could also not be established experimentally.

The heating rate (relating to laser power) influences the time required to heat the particles to the ignition point, but does not affect the ignition temperature. The heating time was much longer than the characteristic time for heat conduction within the particle, ensuring a homogeneous distribution of the temperature over the particle volume. The high thermal conductivity of the metals thus ensures that the temperature is homogeneously distributed over the entire particle volume. Reaction takes place only at the surface of the particles. Taking the rate of the oxide layer formation into account, the pre-exponential factor and the activation energy of the combustion reaction of the metal to its stable oxide can be calculated. Conversely, knowing the kinetic parameters, the minimum ignition temperature of the metal can be calculated.

The spark efficiency (i.e. the efficiency by which the total spark energy is absorbed by the particles and converted into particle thermal energy, and thus particle temperature rise) is very low (in the order of a factor 1000) if the amount of energy absorbed by the critical number of particles - required for sustained combustion - is considered. However, a spark in an industrial unit will suffer from the same low efficiency as a spark generated with the standardized technique. The energy determined with the spark technique is solely applicable when electrostatic hazards are evaluated. The minimum spark energy is not the absolute minimum energy of all possible ignition sources.

The laser ignition technique is not an answer for the shortcomings of the standardized techniques. It merely confirms the fact that these systems have shortcomings, but will not replace them as an alternative technique, because of the complexity, and as of yet, the limited experience with this technique. This is most clearly shown in literature data. At best the minimum required power levels to achieve ignition were determined, a quantity that can not be used universally due to the wavelength dependence of the absorption characteristics. The success of the technique depends on having full knowledge of all relevant parameters of the material to be studied. Alternatively, if all but one parameters are known, in inert environments the missing parameter can be fitted with high accuracy.

The T-matrix method was validated for single particles and yields, given enough computational effort, exact solutions of the absorption and scattering of multiple particles. The technique needs to be further expanded to include the absorption terms and the en-
energy balances over the particles, even if the model will not be used for ignition purposes.

7.2 Perspectives

To more solidly validate the results reported here, more metals and other heterogeneously igniting substances should be considered. For single particle experiments, other materials, like boron, beryllium, zinc, and carbon need to be tested. Zinc ignites heterogeneously, but in a different mode compared to other metals. Furthermore its transition temperature is allegedly higher than its melting point. For carbon particles previous research, performed by other researchers, has indicated that carbon is not likely to be ignitable in ambient air.

In addition to carrying out more experiments, the experimental methodology should also be improved. A setup similar to that of the Electrostatic Particulate Suspension equipment needs to be built and the results of the current study implemented. The concept of the ultrasonic three dimensional levitator needs to be pursued, even if its application is not related to ignition work.

The effect of acoustic streaming on the heat and mass transfer also needs to be quantified. The heat transfer enhancement can be determined by heating an inert particle (for instance alumina) of known size to its equilibrium temperature. With all parameters known, the enhancement of the heat transfer can be elucidated. Using the well known Lewis relationship, under the condition that the Reynolds number is not too small, the effect on the mass transfer can be quantified.

The carbon dioxide laser can be replaced by a continuous YAG laser. Despite the fact that the power output of YAG lasers is considerably lower and the absorption bands of materials are weaker, the lower limit of the particle sizes used can be reduced by a factor of 10. Preferably metal substances need to be tested.

Homogeneous ignition in the ignition facility is less likely due to the acoustic streaming effect. Heated polypropylene particles of all sizes were seen to merely evaporate without ignition. Hence, these particles may forcedly ignite heterogeneously, if at all ignitable. This is inherent to the acoustic levitation technique. Although also limited in applicability, a comparative study of, for instance, polypropylene and sulphur in the electrodynamic balance for single particle ignition is envisioned. This under the condition that all relevant properties are known and that the swelling of the particles is limited. If the swelling is considerable, this factor would need to be carefully studied and quantified.

An alternative principle is combining the levitation technique with the furnace technique. By creating a very small furnace were multiple particles can be levitated, the effect of residence time is eliminated while adapting the advantages of the established furnaces. With this straightforward setup, the ignition behaviour of intrinsic homogeneously igniting particles can be studied in detail, including the cooperative effect of the particles. The problem with the technique is the fact that with increasing temperature, the levitation force will decline due to the decreasing density of the gaseous medium.

The concept of pyrophoricity needs to be expanded, and research should focus on the run-away temperature of the particles.
The current T-matrix model needs to be expanded to include particle size distributions of non-spherical particles and incident non-planar waves. The internal field algorithms (absorption) need to be coupled with heat transfer equations. To ease the computational efforts, the particle size parameter should initially be reduced to unity.
Bibliography


BIBLIOGRAPHY


Appendix A

Drude’s free electron theory

Drude developed his free electron theory [150, 151, 152] after J.J. Thomson’s discovery of the electron in 1897 by applying the kinetic theory of gases to a metal, considering the metal as a gas of electrons.

The interaction between a photon and an electron causes either an interband transition or an intraband transition of the electron. For an interband transition to occur a minimum photon energy is required, associated with an electron transition from a filled band to an empty band. On the other hand, if one or more bands are only partially occupied by electrons, intraband transitions of electrons to an empty state within the same band occur by absorption of photons with energies lower than the threshold value for interband transitions. Hence, for most metals the effects of intraband transitions on the optical absorption and dispersion, which can be modeled by Drude’s theory, are dominated in the infrared.

The mathematical formulation of Drude’s free theory is as follows. Besides the complex index of refraction, one can also use the complex dielectric function to describe the optical properties of a given material, assuming that the relaxation frequency of the free electron is constant over the Fermi surface:

$$\epsilon = \epsilon' - i\epsilon''$$  \hspace{1cm} (1)

For a “free” electron material, the complex dielectric function is

$$\epsilon = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$  \hspace{1cm} (2)

with

$$\epsilon' = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2}$$  \hspace{1cm} (3)

$$\epsilon'' = \frac{\omega_p^2\gamma}{\omega(\omega^2 + \gamma^2)}$$  \hspace{1cm} (4)

where $\gamma$ denotes the relaxation frequency of the free electron. The complex index of refraction and the complex dielectric function are coupled through

$$\epsilon' = n^2 - k^2$$  \hspace{1cm} (5)

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\[ \varepsilon'' = 2nk \]  

(6)

For a given set of frequencies of the laser, plasma and relaxation, one can calculate the values of the real and imaginary part of the complex index of refraction.

The plasma frequency of the electrons, \( \omega_p \), relative to the circular frequency of the laser light, \( \omega \), determines the optical behaviour of the particle. If the frequency of the laser light is smaller than the plasma frequency, the particle behaves like an opaque material. For frequencies larger than the plasma frequency, the particle becomes transparent. For most metals the plasma frequency lies in the ultraviolet region.

Summarizing:
\[
\begin{align*}
\omega & \ll \omega_p : \quad k > n \gg 1 \text{ (reflecting)} \\
\omega & \approx \omega_p : \quad k = n \ll 1 \text{ (absorbing)} \\
\omega & \gg \omega_p : \quad n \to 1, k \to 0 \text{ (transparent)}
\end{align*}
\]

Despite the (mathematical) simplicity of Drude's free electron theory, care should be taken when applying the theory. In metals, intraband transitions will take place from an energy state just below the Fermi level to one just above the Fermi level. This is actually only true for the alkali metals, which exhibit nearly free electron behaviour and to a lesser extent also for the noble metals. The transition metals, for instance, have d-bands which intersect the Fermi level. Hence, their optical and dispersion properties are to a considerable degree dominated by the "bound" d-band electrons. Although Drude's free electron theory is not valid in all cases, it can be used by approximation for all other metals, non-conductors and semiconductors containing impurities.

In general, Drude's theory predicts the imaginary part of the complex index of refraction, \( k \), well for most infrared wavelengths. The predicted value for the real part, \( n \), starts to deviate from measured data at wavelengths smaller than \( \lambda \approx 5\mu m \). This can be explained as follows. The complex dielectric function can be separated in a "bound" and a "free" component
\[
\varepsilon(\omega) = 1 + \varepsilon_b(\omega) + \varepsilon_f(\omega)
\]

(7)

Below the threshold value of interband transitions, the imaginary part of the bound complex dielectric function is zero, while the real part becomes constant. Hence,
\[
\begin{align*}
n^2 &= 1 + \varepsilon_b' + \varepsilon_f(\omega) \\
2nk &= \varepsilon_f''(\omega)
\end{align*}
\]

(8)

(9)
The imaginary part of the "free" dielectric function determines the imaginary part of the complex index of refraction, while the real parts of the "bound" and "free" dielectric functions determine the real part of the complex index of refraction.

Qiu et al [45] applied Drude’s theory to aluminum, chromium and nickel particles. The literature values of the optical constants of aluminum agree (see Table 3.1) with the predicted values of Drude’s theory. Although not an alkali metal, aluminum has a partially
filled p-band and lacks a d-band. The latter two metals, however, are transition metals. Although it is not stated here that the literature values are correct, Drude's theory cannot be expected to predict correct values. Especially the real part of the complex index of refraction deviates from literature values. When using Drude's theory to predict the complex index of refraction at room temperature, the absorption efficiency based on these values of chromium particles is underestimated by approximately 20%, while for the nickel particles the efficiency is overestimated by approximately 30%, compared to literature based efficiencies.
Appendix B

Poynting’s Theorem

Poynting’s theorem [38, 41, 124, 153] provides a relation of the energy carried by an electromagnetic wave per unit time and unit of surface area through the Poynting vector. Consider an electromagnetic field \((\mathbf{E}, \mathbf{H})\), which is not necessarily time harmonic, incident on a spherical particle. The particle will absorb the incident radiation energy by so-called Joule heating.

The energy of the beam can be found from the time-average of the Poynting factor, \(S\), and is given by:

\[
I_0 = \int S \, dt = \int \mathbf{E} \times \mathbf{H} \, dt = \frac{1}{2\mu_0 c} E_0^2 \tag{10}
\]

This integration is taken over a time period much greater than that required for the energy to propagate one wavelength \((\tau \gg \frac{1}{\omega})\). The time-averaged absorption is then

\[
Q(r, \theta, \phi) = \frac{\sigma_c}{2} |\mathbf{E}(r, \theta, \phi)|^2 \tag{11}
\]

The conductivity is given by

\[
\sigma_c = \frac{4\pi nk}{\lambda_0} \tag{12}
\]

Equations 11 and 12 can be expressed in terms of the incident radiation intensity \(I_0\) as follows

\[
Q(r, \theta, \phi) = \frac{4\pi nkI_0}{\lambda} S(r, \theta, \phi) \tag{13}
\]

with

\[
S(r, \theta, \phi) = \left| \frac{\mathbf{E}(r, \theta, \phi)}{E_0} \right|^2 \tag{14}
\]
Appendix C

The Vector Wave Equation

Let the scalar function $\psi$ be a solution of the equation

$$\nabla^2 \psi + k^2 \psi = 0. \quad (15)$$

Solutions of the vector wave equation in spherical coordinates can be deduced directly from the characteristic functions of the corresponding scalar equation. Following the notation done by Stratton [127] and in other literature we shall put $\psi_{m,n} = f_{m,n} \exp(-i\omega t)$, where $f_{m,n}$ is the characteristic solution

$$f_{m,n} = z_n(kr) P_n^{ml} \cos(\theta) \exp(i\phi), \quad (16)$$

where $z_n(kr)$ is just one of the Bessel functions, depending on the ingoing or outgoing character of the considered wave. One solution of the vector wave equation

$$\nabla(\nabla \cdot C) - \nabla \times \nabla \times C + k^2 C = 0 \quad (17)$$

can be found by taking the gradient of the $f_{m,n}$ defined in Equation (16). We define $L = \nabla \psi$, and split off the time factor by writing $L = l \exp(-i\omega t)$. The other two independent vector solutions can be constructed as follows:

$$M = (-1)^m \nabla \times \nabla \psi = L \times r = \frac{1}{k} \nabla \times N, \quad (18)$$

$$N = \frac{1}{k} \nabla \times M. \quad (19)$$

To obtain explicit expressions for the vector wave functions $L$, $M$ and $N$, we need only carry out the differentiation of Equation (17) as required by the following vector properties:

$$L \cdot M = 0, \quad \nabla \times L = 0, \quad \nabla \cdot L = \nabla^2 \psi = -k^2 \psi,$$

$$\nabla \cdot M = 0, \quad \nabla \cdot N = 0.$$

When properly done and splitting off the time factor, we find

$$l_{m,n} = \frac{\partial}{\partial r} z_n(kr)(-1)^m P_n^{ml} \cos(\theta) \exp(i\phi) i_1 + \frac{1}{r} z_n(kr)(-1)^m \frac{\partial}{\partial \theta} P_n^{ml} \cos(\theta) \exp(i\phi) i_2 + \ldots$$

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\[
\begin{align*}
\mathbf{m}_{m,n} &= \frac{im}{r \sin \theta} z_n(kr)(-1)^m \mathbf{P}_n^m(\cos \theta) \exp(im \phi) \mathbf{i}_2 - \\
&\quad z_n(kr)(-1)^m \frac{\partial}{\partial \theta} P_n^m(\cos \theta) \exp(im \phi) \mathbf{i}_3,
\end{align*}
\]  

\[
\begin{align*}
\mathbf{n}_{m,n} &= \frac{n(n+1)}{kr} z_n(kr)(-1)^m P_n^m(\cos \theta) \exp(im \phi) \mathbf{i}_1 + \\
&\quad \frac{1}{kr \frac{\partial}{\partial r}} |rz_n(kr)| (-1)^m \frac{\partial}{\partial \theta} P_n^m(\cos \theta) \exp(i \phi) \mathbf{i}_2 + \\
&\quad \frac{im}{kr \sin \theta \frac{\partial}{\partial r}} |rz_n(kr)| (-1)^m P_n^m(\cos \theta) \exp(im \phi) \mathbf{i}_3,
\end{align*}
\]  

where \( \mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3 \) are the unit vectors in the direction of increasing \( r, \theta \) and \( \phi \) such as to constitute a right-hand base system. The expression for the Legendre polynomials taken in this appendix are given as

\[
P_n^m(\cos \theta) = (-1)^m (1 - \cos^2 \theta)^{m/2} \frac{d^m P_n(\cos \theta)}{d \cos^m \theta}.
\]  

These are the same as in the literature except for Stratton [127], where the factor \((-1)^m\) has been left out for convenience. Some expressions differ from the expressions found in Stratton [127] and the reason lies in the definition of the Legendre functions. Now consider the vector function

\[
f(z) = \mathbf{a} \exp(ikz) = \mathbf{a} \exp(ikr \cos \theta),
\]  

where \( \mathbf{a} \) is an amplitude vector oriented arbitrarily with respect to a rectangular reference system. Let \( \mathbf{a} \) be resolved into three unit vectors directed along the \( x-, y-, z- \)-axis respectively. Then

\[
\begin{align*}
\mathbf{a}_x &= \sin \theta \cos \phi \mathbf{i}_1 + \cos \theta \cos \phi \mathbf{i}_2 - \sin \phi \mathbf{i}_3, \\
\mathbf{a}_y &= \sin \theta \sin \phi \mathbf{i}_1 + \cos \theta \sin \phi \mathbf{i}_2 + \cos \phi \mathbf{i}_3, \\
\mathbf{a}_z &= \cos \theta \mathbf{i}_1 - \sin \phi \mathbf{i}_2.
\end{align*}
\]  

Now the divergence of the vector functions \( \mathbf{a}_x \exp(ikz) \) and \( \mathbf{a}_y \exp(ikz) \) is zero and consequently may be expanded in terms of the characteristic functions \( \mathbf{m} \) and \( \mathbf{n} \) alone. At \( r = 0 \) the field is finite and we shall, therefore, require functions of the first kind. It is apparent, moreover, that the dependence of Equations (25-26) on \( \phi \) limits us to \( m = 1 \). If we compare Equations (21-22) with Equation (25), obviously we have to split \( \mathbf{m} \) and \( \mathbf{n} \) in ‘odd’ and ‘even’ parts. From this it follows that we only take the odd contribution of \( \mathbf{m} \) and the even contribution of \( \mathbf{n} \). We set up the expansion

\[
\mathbf{a}_x \exp(ikr \cos \theta) = \sum_{n=0}^{\infty} a_n \frac{m_1^{(1)} - m_{-1,n}^{(1)}}{2i} + b_n \frac{n_1^{(1)} + n_{-1,n}^{(1)}}{2i}.
\]
Using the orthogonality relations for vector wave functions, see Stratton [127], we find for this expansion

\[ a_x \exp(ikz) = \sum_{n=0}^{\infty} i^{n+1} \frac{2n + 1}{2n(n+1)} \left[ m_{-1,n}^{(1)} - m_{1,n}^{(1)} - (n_{-1,n}^{(1)} + n_{1,n}^{(1)}) \right]. \]  

(29)

In other literature it is also customary to write \( m \) and \( n \) explicitly in odd and even parts as

\[ m_{o1n} = \frac{m_{1,n} - m_{-1,n}}{2i}, \]

(30)

\[ n_{e1n} = \frac{n_{1,n} + n_{-1,n}}{2}, \]

(31)

where the subscripts \( o \) and \( e \) mean that we are dealing with the odd and the even part, respectively. The same process gives for the wave polarized in the \( y \)-direction the expansion

\[ a_y \exp(ikz) = -\sum_{n=0}^{\infty} i^n \frac{2n + 1}{n(n+1)} \left[ m_{e1n}^{(1)} + in_{o1n}^{(1)} \right], \]

(32)

which obviously results in

\[ a_y \exp(ikz) = -\sum_{n=0}^{\infty} i^n \frac{2n + 1}{2n(n+1)} \left[ m_{-1,n}^{(1)} + m_{1,n}^{(1)} - (n_{-1,n}^{(1)} - n_{1,n}^{(1)}) \right]. \]

(33)

Furthermore, the \( \psi \) from Equation (18) is constituted out the spherical wave functions, written as

\[ \psi_{m,n}(r) = h_n^{(1)}(k_0r)Y_{m,n}(\theta, \phi), \]

(34)

where \( h_n^{(1)}(x) \) is the \( n \)-th order spherical Hankel function of the first kind and

\[ Y_{m,n}(\theta, \phi) = \sqrt{\frac{(2n + 1)(n - |m|)!}{4\pi (n + |m|)!}} P^{|m|}_n(\cos \theta) \exp(im\phi). \]

(35)

The regular part of \( \psi \), \( \Re \psi_{m,n} \), is obtained by substituting \( h_n^{(1)} \) with \( j_n \), the \( n \)-th order spherical Bessel function. The expression for the Legendre polynomials taken in this appendix are given as

\[ P_n^m(\cos \theta) = (-1)^m (1 - \cos^2 \theta)^{\frac{m}{2}} \frac{d^m P_n(\cos \theta)}{d \cos^m \theta}. \]

(36)
Appendix D

Waterman Method

The multiple scattering of electromagnetic fields is a research topic that finds applications in many fields. In this appendix, a method will be discussed which can be applied to arbitrarily shaped scatterers. Although the transition matrix of each individual sphere can be found in closed form, the general theory of the T-Matrix method shall, for both apprehensive and comprehensive reasons, be discussed here. For simplicity, we shall give the scalar expressions. The resulting equations are easily adapted to the vector electromagnetic scattering problems.

Surface Integral Equations

An integral equation can be viewed as an operator equation. Thus, the matrix representation of such an operator equation can be obtained, and then the unknown is easily solved for with a computer. We shall show how such integral equations with only surface integrals are derived, using the scalar wave equation. First we look at the following two-region problem as shown in Figure 1.

The governing equations are given by

\begin{align}
(\nabla^2 + k_1^2)\phi_1(r) &= Q(r), \\
(\nabla^2 + k_2^2)\phi_2(r) &= 0,
\end{align}

for region 1 and 2, respectively. If we now introduce the Green's functions through

\begin{align}
(\nabla^2 + k_1^2)g_1(r, r') &= -\delta(r - r'), \\
(\nabla^2 + k_2^2)g_2(r, r') &= -\delta(r - r'),
\end{align}

then by writing Equations (37-40) out, the following equations can be found,

\begin{align}
g_1(r, r')\nabla^2\phi_1(r) - \phi_1(r)\nabla^2g_1(r, r') &= Q(r)g_1(r, r') + \delta(r - r')\phi_1(r), \\
g_2(r, r')\nabla^2\phi_2(r) - \phi_2(r)\nabla^2g_2(r, r') &= \delta(r - r')\phi_2(r),
\end{align}

for region 1 and 2, respectively. By integrating Equation (41) over region 1, we get

\[
\int_{V_1} [g_1(r, r')\nabla^2\phi_1(r) - \phi_1(r)\nabla^2g_1(r, r')] dV = \int_{V_1} g_1(r, r')Q(r) dV + \phi_1(r'),
\]

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where \( r' \in V_1 \). If we apply Gauss' theorem to the left-hand side of Equation (43) and since \( \nabla \cdot (g \nabla \phi - \phi \nabla g) = g \nabla^2 \phi - \phi \nabla^2 g \), this volume integral becomes a surface integral over the surface bounding \( V_1 \) and reads as

\[
- \int_{S + S_{inf}} \hat{n} \cdot \left[ g_1(r, r') \nabla \phi_1(r) - \phi_1(r) \nabla g_1(r, r') \right] dS = -\phi_{inc}(r') + \phi_1(r'),
\]

where \( r' \in V_1 \) and \( \phi_{inc} \) is the field generated by the source \( Q(r) \):

\[
\phi_{inc}(r') = -\int_{V_1} g_1(r, r')Q(r)
\]  

(45)

Now, by swapping \( r \) and \( r' \) and when \( S_{inf} \to \infty \), we get

\[
\phi_1(r) = \phi_{inc}(r) - \int_S \hat{n}' \cdot \left[ g_1(r, r') \nabla' \phi_1(r') - \phi_1(r') \nabla' g_1(r, r') \right] dS', \quad r \in V_1.
\]  

(46)

Notice that when \( r' \notin V_1 \) in (43), the second term on the right-hand side becomes zero, so we have

\[
0 = \phi_{inc}(r) - \int_S \hat{n}' \cdot \left[ g_1(r, r') \nabla' \phi_1(r') - \phi_1(r') \nabla' g_1(r, r') \right] dS', \quad r \in V_2.
\]  

(47)

For region 2 the results read as

\[
\phi_2(r) = \int_S \hat{n}' \cdot \left[ g_2(r, r') \nabla' \phi_2(r') - \phi_2(r') \nabla' g_2(r, r') \right] dS', \quad r \in V_2,
\]  

(48)

\[
0 = \int_S \hat{n}' \cdot \left[ g_2(r, r') \nabla' \phi_2(r') - \phi_2(r') \nabla' g_2(r, r') \right] dS', \quad r \in V_1.
\]  

(49)

By using Equations (47) and (49) and introducing homogeneous-medium Green's functions,

\[
g(r, r') = \frac{\exp(ik|r - r'|)}{4\pi|r - r'|},
\]  

(50)
we can eliminate two of the four unknowns in these equations by using the boundary conditions:

\[
\phi_1(r) = \phi_2(r), \quad r \in S, \tag{51}
\]
\[
p_1 n \cdot \nabla \phi_1(r) = p_2 n \cdot \nabla \phi_2(r), \quad r \in S. \tag{52}
\]

**Extended-Boundary-Condition Method**

The extended-boundary-condition (EBC) method, developed by Waterman [154, 155, 124], is also known as the null-field approach. It is an alternative to solve the surface integral equation, but now imposed on some surfaces \(S_1\) and \(S_2\) away from \(S\) as shown in Figure 2, in order to simplify the solutions. The scalar integral equations are

\[
\phi_{inc}(r) = \int_S [g_1(r, r') n' \cdot \nabla \phi_1(r') - \phi_1(r') n' \cdot \nabla' g_1(r, r')] dS', \quad r \in V_2, \tag{53}
\]
\[
0 = \int_S [g_2(r, r') n' \cdot \nabla \phi_2(r') - \phi_2(r') n' \cdot \nabla' g_2(r, r')] dS', \quad r \in V_1. \tag{54}
\]

![Figure 2: Two-region](image)

where Equation (53) is valid for \(r\) anywhere in \(V_2\) bounded by \(S\) and Equation (54) for \(r\) anywhere in \(V_1\) outside \(S\). If we now assume that \(S_1\) and \(S_2\) are spherical surfaces, this will simplify the solutions of the integral equation when spherical harmonics are used in the expansion of the field. It can be shown that the Green's function in a homogeneous medium can be expanded as

\[
g(r, r') = ik \sum_n \psi_n(k, r_\geq) \Re g \psi_n(k, r_\leq), \tag{55}
\]

where \(\psi_n(k, r)\) represents an outgoing wave spherical harmonic, \(\Re g \psi_n(k, r)\) is the regular part of \(\psi_n(k, r)\) and \(r_\geq\) represents the larger of the \(r\) and \(r'\) and \(r_\leq\) is the smaller of the
\( \mathbf{r} \) and \( \mathbf{r}' \) in magnitudes. Since the incident wave is regular about the origin, it can be expanded as the regular spherical wave functions, i.e.,

\[
\phi_{\text{inc}}(\mathbf{r}) = \sum_n a_n \mathcal{R} \psi_n(k_1, \mathbf{r}).
\]  

(56)

Now we can write Equations (53-54) into the spherical harmonics as

\[
\sum_n a_n \mathcal{R} \psi_n(k_1, \mathbf{r}) = ik_1 \sum_n \mathcal{R} \psi_n(k_1, \mathbf{r}) \int_{S'} [\psi_n(k_1, \mathbf{r}') \hat{n}' \cdot \nabla' \phi_1(\mathbf{r}')] - \phi_1(\mathbf{r}') \hat{n}' \cdot \nabla' \psi_n(k_1, \mathbf{r}')] dS', \quad \mathbf{r} \in S_2,
\]

(57)

\[
0 = ik_2 \sum_n \psi_n(k_2, \mathbf{r}) \int_{S'} [\mathcal{R} \psi_n(k_2, \mathbf{r}') \hat{n}' \cdot \nabla' \phi_2(\mathbf{r}') - \phi_2(\mathbf{r}') \hat{n}' \cdot \nabla' \mathcal{R} \psi_n(k_2, \mathbf{r}')] dS', \quad \mathbf{r} \in S_1.
\]

(58)

These equations can be further simplified to

\[
a_n = ik_1 \int_{S'} [\psi_n(k_1, \mathbf{r}') \hat{n}' \cdot \nabla' \phi_1(\mathbf{r}') - \phi_1(\mathbf{r}') \hat{n}' \cdot \nabla' \psi_n(k_1, \mathbf{r}')] dS',
\]

(59)

\[
0 = ik_2 \int_{S'} [\mathcal{R} \psi_n(k_2, \mathbf{r}') \hat{n}' \cdot \nabla' \phi_2(\mathbf{r}') - \phi_2(\mathbf{r}') \hat{n}' \cdot \nabla' \mathcal{R} \psi_n(k_2, \mathbf{r}')] dS',
\]

(60)

and both valid \( \forall n \). Now these equations only depend on \( \mathbf{r}' \) and if we let

\[
\phi_2(\mathbf{r}') = \sum_m \alpha_m \mathcal{R} \psi_m(k_2, \mathbf{r}'),
\]

(61)

\[
\hat{n}' \cdot \nabla' \phi_2(\mathbf{r}') = \sum_m \alpha_m \hat{n}' \cdot \nabla' \psi_m(k_2, \mathbf{r}'),
\]

(62)

and using Equations (61-62) and (51-52) in Equation (59), (59) becomes

\[
a_n = ik_1 \sum_m \alpha_m \int_{S'} [\psi_n(k_1, \mathbf{r}') \hat{n}' \nabla' \mathcal{R} \psi_m(k_2, \mathbf{r}') \frac{P_2}{P_1} - \mathcal{R} \psi_m(k_2, \mathbf{r}') \hat{n}' \nabla' \psi_n(k_1, \mathbf{r}')] dS'.
\]

(63)

From this we can conclude that

\[
a_n = i \sum_m \alpha_m Q_{nm},
\]

(64)

where

\[
Q_{nm} = k_1 \int_{S'} [\psi_n(k_1, \mathbf{r}') \hat{n}' \nabla' \mathcal{R} \psi_m(k_2, \mathbf{r}') \frac{P_2}{P_1} - \mathcal{R} \psi_m(k_2, \mathbf{r}') \hat{n}' \nabla' \psi_n(k_1, \mathbf{r}')] dS'.
\]

(65)
Transition and Scattering Matrices

Similarly we can find for the scattered field:

$$\phi_{sca} = \sum_n f_n \psi_n(k_1, r) = - \sum_{nm} i k_1 \alpha_m \psi_n(k_1, r) \int_S |\Re g\psi_n(k_1, r')| \hat{n}' \cdot \nabla' \Re g\psi_m(k_2, r') \frac{P_2}{P_1} - \Re g\psi_m(k_2, r') \hat{n}' \nabla' \Re g\psi_n(k_1, r') |dS'. \quad (66)$$

From this, we deduce that

$$f_n = -i \sum_m \alpha_m \Re g Q_{mn}, \quad (67)$$

where $\Re g Q_{nm}$ is the regular part of the $Q_{nm}$ as defined in Equation (65). By now defining $\overline{Q}$ as a matrix with elements $Q_{mn}$, we obviously find

$$a = i \overline{Q} \cdot \alpha, \quad (68)$$
$$f = -i (\Re g \overline{Q}) \cdot \alpha, \quad (69)$$

where $a$, $f$ and $\alpha$ are vectors containing $a_n$, $f_n$ and $\alpha_n$, respectively. From these equations $\alpha$ can be eliminated and one equation is left which gives the relation between the scattered wave amplitude and the incoming wave amplitude:

$$f = \overline{T} \cdot a, \quad (70)$$

where $\overline{T}$ is defined as

$$\overline{T} = -(\Re g \overline{Q}) \cdot \overline{Q}^{-1}. \quad (71)$$

As usually, the total field can be written as $\phi = \phi_{inc} + \phi_{sca}$; if we use this together with Equations (56) and (66) we find

$$\phi = \sum_n \left[ a_n \Re g \psi_n(k_1, r) + f_n \psi_n(k_1, r) \right]$$
$$= \sum_n \left[ a_n \Re g \psi_n(k_1, r) + \left( \sum_m T_{nm} a_m \right) \psi_n(k_1, r) \right]. \quad (72)$$

Once the $T$ matrices for every isolated scatterer are found, they can be used to construct the solution of scattering by many scatterers. When more than one scatterer are present, multiple scattering exists between the scatterers. The solution to such a problem can be found recursively by using the translational addition theorem for spherical or cylindrical harmonics.
Samenvatting in het Nederlands

Laserontsteking van enkelvoudige deeltjes en deeltjeswolken

De explosiegevoeligheid van poeder-lucht mengsels wordt gekarakteriseerd door twee groot- heden, te weten de minimale ontstekingsenergie (MOE) en de minimale ontstekingstemperatuur (MOT). Zoals de termen al aangeven, is er een zekere minimale hoeveelheid energie nodig, voordat een poeder-lucht mengsel ontsteekt en er een explosie ontstaat. Eenzelfde redenering geldt voor de minimale ontstekingstemperatuur. Deze twee grootheden werden vandaag de dag bepaald met apparatuur gebouwd op basis van internationale richtlijnen. In het onderzoek, dat de basis vormt voor dit proefschrift, zijn beide grootheden onderzocht op fundamentele gronden, gebruik makend van een laser als ontstekingsbron. Bij een laser zijn zowel de hoeveelheid energie per laserpuls als de duur van de laserpuls nauwkeurig bekend.


Voor de bepaling van de minimale ontstekingstemperatuur worden ovens gebruikt en voor de bepaling van de minimale ontstekingsenergie, apparatuur met een vonksysteem als ontstekingsbron. De belangrijkste tekortkomingen van de verschillende apparaten zijn geïdentificeerd en worden besproken.

Voor de verschillende ovens is de verblijftijd van de gesuspendeerde deeltjes het grootste bezwaar. Met toenemende deeltjesgrootte, neemt de verblijftijd van de deeltjes in de oven af en dientengevolge hebben de deeltjes minder tijd om op te warmen tot hun ontstekingstemperatuur. Om de kleinere verblijftijd te compenseren kan de oven-temperatuur worden verhoogd om alsnog ontsteking te bewerkstelligen. De minimale ontstekings-temperatuur, bepaald met de ovens, is daarom afhankelijk van de deeltjes- grootte.

De energie, opgeslagen in een condensator, wordt over twee electrodens ontladen om hiermee een bekende hoeveelheid gesuspendeerd poeder te ontsteken. Indien de capaciteit
en voltage van de condensator bekend zijn, kan de minimale onstekingsenergie worden uitgerekend. De energie-efficiency van de vonkmethode wordt sterk betwijfeld, in die zin, dat slechts een fractie van de opgeslagen energie in de condensator nuttig wordt gebruikt om de deeltjes op te warmen tot hun onstekingspunt.

Met de laserontstekingstechniek wordt het principe toegepast om eerst de onstekingscharacteristieken van een enkelvoudig deeltje te bepalen. Daarna worden de onstekingscharacteristieken van een cluster van een aantal deeltjes bestudeerd, om uiteindelijk het onstekingsgedrag van een deeltjeswolk te bestuderen.

Om de laserontstekingstechniek een fundament te geven, zijn metaaldeeltjes gekozen als de aanvankelijk te ontsteken deeltjes. De metaaldeeltjes, die ontkoken zijn met een laser in dit werk, ontsteken via het heterogene mechanisme. Als zodanig is een volledige beschrijving van de gas-atmosfeer om het deeltje overbodig.

Met een zogenaamde ultrasonische levitator en een optische thermometer, is de temperatuurstijging gemeten van een enkelvoudig deeltje. De gemeten temperatuurstijging is beschreven met de energiebalans voor het deeltje. De gemeten temperatuurstijging kon nauwkeurig worden gemodelleerd. De deeltjes werden bestraald met de laser, totdat de deeltjes ontkoken. Met andere woorden, tijd was geen variabele. De gemeten minimale onstekings-temperatuur is onafhankelijk van de deeltjesgrootte. Het oppervlakte onder de temperatuur-tijd curve geeft de minimale onstekingsenergie van dat deeltje. Door de aldus gevonden minimale onstekingsenergie te delen door het deeltjesvolume gaf wederom een deeltjesgrootte onafhankelijk verband. Belangrijker, de twee explosiegevoeligheidsparameters, tot op heden onafhankelijk van elkaar bepaald (oven en vonk), zijn direct aan elkaar gerelateerd. Dit is een direct gevolg van de energiebalans over het deeltje.

De verkregen resultaten van de enkelvoudige deeltjesexperimenten kunnen worden vertaald naar een wolk deeltjes van hetzelfde materiaal. De hypothese is dat de minimale onstekingsstemperatuur van een deeltjeswolk gelijk is aan de minimale onstekingsstemperatuur van het overeenkomstige enkelvoudige deeltje. De minimale onstekingsenergie kan worden berekend wanneer het aantal deeltjes, nodig om het kritische onstekingsvolume te bewerkstelligen, bekend is. Vermenigvuldiging van de met deeltjesvolume genormaliseerde onstekingsenergie van de enkelvoudige deeltjes met de som van volumina van de deeltjes uit het kritische onstekingsvolume, resulteert in de minimale onstekingsenergie van de deeltjeswolk. In praktijk zal de als zodanig bepaalde minimale onstekingsenergie van de deeltjeswolk lager zijn, ten gevolge van het collectieve effect van de, door de laser opgewarmde deeltjes. Dit collectieve effect kan worden gekwantificeerd door de electromagnetische vergelijkingen voor de absorptie van laserlicht door de deeltjes, te koppelen met de energiebalansen over de enkelvoudige deeltjes in de wolk.

De T-matrix methode is de meest attractieve methode om de electromagnetische vergelijkingen voor de absorptie van laserlicht door meerdere deeltjes te modeleren. Het gegeven T-matrix model is gevalideerd met literatuurdata voor het verstrooien van laserlicht. Het model is vervolgens uitgebreid met meerdere deeltjes.

John Zevenbergen
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In my opinion, for a researcher, a university has two important assets: the students and the non-academic personnel. Without these people science is no longer worthwhile. I therefore start this acknowledgement by thanking all the students, who, somewhere in time, were part of the Explosion Group of the Delft University of Technology. First my graduate students.

Michaël Kortekaas. After finishing your "scriptie" (literature survey) on the Mie theory, you embarked on a project that was not at all related to chemistry, but had to do with electromagnetism. Parts of your scriptie and thesis you will find in Chapter 5. Despite the complexity of the project, you did a wonderful job that resulted in for me probably the most satisfying chapter of my thesis.

Joep Beukers. Your project was not related to laser ignition. You chose to do a project with a company on mineral flame retardants. The project was practical in nature. It opened my eyes that fundamental research is nice, but without an application, for me such research is less interesting. Without you knowing, you triggered me to do more contracting research after your project in those fields where fundamental and practical research coincide.

Bas de Ruiter. You started with me with a scriptie on brush discharges and decided that igniting metal particles with a laser was rather cool. You explored the limits of the technique and generated a lot of data, forming the basis for two conference articles, one article published in a book and an award winning poster (sorry, but I collected the prize). You will find your results in Chapter 6.

Marco Hoogendijk. After finishing your scriptie on levitation techniques, you spent several months in the USA, working in the group of Professor Apfel at Yale University. You were allowed to reproduce (people at Yale still talk about they way you used machining tools!) the two-dimensional levitator that Professor Apfel had developed for NASA. Your work resulted in very intriguing results, which you will find in Chapter 6. The full description of the levitator is mentioned in Chapter 4. Thank you for the hard work and the machining skills. Your two-dimensional levitator is still in our laboratory.

Björn Rommen. The only non-chemical engineer in this list of graduate students. Coming from the faculty of Electrical Engineering, Section of Electromagnetism, you started at the point where Michaël Kortekaas stopped. You spent several months, just like your housemate Marco Hoogendijk, in the USA. You went to the group of Professor Chew at the University of Illinois at Urbana-Champaign. You had the possibility of working with some of the greatest professors in the field of electromagnetism during your
project. The results of this brilliant "journey" you will find as Chapter 5 in my thesis.

Christiaan Poelma. The only graduate student of the Explosion Group that decided to do a PhD, albeit in a different field. You first wrote a scriptie on optical levitation techniques. For your thesis you worked on the determination of turbulent flow fields inside the standard 20 liter sphere and the Hartmann tube, results of which were and are used for a European Union project. Your results are actually included in a commercial CFD code for predicting explosion severity in chemical plants and on offshore rigs. Great piece of work. By the way, once we made a bet, and the prize was a stack of AKP’tjes. I believe you lost this bet, so ......

Sander van den Ban. Thus far my only graduate student to graduate cum laude. I believe that that says it all. Most professors in the building tried to persuade you to join their group, but they lost this battle. Giving you the simple freedom of allowing you to play with fire and explosives in the broadest sense possible, did the trick for me. I will remember the AKP’tjes and I believe you still owe me a few. Despite the fact that I was born and raised in Amsterdam and familiar with quite some "non-standard" words, you were able to extend that specific part of my vocabulary. You did a scriptie with us, and a research practicum, before starting your graduation work. You extended the work of Christian Poelma, using higher pressures in the 20 liter sphere. As well as Christian’s work, your results are implemented in the same CFD code.

Gijsbert-Jan Portheine. Having two supervisors, myself and Andrzej, you also did both your research practicum and graduation work with the Explosion Group. Your thesis dealt with an assignment from industry, that enabled the company in question to improve the efficiency of their process. To a large extent our characters are similar. With this information you will know what I mean when I say, "just write that letter".

Ferry Liem. The person with the most durable link with Explosion Group as of this moment. You did the entire trajectory with the Explosion Group: scriptie, research practicum and graduation. But it did not stop there: you also became a member of the Explosion Group. This time not as a student, but as an employee. With your graduation work, you extended the project of Bas de Ruiter. You found the limits of the equipment. You will find parts of your scriptie and graduation work in Chapters 2, 6 and 7. Moreover, most of the drawings in Chapters 2 to 6 were made by you. Thank you very much for all your efforts. You are a valuable asset for the Explosion Group and for any company/institute/university you might work for in the future.

Walter Oudshoorn. Your arrival in the Group in the year 2000 meant a radical change of my interest within the Explosion Group. You had arranged a project on rocket propulsion with TNO, and you were looking for a supervising professor and a daily supervisor. My promoter, Professor Scarlett, was willing to supervise you, under the condition that you were able to persuade me to assist you on a daily basis. I recall that you did not need to make that much of an effort to do so. Thank you for that. Your project was complex, but rewarding, as you took a new generation of solid propellants one step closer to commercialization. TNO is still doing testing work on the basis of your recommendations.

Raoul Zweevel. After teaming up with Rene Rozendal, writing a scriptie about the synthesis of an energetic material, you made a conceptual plant design for this energetic
material. This plant is actually envisioned to be constructed in the near future. Your project had it all: pure chemistry, developing synthesis routes, brain storming about possible derivatives, and "constructing" the plant in the computer. This all for a product that will be produced on a large scale one day. You did a fantastic job.

**Rutger Wilts.** After performing an actual accident investigation for your research practicum, together with your housemate Hans van de Rijt, you returned to the Explosion Group sometime later, to do your graduation work. You decided to work on the synthesis of trinitromethane, an ingredient for a new generation of solid propellants. The actual synthesis was easy, but the analysis of the liquid and gas phase proved to be less easy. "Giving up" was not found in your vocabulary and you produced a thesis that will serve as basic reading material for anyone who wants to synthesize and analyse trinitromethane in the years to come. The ultimate goal of the research on trinitromethane is to come to a full scale industrial plant. Your work can be considered to be part of the foundation of this (these) plant(s).

**Hans van de Rijt.** You also did the entire trajectory with the Explosion Group: scriptie, research practicum (with Rutger Wilts) and graduation work. At the moment of this writing, you have three more months to go before your graduation. Just like Walter Oudshoorn, you look at improving a solid propellant, albeit via another route compared to Walter. The prospects of improving the solid propellant are good. Time will tell.

**Barbara Slettenhaar.** After you finished your scriptie on a subject related to solid propellants, you decided to return to the Explosion Group for your graduation project. A few more months and you are finished with your project on a new generation of mono-propellants. It is a pleasure of having you in the Group.

My scriptie students:

**Rutger Jakobsen.** Parts of your scriptie on the complex index of refraction you will find in Chapter 3.

**Moussa Aberkani.** Your scriptie on the production of ethylene oxide is used for a large project on the explosion safety of ethylene oxide decomposition, involving several companies.

**Jan van Leeuwen.** Acoustic ignition was your topic. Currently a PhD student is working on this subject.

**Micha Sprengers.** Valuable information on heterogeneous ignition I implemented in Chapter 2.

**Irene Sustantio.** Pyrophoric behaviour of substances is a well known phenomenon, but nobody investigated this elaborately. That is the main conclusion from your work. Moreover, your scriptie enabled me to come to the hypothesis that this phenomenon is all about a careful choice of the temperature reference point as you can read in Chapter 6.

**Ulven Aurich.** International standards on the determination of the minimum ignition temperature was the title of your scriptie. The results of this work you will find in Chapter 2.

**Geert-Jan ten Holder.** You wrote a scriptie on the topic "can flammable dust atmospheres be ignited by broken optical fibres?" The answer to this question as of now
ACKNOWLEDGEMENTS

is a firm no. At the moment of this writing, you are working on your graduation project with Andrzej in the field of high temperature/high pressure explosions. Almost there, Pepijn.

**Rene Rozendaal.** You did your scriptie together with Raul Zweeveld. You had to find, according to some people, impossible information: the synthesis route of a certain energetic material. I believe the two of you together found three binders full of literature on this compound. Even better, for your research practicum you actually synthesized the material. I think you are able to finish the following sentences. Concerning the scriptie: "If I am not part of the greatest........" and for your practicum: "Mixing three energetic solids will result in ....""

**Vincent Lukkien.** Your scriptie on the theoretical calculation of the heats of formation of energetic materials was a real good piece of work. We have decided to make three conference articles out it and one, or maybe two, journal articles. After that, you teamed up with Robert Meijer for your research practicum.

**Robert Meijer.** Safety is important, certainly with energetic materials, but even more with cumbersome side products of energetic materials. Your scriptie was on one of these side products. Currently investigations have started to come to some kind of sensor for the side product you studied. You gathered very useful information. Your research practicum, with Vincent Lukkien, took a certain part of Raul Zweeveld’s work one step further. Thank you for that.

**Coen Schuurbers.** Together with Marnix Teuling you wrote a heavy scriptie (and I will not explain the weight of the scriptie here) on the synthesis of several oxidising agents for solid propellants and perhaps for monopropellants.

**Marnix Teuling.** After finishing your scriptie with Coen Schuurbers, you teamed up with him again for the research practicum to actually synthesize some of the compounds you had found while writing your scriptie. Very interesting reaction conditions!

**Igor van der Hel.** Ways of purifying huge gaseous flows, that are only present for a few seconds, was the topic for your scriptie. You tackled this project in a structured manner. Well done.

**Michiel Regenbogen.** It was hard for you to let go of your scriptie on monopropellants. You had to finish it in six weeks, but you devoted considerably more time and it clearly shows. The end result is basic reading material for the next few graduate students who will work on monopropellants. Job well done!!

**Annelieke de Winter.** The conclusions of your scriptie on gas generators yielded very valuable information, to be used in future upgrades of these generators. You produced a magnificent piece of work.

**Lillian Chang.** Synthesis and physical properties of yet another energetic material was the topic for your scriptie. Again, basic reading material for the next few graduate students. Eventually a chemical plant needs to be built for this material. Your scriptie forms the starting point of that plant.

**Simone Wiers.** Looking at ways to improve the performance of monopropellants formed the basis for your scriptie. For your research practicum you used your own recommendations of your scriptie, to experimentally confirm the possible improvements. You
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All the other students who were part of the Explosion Group: Wouter de Heij, Macco Spaans, Cristhian Almeida Rivera, Edgar Nettl, Serge Smallegange, Marco Blokland, Erkan Terli, Tom Kers, Anton Vleeshouwers, Ashkan Taheri, Luis Ibanez, Marta Velez, Koen van der Nat, Joost van der Weijst, and Mark Pursell.

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The staff members of the Particle Group of Delft University of Technology. Thank you Professor Scarlett for giving me this opportunity. Once Andrzej and myself started to do some contracting research, you gave us the freedom to do so. However, at one stage, at least in my perception, you probably felt that you had given us too much freedom, since both Andrzej and myself diverted significantly from the tasks you had hired us for. I remember the discussions I had with you, when, every now and then, you came over from Florida for a couple of weeks. You sat down with me and always started the conversation with the same words: "John, I am worried about your thesis...". However, I kept my word by finishing the draft of the thesis before the end of 2001. I want to thank you for actually giving me that luxury of freedom and allowing me to embark in those numerous fields that fit my character and expertise. It resulted in, amongst others, the Center of Expertise and a very lively collaboration with scientists in the field of Rocket Propulsion.

Professor Pasman. After being instrumental in the development of the strengthened 20 liter sphere, you became professor of Chemical Risk Assessment. You have given me the freedom, just like Professor Scarlett, to get some things of the ground, most notably the Center of Expertise. You were again instrumental during the negotiations. Thank you very much for that.

Professor Schmidt-Ott. Being the successor of Professor Scarlett, you will keep the tradition of Particle Technology at the Delft University of Technology alive. Your main focus will be on nanoparticles and there are plenty of links between explosions and rocket propulsion on the one hand and nanoparticles on the other. We need to start working on
getting some (PhD) projects of the ground with the Center.

Saul Lemkowitz. You were the person who got me involved in this explosion world in the first place. You were also there at the very last moment, thoroughly going through my thesis. After graduating, I stated that I would never return to the University. Three months later I was making explosions and burning cornstarch in a powder burner under our guidance. The Explosion Group got established and things went fast, maybe too fast. However, without that acceleration in the late nineties, we would not have been where we are today, doing the things that we do right now. On the other hand I also feel that we have to sit down one day and discuss that acceleration and all the consequences it had for all of us. Currently, you have taken the responsibility for a huge project of the Center, explosion safety in tunnels. Let’s do this!!

Henk Merkus. Within the Particle Technology Group you were responsible for one of my favorite topics: money! Without money, no science. We had numerous discussions on this topic and especially on how to get more money from industry and government. Thank you for sharing your experience with me in this field. Thank you for all your help during my presence in the group and for carefully reading the draft version of my thesis.

Jan Marijnissen. Whenever I needed help in some way or another you were there. I am grateful to you for this.

The other staff members of the Particle Technology Group: Stefan Luding, Henk Nugteren, and Gabrie Meesters.

One day you, dear Andrzej Pekalski, walked in, coming from the University of Wrocław, Poland. Officially for a period of six months. At this moment you are getting close to six years (try six decades for a change!!). Time flies when you are having fun (not to mention safety reports)! You extensively helped me in the beginning of my PhD project to establish the laser ignition facility. We traveled throughout the Netherlands to prove the fact that the carbon dioxide laser was the most appropriate laser to use for the purpose of laser ignition. I also was glad to have somebody around me who had better eyes than I, otherwise I would have never been able to focus the laser beams on those small particles in the ultrasonic levitator. More importantly, however, we established the Explosion Group as we know it today. We were also engaged in numerous contract research projects, with all the ups and downs you can imagine. In the end, these projects formed the foundation for your current PhD project on high temperature/high pressure explosions. A really perfect project: combining fundamental research with real application, directly applicable in industry. Just like me, you also diverted slightly from your PhD work. However, I firmly believe that without these "distractions" we would not have been where we are today. Aside from work, we were engaged in numerous, let’s call it, private projects. We are more than colleagues. We have different characters, but the team spirit will always be there. As mentioned previously, the Explosion Group accelerated in the late nineties. At this moment the acceleration rate is even higher, with the Center established, the enormous EU project being granted on high temperature/high pressure gas phase explosions of which you are the coordinator, and my interest in rocket propulsion. It should not go any faster than this.
Dear Elzbieta "Ela" Pekalska, if I have to express myself in one sentence, I just would like to say, thank you very much for being such a wonderful woman.

The members of the Center of Expertise: Bart vd Graaf, I hope you will have a great time as a PhD student with us. Arne Dijksman, Maarten de Jong, and August Roelofsen.

The current and former members of the Particle Technology Group: Ramanan Pitchumani, Flip Wauters, Evelien Nijman, Damien Camelot, Arjan van Wuyckhuyse, Richard Janssen, Zhenhua Ma, Daan Verkoeijen, Kees Geerse, Sjoerd Verdoold, Michael Stowers, Tommy Ciach, Olaf Klevit, Erik Goonmeren, Ilse Tuinman, Michiel van Drunen, Marcel van de Kraan, Rob Hartmann, Martin Weiss, Wim Oostra, Machida, Alexander Willemse, and Jan de Smet. A special thank you in this respect to Peter van der Wel, Frank Kuhn and Silvia Leschonski.

Professor Braithwaite. Dear Martin, thank you very much for all the help and support the last couple of years.

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Professor Apfel, Yale University, USA. Thank you for your kindness and support that enabled Marco Hoogendijk to reproduce the two-dimensional levitator.

Sergei Koponenko. The three-dimensional was and still is an enormous challenge, especially from a practical point of view. Who knows, one day .....

Sabine Schenk. The only person in this world engaged in the field of laser ignition of flammable atmospheres. Thank you for all the discussions we had on this topic.

Kees Braun. Thank you for all your help with the Optical Fiber Thermometer.

Edward Maloney. To say it in your words: “one day it is going to happen”. All the best with Everest Coatings.

The Explosion Safety group of TNO Prins Maurits Laboratory: Jaap Weerheijm, Rolf van Wees, Piet Timmers, Peter de Bruin, Peter van Ierschot, Bert vd Berg, Louk Absil, Arjan Klein, Matthijs de Maaijer, Ronald Kersten, Marco Broere, Conny Huijsmans, and Albert vd Steen.

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Finally, my parents for being there whenever I needed you. Thank you very much.

So many have been there before, during and throughout my presence at the faculty, if I have neglected to mention you, please blame it on my head and not my heart.
Curriculum Vitae

John Zevenbergen is geboren op 12 November 1970 te Amsterdam.

1983-1989 VWO, Augustinus College Amsterdam
1995-1996 Research Fellow (Toegevoegd Onderzoeker), Delft University of Technology, Faculty of Applied Sciences, Section of Particle Technology, Research Field: Explosion Science.
1996-2001 PhD research, Delft University of Technology, Faculty of Applied Sciences, Section of Particle Technology, Subject: Laser ignition of single particles and particle clouds. Promoters: Prof. dr B. Scarlett MSc and Prof. dr ir H.J. Pasman. Co-promotor: Dr ir S.M. Lemkowitz
1997- Group Leader of the Explosion Group of the Delft University of Technology.
2000- Co-founder and Scientific Director of the Center of Expertise "Reactive Gasdynamics and Explosion Safety”. Center established between the Delft University of Technology and TNO Defense Laboratory.