Doctoral Thesis

Transient radiative heat transfer in chemically reacting media

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TRANSIENT RADIATIVE HEAT TRANSFER
IN CHEMICALLY REACTING MEDIA

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of
DOCTOR OF TECHNICAL SCIENCES

presented by
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Prof. Dr Konstantinos Boulouchos, co-examiner

2004
To my parents
Preface

This work is focused on the transient analysis of radiative heat transfer in participating media undergoing thermochemical transformation and on the methodology for this type of problem for the purpose of obtaining a better understanding of the time-dependent phenomena taking place in solar thermochemical reactors. No attempt has been made to cover exhaustively the vast amount of issues arising from considerations on the transient character of chemical systems with thermal radiation as the dominant heat transfer mode, and to consider all available methods for modelling such systems. The methods used in this work were chosen due to their universal applicability to complex problems at a relatively low implementation cost. This especially applies to the Monte Carlo method, which is used in the simulations throughout this study.

The major motivation behind this work is to learn to model reactors used in solar thermochemical applications. Solar thermochemistry is one of the viable routes to sustainable energy supply which can significantly reduce the dependence on fossil fuels and environmental pollution by gathering the abundant but diluted and intermittent solar energy, and converting it into storable chemical energy. A number of scientists and engineers from around the world do research in this field because they realise the fact that using only 0.1% of the earth's land space for collecting sunlight with collection efficiency of merely 20%, one could gather more than enough energy to supply the current energy needs of all the citizens of the planet.

I would like to take the opportunity to thank all the people and institutions who have made this work possible and helped me in any way. The work was carried out at the Laboratory for High Temperature Solar Technology at Paul Scherrer Institute, and at the Professorship in Renewable Energy Carriers at ETH Zurich.

I am particularly indebted to Prof. Aldo Steinfeld, who supervised my doctoral studies and the preceding exchange fellowship at ETH Zurich. His strong enthusiasm and support in every part of this work helped me so much to accomplish my dissertation and achieve my educational goals during the last four years.

I thank Prof. Konstantinos Boulouchos for taking over my final examination as a co-examiner.

Special thanks go to Prof. Robert Palumbo for the numerous discussions on various problems I was working on, and for his comments helping me greatly in improving this thesis.

I would like to thank Dr Anton Meier, Daniel Wuillemin, and Enrico Bonaldi, with whom I was working on the solar production of lime, for their kind co-operation,
and Dr Christian Wieckert, Max Brack, Peter Häberling and Ulrich Frommherz for their assistance during the experimental campaign in the solar furnace.

I am grateful to Daniel Wuillemin, Philipp Haueter, Max Brack, Peter von Zedtwitz, and Dr David Hirsch for their help during the preparation and conduction of the experiments at the sun simulator.

I am deeply indebted to Dr Valeri Markushin, who taught me the basics of scientific computing, and who helped me to build the computational facility and to solve a lot of problems of computational nature.

I thank Dr Stefan Kräupl, Dr Michael Keunecke, Dr David Hirsch, doctoral students Jörg Petrasch, Reto Müller, Andreas Z’Graggen, Peter von Zedtwitz, Thomas Osinga and Dominic Trommer for discussions of the experimental and theoretical work and for their co-operation on organising the series of meetings devoted to modelling.

I thank Prof. Stanisław Pisarczyk, Dr Andrzej Szamowski, Prof. Roman Domański, and Prof. Antoni Adamczyk for their encouragement from the beginning of my research as an undergraduate student, which has had an enormous influence on my later educational choices.

The effort of many people around the world who created and made available \TeX, \LaTeX, Vim, Gnuplot, Ghostscript, XFig, MPICH, GNU/Linux operating system, and other smart software, is greatly appreciated.

I thank my nearest friends for the numerous and lively conversations, for encouraging me in my activities, and for accompanying me in challenging moments.

My family has been always giving me hope and courage for things I do, and supporting me in my career choice. I thank my parents, Grażyna and Henryk, and my sister Basia.

Villigen, August 2004

Wojciech Lipiński
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Abstract

Unsteady radiative heat transfer problems involving time-dependent directional and spectral radiative properties, anisotropic scattering and irregular geometries are typical for high temperature heterogeneous reacting systems. Only a transient model of a reacting system may give enough insight into the process and its complexity, so that correct prediction of the conditions under which a chemical reaction is conducted is possible in order to optimally match the rate of the reaction to the rate of the radiative heat transfer. There is no example of previous modelling work applied to solar thermochemistry that incorporates transient analysis of a directly-irradiated reacting medium in which the influence of the reaction progress on the time variation of the radiative properties is taken into account.

In this work, two methodologies are proposed to treat the unsteady radiative heat transfer. The first one makes use of the Rosseland diffusion approximation and, therefore, is limited to optically thick participating media. In the second methodology, the Monte Carlo method is employed to obtain the distribution of the radiative source. A low-pass smoothing filter and parallel computational techniques are proposed to improve the Monte Carlo accuracy and to shorten the computational time. Both methodologies are based on the finite volume method for space discretisation of the mass and energy equations, and on the time integration schemes for time discretisation. Combination of the Monte Carlo method with time integration schemes preserves the robustness and relatively easy implementation of the method, demonstrated extensively for steady-state conditions in numerous works. As long as such a procedure is followed, a solution to unsteady radiative heat transfer problems involving the mutual coupling between temperature, composition, material properties and rate of chemical reaction within non-gray, non-uniform, and anisotropically scattering media with arbitrary values of the optical thickness and scattering albedo may be found.

A transient analysis of reacting media is carried out in order to demonstrate the applicability of the selected methods and to show the importance of transient effects for practical applications. A three-dimensional model that links thermal radiation, conduction and natural convection heat transfer to the chemical reaction is applied for a packed bed of calcium carbonate particles undergoing thermal decomposition under direct irradiation. The model uses the Monte Carlo ray tracing technique for determining the radiative flux at boundaries and the Rosseland diffusion approximation for obtaining the internal radiative flux. This model enables one to treat a non-isothermal non-grey chemical system involving optically thick media with a
time dependent chemical composition. The computed temperature field and overall reaction extent are in good agreement with the experimentally measured values.

Another group of models concerns one-dimensional suspensions of particles undergoing chemical reaction. A model of a suspension of small reacting particles having radiative properties predicted from Mie theory and undergoing a decomposition reaction is formulated for non-shrinking and shrinking particles. The comparison of the two cases shows that radiation absorption is superior in the non-shrinking particle case resulting in higher attained temperatures and a faster reaction rate. In the shrinking particle case, radiative properties vary strongly with time as the reaction progresses due to their strong dependence on the particle size parameter. The comparison shows the necessity of taking the effect of time-dependent particle size into consideration in order to avoid an over-prediction of the reaction conversion.

Simulation of a suspension of Mie-scattering coal particles undergoing shrinking due to the gasification reaction showed that radiation in the visible and near infrared spectrum incident on the particles greater than 2.5 \( \mu \text{m} \) is more likely to be forward scattered than absorbed, but the opposite is true as the particles shrink below 1.3 \( \mu \text{m} \). As in the previous problem, particle shrinking resulted in temperature decrease. In contrast, increasing temperature with time was observed for a suspension of large coal particles, whose radiative properties were predicted from the geometric optics. Shrinking of the particles resulted in this case in a faster decrease of heat consumption by the chemical reaction than of heat absorption due to decreasing absorption coefficient.

The models presented can be applied for solving transient radiative heat transfer problems involving high-temperature solid-gas thermochemical reactions with changing radiative properties due to changing composition, particle size, and temperature dependence as is typical for combustion, decomposition, cracking, and gasification processes. If the transient effects are accounted for, the temperatures, reaction rates, and residence time requirements for a particular solar thermochemical system are predicted more precisely, and therefore, the assessment of the expected performance of a chemical reactor is more accurate than by considering only the steady-state conditions.
Zusammenfassung


Eine zeitabhängige Analyse von reagierenden Medien wird durchgeführt, um die Anwendung der gewählten Methoden zu veranschaulichen und die Bedeutung der instationären Effekte für praktische Anwendungen zu zeigen. Ein dreidimensionales Modell, das die Wärmestrahlung, die Wärmeleitung und die freie Konvektion an die chemische Reaktion koppelt, wird für ein direkt bestrahltes Festbett mit thermisch zersetzten Kalziumkarbonat-Partikeln angewendet. Die Monte Carlo Methode wird für die Bestimmung des Strahlungsflusses an den Rändern benutzt und die Rosseland Diffusionsapproximation für die Berechnung des internen Strahlungsflus-
Zusammenfassung


Eine andere Gruppe von Modellen betrifft eindimensionale Suspensionen von reagierenden Partikeln. Ein Modell einer Suspension kleiner reagierender Partikel, deren Strahlungseigenschaften durch die Mie-Theorie bestimmt und die einer Zersetzungreaktion unterzogen werden, wird für nicht-schrumpfende und schrumpfende Partikel formuliert. Der Vergleich der zwei Fälle zeigt, dass die Absorption der Strahlungswärme im Fall der nicht-schrumpfenden Partikel höher liegt, was zu höheren Temperaturen und einer schnelleren Reaktion führt. Im Fall der schrumpfenden Partikel variieren die Strahlungseigenschaften stark mit fortschreitender Reaktionszeit als Folge ihrer starken Abhängigkeit von der Partikelgrösse. Der Vergleich beweist die Notwendigkeit, zeitabhängige Partikelgrössen zu berücksichtigen, um eine Überschätzung der chemischen Umwandlungsrate zu vermeiden.

Die Simulation einer Suspension Mie-streuerender Kohlepartikel, die als Folge der Vergasungsreaktion schrumpfen, zeigt, dass die auf Partikel grösser als 2.5 µm einfallende Strahlung im sichtbaren und nahen Infrarot-Bereich eher vorwärts gestreut als absorbiert wird. Das Gegenteil gilt für Partikel, die kleiner als 1.3 µm sind. Ähnlich wie im vorangegangenen Problem führt das Schrumpfen von Partikeln zu einer Temperaturabnahme. Im Gegensatz dazu wird eine mit der Zeit ansteigende Temperatur für die Suspension grosser Kohlepartikel beobachtet, deren Strahlungseigenschaften durch die geometrische Optik bestimmt sind. In diesem Fall bewirkt das Schrumpfen der Partikel, dass der Wärmeverbrauch durch die chemische Reaktion schneller abnimmt als die durch den abnehmenden Absorptionskoeffizienten verursachte Wärmeeabsorption.

Die beschriebenen Modelle können zur Lösung zeitabhängiger Probleme der Strahlungswärmeübertragung in Hochtemperaturprozessen mit Gas-Feststoff-Gemischen angewendet werden, bei denen sich die Strahlungseigenschaften auf Grund der variierenden Zusammensetzung, Partikelgrösse und Temperaturabhängigkeit ändern, was typischerweise bei Verbrennungs-, Zersetzung-, Cracking- und Vergasungsprozessen der Fall ist. Wenn der Einfluss der instationären Phänomene berücksichtigt wird, können die Temperaturen, die Reaktionsraten und die Verweilzeitbedingungen eines bestimmten solaren thermochemischen Systems exakter vorhergesagt und somit die erwartete Leistung eines chemischen Reaktors genauer abgeschätzt werden als wenn nur die stationären Bedingungen in Betracht gezogen werden.
Symbols

\( a \)  
mass specific active surface area, \( m^2 \text{kg}^{-1} \)

\( A \) 
active surface area, \( m^2 \)

\( A \)  
area, \( m^2 \)

\( c \)  
specific heat, \( J \text{kg}^{-1} \text{K}^{-1} \)

\( c_0 \)  
speed of light in vacuum, \( c_0 = 2.99792458 \times 10^8 \text{m s}^{-1} \)

\( C \)  
cross section for radiation attenuation, \( m^2 \)

\( C \)  
molar specific heat, \( J \text{mol}^{-1} \text{K}^{-1} \)

\( C_1 \)  
constant in Planck’s spectral energy distribution,  
\( C_1 = 0.59552137 \times 10^{-16} \text{W m}^2 \)

\( C_2 \)  
constant in Planck’s spectral energy distribution,  
\( C_2 = 0.014387752 \text{m K} \)

\( d \)  
diameter, \( m \)

\( E_a \)  
activation energy; apparent activation energy, \( J \text{mol}^{-1} \)

\( E \) 
electric field vector

\( E_n \)  
exponential integral function

\( E_{\lambda} \)  
spectral emissive power, \( W \text{m}^{-2} \text{m}^{-1} \)

\( f \)  
force vector

\( f_v \)  
particle volume fraction, –

\( G_{\lambda} \)  
spectral direction-integrated intensity, \( W \text{m}^{-2} \text{m}^{-1} \)

\( h \)  
heat transfer coefficient, \( W \text{m}^{-2} \text{K}^{-1} \)

\( h \)  
molar specific enthalpy, \( J \text{mol}^{-1} \)

\( h \)  
Planck’s constant, \( h = 6.62606876 \times 10^{-34} \text{Js} \)

\( H \)  
enthalpy, \( J \)

\( H \)  
height, \( m \)

\( \mathbf{H} \)  
magnetic field vector

\( H'_{\lambda} \)  
spectral directional irradiation onto a surface, \( W \text{m}^{-2} \text{m}^{-1} \text{sr}^{-1} \)

\( I_{\lambda} \)  
spectral intensity of radiation, \( W \text{m}^{-2} \text{m}^{-1} \text{sr}^{-1} \)

\( k \)  
Boltzmann’s constant, \( k = 1.3806503 \times 10^{-23} \text{JK}^{-1} \)

\( k \)  
imaginary part of the complex refractive index, –

\( k \)  
reaction rate constant, \( s^{-1} \)

\( k \)  
Rosseland coefficient, \( W \text{m}^{-1} \text{K}^{-1} \)

\( k \)  
thermal conductivity, \( W \text{m}^{-1} \text{K}^{-1} \)

\( \hat{k} \)  
unit vector in \( z \) direction

\( k_0 \)  
frequency factor, \( s^{-1} \)

\( K \)  
complex reaction rate constant, \( \text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1} \), \( \text{Pa}^{-1} \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_0 )</td>
<td>complex frequency factor, ( \text{mol m}^{-2}\text{s}^{-1}\text{Pa}^{-1}, \text{Pa}^{-1} )</td>
</tr>
<tr>
<td>( l_m )</td>
<td>mean free path to attenuation, m</td>
</tr>
<tr>
<td>( L )</td>
<td>characteristic length, m</td>
</tr>
<tr>
<td>( L )</td>
<td>layer thickness, m</td>
</tr>
<tr>
<td>( m )</td>
<td>complex refractive index, -</td>
</tr>
<tr>
<td>( m )</td>
<td>mass, kg</td>
</tr>
<tr>
<td>( M )</td>
<td>molar mass, ( \text{kg mol}^{-1} )</td>
</tr>
<tr>
<td>( n )</td>
<td>molar amount, mol</td>
</tr>
<tr>
<td>( \dot{n} )</td>
<td>molar flow rate, ( \text{mol s}^{-1} )</td>
</tr>
<tr>
<td>( n )</td>
<td>real part of the complex refractive index, -</td>
</tr>
<tr>
<td>( N_p )</td>
<td>number of particles per unit volume, ( \text{m}^{-3} )</td>
</tr>
<tr>
<td>( n_{\text{rays}} )</td>
<td>number of rays in the sample for each Monte Carlo run, -</td>
</tr>
<tr>
<td>( p )</td>
<td>porosity, -</td>
</tr>
<tr>
<td>( p )</td>
<td>pressure, Pa</td>
</tr>
<tr>
<td>( P )</td>
<td>perimeter, m</td>
</tr>
<tr>
<td>( q )</td>
<td>heat rate, W</td>
</tr>
<tr>
<td>( q^\prime )</td>
<td>heat flux, ( \text{W m}^{-2} )</td>
</tr>
<tr>
<td>( q^\prime\prime )</td>
<td>heat rate per unit volume, ( \text{W m}^{-3} )</td>
</tr>
<tr>
<td>( Q )</td>
<td>efficiency factor, -</td>
</tr>
<tr>
<td>( r )</td>
<td>reaction rate, ( \text{mol s}^{-1} ); reaction rate per unit mass, ( \text{mol kg}^{-1}\text{s}^{-1} )</td>
</tr>
<tr>
<td>( r^\prime )</td>
<td>reaction rate per unit active surface area, ( \text{mol m}^{-2}\text{s}^{-1} )</td>
</tr>
<tr>
<td>( R )</td>
<td>overall layer reflectance, -</td>
</tr>
<tr>
<td>( R )</td>
<td>radius, m</td>
</tr>
<tr>
<td>( R )</td>
<td>random number, -</td>
</tr>
<tr>
<td>( R )</td>
<td>universal gas constant, ( R = 8.31441 \text{ J mol}^{-1}\text{K}^{-1} )</td>
</tr>
<tr>
<td>( \Re )</td>
<td>real part of a complex number</td>
</tr>
<tr>
<td>( s )</td>
<td>geometric cross section, ( \text{m}^2 )</td>
</tr>
<tr>
<td>( S )</td>
<td>elements of the amplitude scattering matrix</td>
</tr>
<tr>
<td>( S )</td>
<td>Poynting vector</td>
</tr>
<tr>
<td>( S_x )</td>
<td>radiative source function, ( \text{W m}^{-2}\text{sr}^{-1} )</td>
</tr>
<tr>
<td>( t_{\nu,p%} )</td>
<td>( P%-\text{quantile from the Student } t\text{-distribution for } \nu \text{ degrees of freedom} )</td>
</tr>
<tr>
<td>( t )</td>
<td>time, s</td>
</tr>
<tr>
<td>( t_{\nu,p%} )</td>
<td>overall transmittance, -</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature, K</td>
</tr>
<tr>
<td>( u )</td>
<td>specific internal energy, ( \text{J kg}^{-1} )</td>
</tr>
<tr>
<td>( U )</td>
<td>internal energy per unit volume, ( \text{J m}^{-3} )</td>
</tr>
<tr>
<td>( U )</td>
<td>total energy per unit mass, ( \text{J kg}^{-1} )</td>
</tr>
<tr>
<td>( x, y, z )</td>
<td>Cartesian co-ordinates, m</td>
</tr>
<tr>
<td>( x, y )</td>
<td>elemental molar ratios of H/C and O/C in coal, -</td>
</tr>
<tr>
<td>( x )</td>
<td>particle size parameter, -</td>
</tr>
<tr>
<td>( X )</td>
<td>extent of chemical reaction, -</td>
</tr>
</tbody>
</table>
### Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>absorptivity, ( - )</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>thermal diffusivity, ( m^2 s^{-1} )</td>
</tr>
<tr>
<td>( \beta )</td>
<td>extinction coefficient, ( m^{-1} )</td>
</tr>
<tr>
<td>( \beta )</td>
<td>volumetric thermal expansion coefficient, ( K^{-1} )</td>
</tr>
<tr>
<td>( \Delta H_T^\circ )</td>
<td>standard reaction enthalpy at temperature ( T ), ( J , mol^{-1} )</td>
</tr>
<tr>
<td>( \Delta t )</td>
<td>time step interval, ( s )</td>
</tr>
<tr>
<td>( \Delta x, \Delta y, \Delta z )</td>
<td>spatial mesh size in ( x, y ) and ( z ) directions, ( m )</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>emissivity, ( - )</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>relative difference, ( - )</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>auxiliary variable, ( \zeta = C_2 / \lambda T )</td>
</tr>
<tr>
<td>( \theta )</td>
<td>polar angle, rad, ( ^\circ )</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>absorption coefficient, ( m^{-1} )</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>wavelength, ( m )</td>
</tr>
<tr>
<td>( \mu )</td>
<td>magnetic permeability, ( N , s^2 , C^{-2} )</td>
</tr>
<tr>
<td>( \nu )</td>
<td>frequency of an electromagnetic wave, ( s^{-1} )</td>
</tr>
<tr>
<td>( \nu )</td>
<td>kinematic viscosity, ( m^2 , s^{-1} )</td>
</tr>
<tr>
<td>( \rho )</td>
<td>density, ( kg , m^{-3} )</td>
</tr>
<tr>
<td>( \rho )</td>
<td>reflectivity, ( - )</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Stefan-Boltzmann constant, ( \sigma = 5.6704 \cdot 10^{-8} , W , m^{-2} , K^{-4} )</td>
</tr>
<tr>
<td>( \sigma_b )</td>
<td>scattering coefficient, ( m^{-1} )</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>viscous stress tensor</td>
</tr>
<tr>
<td>( \tau )</td>
<td>optical thickness, ( - )</td>
</tr>
<tr>
<td>( \tau )</td>
<td>transmissivity, ( - )</td>
</tr>
<tr>
<td>( \phi )</td>
<td>azimuthal angle, rad, ( ^\circ )</td>
</tr>
<tr>
<td>( \omega )</td>
<td>single scattering albedo, ( - )</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>solid angle, sr</td>
</tr>
</tbody>
</table>

### Subscripts

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>absorbed</td>
</tr>
<tr>
<td>air</td>
<td>referring to air</td>
</tr>
<tr>
<td>b</td>
<td>blackbody; boundary</td>
</tr>
<tr>
<td>baseline</td>
<td>referring to baseline parameter set</td>
</tr>
<tr>
<td>c</td>
<td>conduction</td>
</tr>
<tr>
<td>cal</td>
<td>calculated</td>
</tr>
<tr>
<td>ch</td>
<td>chemistry</td>
</tr>
<tr>
<td>cv</td>
<td>convection</td>
</tr>
<tr>
<td>e</td>
<td>emitted; external variable</td>
</tr>
<tr>
<td>i, j, k, l</td>
<td>dummy indexes</td>
</tr>
<tr>
<td>in</td>
<td>incident</td>
</tr>
<tr>
<td>int</td>
<td>sample-plate interface</td>
</tr>
<tr>
<td>L</td>
<td>referring to a whole layer</td>
</tr>
<tr>
<td>meas</td>
<td>measured</td>
</tr>
<tr>
<td>ov</td>
<td>overall</td>
</tr>
</tbody>
</table>
Symbols

\( p \) at constant pressure
\( p \) particle; plate
\( p_1, p_2, \ldots, p_5 \) measurement points
\( P \) Planck mean value
\( r \) radiation
\( \text{ref} \) reference
\( \text{refl} \) reflected
\( s \) sample; scattering; specular
\( \text{source} \) source of radiation
\( \text{surr} \) surroundings
\( \text{total} \) total value
\( v \) at constant volume; referring to a volume
\( w \) wall
\( x, y, z \) in \( x, y, \) and \( z \) direction
\( \lambda \) spectral
\( \tau \) transmitted
\( 0 \) initial value; in vacuum
\( \infty \) free stream value

Superscripts
\( f \) filtered
\( i \) iteration level
\( n \) time level
\( ^\circ \) standard conditions
\( * \) dummy variable of integration
\( ' \) directional quantity

Overbar
\( - \) surface-averaged conditions; volume-averaged value; sample mean value

Dimensionless groups
\( \text{Bi} \) Biot number
\( \text{Nu} \) Nusselt number
\( \text{Ra} \) Rayleigh number
\( \text{Pr} \) Prandtl number
Chapter 1

Introduction

The analysis of radiative heat transfer within a system undergoing a chemical transformation, in which the chemical species, phases, and properties of the system vary with time as the reaction progresses, is a complex transient problem encountered in such research areas as atmospheric sciences, combustion, and chemical and process engineering. Endothermic processes involving radiative heat exchange in reacting two-phase solid-gas flows like thermal cracking, gasification, reforming, decomposition, and reduction are found in a wide range of industrial applications, including extractive metallurgy, advanced material and fuel processing, and lime and cement production. They are characterised by their high energy requirement and the concomitant emission of pollutants, derived mainly from the combustion of fossil fuels for heat generation. Process heat is supplied either directly by internal combustion, resulting in the contamination of products, or indirectly by external combustion, leading to lower thermal efficiency because of the irreversibilities associated with indirect heat transfer. Alternatively, the process heat can be supplied directly to the reaction site by thermal radiation, which offers some advantages, namely, the reaction products are not contaminated, and the heat is transferred efficiently, bypassing the limitations imposed by heat exchangers. If the radiative source is derived from renewable energy, e.g. concentrated solar energy, the emission of greenhouse gases due to heat generation is avoided. In the case of the solar production of fuels or the upgrade of existing fuels, the final product contains chemically stored solar energy.

An overview of solar thermochemical processes is given by Fletcher [19], and Steinfeld and Palumbo [78]. The main solar thermochemical research activities are oriented towards hydrogen production, either directly by water or hydrogen sulfide splitting, or indirectly by multi-step thermochemical cycles involving thermal reduction of metal oxides. Other applications include the upgrading and decarbonisation of fossil fuels, production of chemicals, detoxification and recycling of waste materials.

Figure 1 illustrates the idea of solar thermochemical processing. Solar radiation is concentrated and redirected into a chemical reactor, where it is absorbed either by reactants undergoing chemical conversion to useful products (direct irradiation), or by reactor walls and transferred as secondary heat flux to the reaction site (indirect
Concentrated solar radiation. In the case of a closed material cycle, the waste formed by end users from products are reused as the reactants.

The design process of a solar chemical reactor based on the concept of direct irradiation aims at optimally matching the radiative flux to chemical kinetics and minimising heat losses from the reactor. Modelling is needed to anticipate the consequences of a given design decision on the reactor's performance [64]. It assists in understanding the phenomena occurring within the reactor and in quantifying them. Although a real system is always simplified, the simplified system will maintain the key features and parameters given by the physics. Models are divided into physical and mathematical. Examples of physical models are reactors on the laboratory scale, which fulfil the requirements of the similarity criteria. A mathematical model establishes a mathematical description of a given process that reflects all the important phenomena by including relevant physical parameters and variables. A mathematical model of a chemical reactor consists of a system of differential equations describing total mass balance, mass balance of every component of a reacting mixture, and momentum and energy balance. Equations describing reaction rates, heat and mass fluxes, material properties, boundary and initial conditions complement the model.

Thermal radiation and chemical reactions are the most important phenomena within a solar thermochemical reactor. Therefore, it is crucial to establish or select existing methods which are compatible and give results which reflect the state of the modelled system at any instant and at any location. In particular, the reaction chamber typically contains a reacting and radiatively participating medium consisting of an irradiated solid-gas mixture, for which the actual velocity, temperature, and composition profiles are sought. If pure interaction between thermal radiation and reacting medium is of primary interest, an idealised mathematical model may be constructed in the first modelling phase by neglecting other phenomena like fluid and particle motion, and heat conduction. However, reacting two-phase flows always couple many phenomena and proper prediction for practical applications requires

![Figure 1.1: Schematic of a solar thermochemical process featuring a chemical reacting system exposed to concentrated solar radiation.](image)
that they are included. Neglecting any motion in the solid-gas mixture will have
an impact on the prediction of the composition, temperatures, reaction rates and
material properties, which in turn may completely obscure the true radiation field.

Radiative heat transfer and studies of physical processes in emitting two-phase
media applied to combustion chambers of heat power plants are discussed exten¬
sively by Adzerikho et al. [3]. Numerical methods and approximate solutions are
proposed for solving complex problems including spectral characteristics of the main
gas components of combustion products. A review of radiative heat transfer phe¬
nomena in dispersed media was carried out by Tien and Drohlen [81], Viskanta and
Mengüç [85], and more recently, by Baillis and Sacadura [4]. A number of studies on
thermal radiation in particulate media was carried out in connection with the anal¬
ysis of the absorption of concentrated solar radiation in receivers containing particle
clouds. Examples include work by Abdelrahman et al. [2], Evans et al. [15], Wang
et al. [88], Miller and Koenigsdorff [50], Mischler and Steinfeld [51], and Bertocchi [7].

Another important field of application concerns heat transfer calculations in
packed beds. Radiative exchange was analysed among others by Singh and Ka¬
viany [74, 75, 76], Kamiuto [33], Wu and Chu [89], and Lu et al. [41]. Mohamad
et al. developed a steady-state model to simulate combustion and heat transfer in
a packed bed including thermal radiation [57]. Belghit et al. proposed a rigorous
pseudo-steady model of a moving chemical bed reactor for coal gasification under
concentrated solar radiation [5]. The variation of the physical properties of the sys¬
tem with temperature and concentration, the velocity of the bed, the variation of
the gas velocity and pressure in the gasifier due to an increase in the number of
moles during the chemical reaction, the variation of the carbon particle diameter
and radiative exchange in porous medium are taken into account. However, the
model does not account for the variation of the radiative properties as the reaction
progresses. Transient heat transfer models for a packed bed and a suspension of
calcium carbonate particles exposed to external concentrated irradiation and under¬
going thermal decomposition, where the time-variation of physical properties was
accounted for, were presented by Lipiński and Steinfeld [37, 38].

Further, general examples of studies coupling chemical reaction and radiative
heat transfer include steady-state models such as a simulation of metalorganic
vapour phase epitaxy growth based on the finite volume solution of coupled flow,
heat, and mass transfer by Bergunde et al. [6], a solution of Navier-Stokes equations
for a non-equilibrium medium existing in rocket exhaust plumes by Vitkin et al. [86],
a model coupling radiative and convective heat transfer with the chemical kinetics
of LPG reforming by Kudo et al. [36], and a simulation of thermal decomposition of
methane in a directly irradiated solar chemical reactor by Hirsch and Steinfeld [27].

Examples of transient problems include a two-phase model to predict ignition tem¬
peratures in an exothermic catalytic chemical reactor by Vortmeyer and Stahl [87],
a two-dimensional model of the ignition of polymethyl-methacrylate by Han and
Baek [24], and a combined convection-conduction-radiation heat transfer model for
an oil-fired furnace [40].

This work deals with the transient radiative heat transfer in chemically react-
ing systems. A brief explanation of fundamental phenomena of thermal radiation, radiative properties of opaque surfaces, and governing relations for radiative heat transfer in participating media is given in Chapter 2. Chapter 3 describes selected numerical techniques, namely the Monte Carlo method, the finite volume method and numerical schemes of time integration, which are used in this work for finding distribution of the radiative source and for solving unsteady conservation equations. In Chapter 4, a series of numerical tests with the Monte Carlo method combined with several time integration schemes is conducted for the purpose of demonstrating the feasibility of the method to treat transient radiative heat transfer problems, and, of showing the qualitative interrelation between the accuracy of the Monte Carlo method, time integration schemes, and the combination of these numerical techniques. The model chemical reactions used in the analyses in this work—the thermal decomposition of calcium carbonate and the steam gasification of coal—and their rate equations are described in Chapter 5. Chapters 6 to 8 present the transient radiative heat transfer models for chemically reacting media. Chapter 6 describes a three-dimensional transient heat transfer model that links conduction, convection and radiation heat transfer to the chemical reaction applied for a packed bed of large calcium carbonate particles undergoing thermal decomposition. Also presented is the experimental validation of the model. A suspension of small reacting particles undergoing a chemical transformation is modelled in Chapter 7. The influence of the non-shrinking and shrinking particle models on the temperature, reaction extent and optical properties of the suspension is investigated. The shrinking particle model is then applied in Chapter 8 to the coal gasification reaction for both small and large coal particles. In addition, an alternative solution methodology involving the direct, or discontinuous, modelling approach of randomly located spheres is proposed for the suspension of large coal particles.

In all problems, the gas phase is assumed as a non-participating medium and the radiative properties are obtained based solely on the actual composition of the solid phase. However, a short introduction to treatment of gas-particle mixtures is given. Further simplifications involve neglecting the effects of hydrodynamics, size distribution and inhomogeneities of a single particle. Most of the material properties were extracted from the literature. The condition of local thermodynamic equilibrium is assumed, implying that the radiative energy is emitted based solely on the temperature and physical properties of emitting bodies, and the properties are unaffected by the characteristics of the surrounding radiation field. This assumption excludes from the analysis the occurrence of luminescence and rapid transients like the heating response of materials to very short energy pulses. Furthermore, only the quasi-steady form of the radiative transfer equation is considered, which means that the effect of the finite time of electromagnetic wave propagation is not accounted for, since this effect is negligible in most engineering applications. The selected model reactions, the calcium carbonate decomposition and the steam gasification of coal, are considered because of their significance to a wide range of industrial applications. Both reactions have been investigated recently in solar thermochemical reactors, demonstrating their feasibility for the solar thermal implementation.
Chapter 2

Radiative heat transfer

The present chapter summarises definitions and equations that form the theoretical background of the radiative heat transfer analysis presented in this work. A brief explanation of fundamental phenomena of thermal radiation, radiative properties of opaque surfaces, and governing relations for radiative heat transfer in participating media is given. Special attention is devoted to radiative properties of particulate media as they are used in this work in all problems that include chemical reactions. A brief introduction to radiative properties of gas-particle mixtures is also given at the end of this chapter.

2.1 Fundamentals

All materials at temperatures above absolute zero continuously emit electromagnetic waves, or photons, due to atomic and molecular agitation. Classical electrodynamics and quantum mechanics are used alternatively to describe this phenomenon called thermal radiation. The spectrum of thermal radiation stretches from the long-wave part of the ultraviolet, through the visible, up to the far infrared region, hence containing wavelengths between $10^{-7}$ m and $10^{-3}$ m. Emission by molecules, atoms, ions, or single electrons results in their translation to lower energy levels, whereas radiation absorption leads to their excitation to higher energy levels. If the radiative energy absorbed by a small volume $dV$ is quickly redistributed into its internal energy and the spectrum of the emitted radiation is based solely on the local temperature and physical properties, which means that the spectrum does not depend on the characteristics of the incoming radiation, $dV$ is considered to be under the condition of local thermodynamic equilibrium. The rapid redistribution of absorbed energy is typical for most problems encountered in engineering. Emission by a medium element remaining in the local thermodynamic equilibrium is called spontaneous and its spectral distribution is described by Planck’s law. For a perfect absorber and emitter, called a blackbody, submerged in a transparent medium with
refractive index \( n \), it is given by

\[
E_{\lambda b}(\lambda, T) = \pi I_{\lambda b} = \frac{2\pi hc_0^2}{n^2\lambda^5 \left[ \exp\left( \frac{hc_0}{n\lambda kT} \right) - 1 \right]}, \tag{2.1}
\]

where \( E_{\lambda b} \) is the blackbody spectral emissive power defined as the rate at which radiative energy is emitted from a surface in all directions per unit wavelength interval around wavelength \( \lambda \) and per unit surface area. \( I_{\lambda b} \) is the spectral intensity of a blackbody defined as the rate at which radiative energy is emitted in a single direction, per unit area of the emitting surface normal to this direction, per unit solid angle around this direction, and per unit wavelength interval around wavelength \( \lambda \). \( h \) is Planck’s constant, \( k \) is the Boltzmann constant, and \( c_0 \) is the speed of light in vacuum. The total blackbody emissive power, which is defined as the rate of radiative energy emitted at all wavelengths, is given by the Stefan–Boltzmann law,

\[
E_b(T) = \int_0^\infty E_{\lambda b}(\lambda, T) \, d\lambda = n^2\sigma T^4, \tag{2.2}
\]

where \( \sigma \) is the Stefan–Boltzmann constant and the refractive index of the surrounding medium \( n \) is assumed as wavelength independent. The blackbody emissive power can be calculated for a finite wavelength interval and a prescribed temperature by use of the blackbody fraction function \( F_{0-n\lambda T} \), which for the refractive index of the surrounding medium \( n \) independent of wavelength is given by \([55, 73]\)

\[
F_{0-n\lambda T} = \int_0^\lambda \frac{E_{\lambda b}(\lambda, T)}{n^2\sigma T^4} \, d\lambda = \int_0^{n\lambda T} \frac{E_{\lambda b}(\lambda, T)}{n^3\sigma T^5} \, d(n\lambda T) = F_{0-n\lambda T}. \tag{2.3}
\]

The evaluation of \( F_{0-n\lambda T} \) is carried out by using the following series form

\[
F_{0-n\lambda T} = \frac{15}{\pi^4} \int_{C_2/(n\lambda T)}^\infty \frac{\zeta^3}{e^\zeta - 1} \, d\zeta = \frac{15}{\pi^4} \sum_{i=1}^\infty \left[ \frac{e^{-i\zeta}}{i} \left( \zeta^3 + \frac{3\zeta^2}{i} + \frac{6\zeta}{i^2} + \frac{6}{i^3} \right) \right], \tag{2.4}
\]

with the substitution \( \zeta = C_2/(n\lambda T) \). The values of the blackbody fraction function were tabulated and are available in standard books on thermal radiation \([55, 73]\).

The quantity of interest used in energy balance calculations is the total radiative heat flux\(^1\). It reads in vector notation

\[
q'' = \int_0^\infty q''_\lambda \, d\lambda, \tag{2.5}
\]

\(^1\)In this work, the term heat flux refers to energy flow per unit time and unit area (\( \text{W m}^{-2} \)), while the term heat transfer rate denotes the energy flow per unit time (\( \text{W} \)).
2.2 Radiative properties of opaque surfaces

which is obtained by integration of the spectral radiative heat flux vector $q''_\lambda$ over the entire spectrum. $q''_\lambda$ is calculated by recalling the definition of the radiative intensity,

$$q''_\lambda = \int_0^{4\pi} I_\lambda(\hat{s}) \hat{s} \, d\Omega,$$

(2.6)

where $\hat{s}$ is the unit vector of a single direction of radiative intensity.

### 2.2 Radiative properties of opaque surfaces

The surface radiative phenomena like emission, absorption, and reflection are, in fact, of volume nature. They take place by virtue of an interaction between the radiation and a layer of atoms or molecules. For opaque solids the effective thickness of this layer is negligible compared to the macroscopic dimensions of the body and the result of the interaction can be viewed as a surface phenomenon.

The most basic radiative property for emission of an opaque surface is the spectral directional emissivity\(^2\) defined as the ratio of the actual spectral directional emissive power to that of a blackbody,

$$\epsilon'_\lambda(\lambda, \hat{s}, T) \equiv \frac{I_\lambda(\lambda, \hat{s}, T) \hat{n} \cdot \hat{s} \, d\Omega}{I_{\text{bb}}(\lambda, T) \hat{n} \cdot \hat{s} \, d\Omega} = \frac{I_\lambda(\lambda, \hat{s}, T)}{I_{\text{bb}}(\lambda, T)}.$$

(2.7)

A radiative property that is used in connection with surface absorption is the absorptivity. Its most basic form, the spectral directional absorptivity, is defined as the ratio of the absorbed part $H'_{\lambda, a}(\lambda, \hat{s}) = -I_{\lambda, a}(\lambda, \hat{s}) \hat{n} \cdot \hat{s}$ of the spectral directional irradiation to the spectral directional irradiation $H'_\lambda(\lambda, \hat{s}) = -I_\lambda(\lambda, \hat{s}) \hat{n} \cdot \hat{s}$ itself,

$$\alpha'_\lambda(\lambda, \hat{s}, T) \equiv \frac{H'_{\lambda, a}(\lambda, \hat{s})}{H'_\lambda(\lambda, \hat{s})} = \frac{I_{\lambda, a}(\lambda, \hat{s})}{I_\lambda(\lambda, \hat{s})}.$$

(2.8)

In general, $\alpha'_\lambda$ can depend on the external radiation field, but, under the condition of local thermodynamic equilibrium, it is a true surface property and the relation between the spectral directional absorptance and the spectral directional emittance called Kirchhoff's law can be written as

$$\alpha'_\lambda(\lambda, \hat{s}, T) = \epsilon'_\lambda(\lambda, -\hat{s}, T).$$

(2.9)

The spectral bidirectional reflectance is the most basic of all surface radiative properties. It depends on two directions—the direction of the incoming radiation $\hat{s}_i$, and the direction into which the energy is reflected $\hat{s}_r$,

$$\rho''_\lambda(\lambda, \hat{s}_i, \hat{s}_r) \equiv \frac{dI_\lambda(\lambda, \hat{s}_i, \hat{s}_r)}{-I_\lambda(\lambda, \hat{s}_i) \hat{s}_i \cdot \hat{n} \, d\Omega}.$$

(2.10)

\(^2\)Throughout this work properties with ending '-ivity' refer to opaque materials, whether for ideal uncontaminated surfaces or for properties with a given surface condition. By contrast, properties with ending '-ance' are extensive quantities such as the transmittance of a partially transmitting participating medium.
Chapter 2. Radiative heat transfer

The basic radiative properties are used to derive total and hemispherical properties, representing spectral and directional averages. A general discussion of all surface properties and their derivation can be found in standard books on thermal radiation [55, 73].

Radiative properties of opaque, perfectly smooth and specularly reflecting surfaces can be predicted from classical electromagnetic theory. In general, a wave can be incident on an interface between two absorbing media with complex refractive indexes $m_1 = n_1 - ik_2$ and $m_2 = n_2 - ik_2$. The wave is then inhomogeneous in both media, which means that the planes of constant amplitude and constant phase are not along the same direction except at the normal incidence, resulting in the two sets of planes being parallel. The directional-hemispherical reflectivity is defined as the ratio of the reflected radiative energy into the whole hemisphere above the surface to the energy incident from only one direction. It is a function of the incidence angle $\theta$, $\cos \theta = -\hat{s}_i \cdot \hat{n}$, the wavelength $\lambda$ and the temperature $T$. The dependence on $\lambda$ and $T$ results from the dependence of the complex refractive index on these quantities. In the following discussion in this section, the temperature dependence is omitted from notation for simplicity.

The magnitude and direction of the radiative energy transfer rate per unit area normal to the propagation direction is given by the Poynting vector,

$$ S = E \times H, \quad (2.11) $$

where $E$ and $H$ are the electric and magnetic field vectors, respectively. The Poynting vector is a rapidly varying function of time as are both $E$ and $H$. More important to an engineer is the time-averaged value of the Poynting vector [55],

$$ \langle S \rangle_{\delta t} = \frac{1}{\delta t} \int_t^{t+\delta t} S(t) \, dt = \frac{n}{2c_0\mu}|E_0|^2 \exp(-\kappa s) s, \quad (2.12) $$

where $\delta t$ is a short time interval, but large enough compared to the wave period $1/\nu$, $E_0$ is the amplitude of the electric field, and $\kappa = 4\pi k / \lambda_0$ is the absorption coefficient of the medium. The directional-hemispherical reflectivity for incident parallel and perpendicular polarised waves are given by

$$ \rho_{\lambda||}(\lambda, \theta) = \frac{|\langle S_{r||} \rangle_{\delta t}|}{|\langle S_{i||} \rangle_{\delta t}|} = \left( \frac{E_{0, r||}}{E_{0, i||}} \right)^2, \quad (2.13) $$

$$ \rho_{\lambda\perp}(\lambda, \theta) = \frac{|\langle S_{r\perp} \rangle_{\delta t}|}{|\langle S_{i\perp} \rangle_{\delta t}|} = \left( \frac{E_{0, r\perp}}{E_{0, i\perp}} \right)^2. \quad (2.14) $$

The ratios of the reflected and incident components of the electric field amplitudes

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3In the following discussion it is assumed that the radiative properties do not depend on the azimuthal angle $\phi$. 

are expressed by [73]

\[
\frac{E_{0,r||}}{E_{0,\|\|}} = \frac{\cos \theta/\cos \chi - m_1/m_2}{m_1/m_2}, \quad (2.15)
\]

\[
\frac{E_{0,r\perp}}{E_{0,\perp\perp}} = \frac{\cos \chi/\cos \theta - m_1/m_2}{m_1/m_2}, \quad (2.16)
\]

where \( \chi \) is a complex angle that obeys Snell's law,

\[
\sin \chi = \frac{m_1 - ik_1}{m_2 - ik_2} \quad (2.17)
\]

If the radiation is arriving at an interface from a non-absorbing medium, \( k_1 = 0 \), the incident wave is homogeneous, and the directional-hemispherical reflectivities can be expressed as [55, 73]

\[
\rho_{\lambda||}(\lambda, \theta) = \frac{(a - n_1 \sin \theta \tan \theta)^2 + b^2}{(a + n_1 \sin \theta \tan \theta)^2 + b^2} \rho_{\lambda\perp}, \quad (2.18)
\]

\[
\rho_{\lambda\perp}(\lambda, \theta) = \frac{(a - n_1 \cos \theta)^2 + b^2}{(a + n_1 \cos \theta)^2 + b^2}, \quad (2.19)
\]

where \( a \) and \( b \) are auxiliary variables given by

\[
2a^2 = \left[ (n_2^2 - k_2^2 - n_1^2 \sin^2 \theta)^2 + 4n_2^2k_2^2 \right]^{\frac{1}{2}} + (n_2^2 - k_2^2 - n_1^2 \sin^2 \theta), \quad (2.20)
\]

\[
2b^2 = \left[ (n_2^2 - k_2^2 - n_1^2 \sin^2 \theta)^2 + 4n_2^2k_2^2 \right]^{\frac{1}{2}} - (n_2^2 - k_2^2 - n_1^2 \sin^2 \theta). \quad (2.21)
\]

Equations (2.18) and (2.19) are known as Fresnel's equations for absorbing media. For non-polarised incident radiation, the reflectivity is an average of the parallel and perpendicular components,

\[
\rho_{\lambda}(\lambda, \theta) = \rho_{\lambda||} + \rho_{\lambda\perp}. \quad (2.22)
\]

### 2.3 Radiative transfer in participating media

As the radiation travels through vacuum, no interactions with matter occurs and the radiative intensity along a certain direction \( \hat{s} \) is constant. Intensity at position \( s_1 \) and instant \( t_1 \) is equal to intensity at position \( s_2 \) at some later instant \( t_2 = t_1 + (s_2 - s_1)/c_0 \),

\[
I_\lambda(s_1, \hat{s}, t_1) = I_\lambda(s_2, \hat{s}, t_2). \quad (2.23)
\]

Since the speed of light in vacuum, \( c_0 \), is the highest possible, and the time scale of light propagation is much smaller than any other time scale in engineering problems, the assumption of instantaneous radiation propagation is often made leading to

\[
I_\lambda(s_1, \hat{s}) = I_\lambda(s_2, \hat{s}). \quad (2.24)
\]
This assumption also holds for radiatively participating media with complex refractive index \( m = n - ik \). Although the speed of light is lower than in vacuum, the time scale of any significant change of physical properties and state variables still immensely exceeds the time scale of radiation propagation.

In a radiatively participating medium, a bundle of rays travelling along direction \( \hat{s} \) is attenuated by absorption and scattering, and augmented by emission within the medium and incoming scattering. The attenuation of radiative intensity is proportional to the actual intensity \( I_\lambda(s) \) and to the infinitesimal distance \( ds \) that the beam travels along,

\[
dI_\lambda(s, \hat{s}) = -\beta_\lambda(s)I_\lambda(s, \hat{s})\, ds. \tag{2.25}
\]

\( \beta_\lambda \) is the extinction coefficient of the medium. It is defined as the inverse mean free path of a photon until it undergoes attenuation in a medium with constant \( \beta_\lambda \) either by absorption or by scattering [73]. The extinction coefficient is a function of temperature \( T \), pressure \( p \), composition of the medium \( C_i \), and wavelength of the incident radiation. It is composed of two parts, the absorption coefficient \( \kappa_\lambda \) and the scattering coefficient \( \sigma_\lambda \),

\[
\beta_\lambda(\lambda, T, p, C_i) = \kappa_\lambda(\lambda, T, p, C_i) + \sigma_\lambda(\lambda, T, p, C_i). \tag{2.26}
\]

In general, \( T \), \( p \), and \( C_i \) depend on the location and time, thus, so does \( \beta_\lambda \). The augmentation by emission within the medium is calculated using the blackbody intensity at the temperature of the medium and with the absorption coefficient of the medium,

\[
dI_\lambda(s, \hat{s}) = \kappa_\lambda(s)I_{\text{bb}}(s, \hat{s})\, ds. \tag{2.27}
\]

Finally, the contribution by incoming scattering from all directions \( \hat{s}_i \) to the intensity in direction \( \hat{s} \) is given by

\[
dI_\lambda(s, \hat{s}) = \frac{\sigma_\lambda ds}{4\pi} \int_0^{4\pi} I_\lambda(\hat{s}_i)\Phi_\lambda(\hat{s}_i, \hat{s})\, d\Omega_i. \tag{2.28}
\]

\( \Phi_\lambda \) is the phase function for scattering defined as

\[
\Phi_\lambda(\hat{s}_i, \hat{s}) = \frac{dI_\lambda(\hat{s}_i, \hat{s})}{\frac{1}{4\pi} \int_0^{4\pi} dI_\lambda(\hat{s}_i, \hat{s}_i)\, d\Omega}. \tag{2.29}
\]

It expresses the angular distribution of the scattered intensity and is interpreted as the scattered intensity in the direction \( \hat{s} \), divided by the intensity that would be scattered in this direction if the scattering were isotropic.

A balance on radiative intensity in direction \( \hat{s} \) leads to the basic equation of radiative transfer in participating media. Recalling the assumption of instantaneous radiation propagation, and introducing the optical thickness,

\[
\tau_\lambda(s) = \int_0^s \beta_\lambda(s^*)\, ds^*, \tag{2.30}
\]
and the single scattering albedo,\[ \omega_\lambda = \frac{\sigma_{al\lambda}}{\beta_\lambda}, \] (2.31)

the compact quasi-steady form of the equation of radiative transfer is obtained [55],\[ \frac{dI_\lambda(\tau_\lambda, \hat{s})}{d\tau_\lambda} + I_\lambda(\tau_\lambda, \hat{s}) = S_\lambda(\tau_\lambda, \hat{s}), \] (2.32)

where \( S \) is the source function for radiative intensity,

\[ S_\lambda(\tau_\lambda, \hat{s}) = (1 - \omega_\lambda)I_{\lambda b} + \frac{\omega_\lambda}{4\pi} \int_0^{4\pi} I_\lambda(\hat{s}_i) \Phi_\lambda(\hat{s}_i, \hat{s}) \, d\Omega. \] (2.33)

Equation (2.32) is derived assuming that the refractive index of the medium is constant across the medium—otherwise waves would not propagate along straight lines. Moreover, the medium is non-polarising, and it is in local thermodynamic equilibrium.

The divergence of the total radiative heat flux is obtained by integrating the equation of radiative transfer (2.32) over the whole wavelength spectrum and all directions, yielding

\[ \nabla \cdot q'' = \int_0^\infty \kappa_\lambda (4\pi I_{\lambda b} - G_\lambda) \, d\lambda, \] (2.34)

with \( G_\lambda \) being the direction-integrated intensity,

\[ G_\lambda = \int_0^{4\pi} I_\lambda(\hat{s}) \, d\Omega. \] (2.35)

The net radiative heat transfer rate into a volume element \( V \) is then found as

\[ q_r = -\int_V \nabla \cdot q'' \, dV = q_s - q_e. \] (2.36)

2.4 Radiative properties of particles

The amount of energy absorbed and scattered by a particle and the scattering direction depend on the shape of the particle, its material, relative size, and the clearance between particles. If scattering does not change the energy of an electromagnetic wave, or a photon, it is called elastic. Elastic scattering prevails in heat transfer problems. If scattering by a single particle is unaffected by the presence of other particles, it is called independent. It occurs when the clearance between particles is sufficiently large relative to both the wavelength and the particle diameter. In this
Figure 2.1: Map of independent and dependent scattering regimes for particulate media [81].

case radiative properties of a particle cloud can be predicted from properties of the single particle. Figure 2.1 shows the map of independent and dependent scattering regimes as a function of particle size parameter \( x \) and particle volume fraction \( f_v \), defined as

\[
x = \frac{\pi d_p}{\lambda},
\]

\[
f_v = N_p V_p,
\]

where \( d_p \), \( N_p \) and \( V_p \) are the particle diameter, number of spherical particles of equal radius per unit volume, and volume of a particle, respectively. In many problems of radiative heat transfer in particulate media, irregularly shaped, randomly located and oriented particles are assumed spherical. Radiative properties can then be calculated based on their optical properties such as the complex refractive index or surface radiative properties such as reflectivity.

The absorption and scattering coefficients of an independently-scattering monodispersed particulate medium can be expressed in terms of the absorption and scattering efficiency factors of a single particle as

\[
\kappa_\lambda = \frac{\pi d_p^2}{4} N_p Q_{a\lambda} = \frac{3}{2} f_v Q_{a\lambda},
\]

\[
\sigma_{a\lambda} = \frac{\pi d_p^2}{4} N_p Q_{a\lambda} = \frac{3}{2} f_v Q_{a\lambda}.
\]
The absorption and scattering efficiency factors are defined as
\[ Q_{a\lambda} = \frac{C_{a\lambda}}{s_p}, \quad (2.41) \]
\[ Q_{s\lambda} = \frac{C_{s\lambda}}{s_p}, \quad (2.42) \]
where \(C_{a\lambda}, C_{s\lambda},\) and \(s_p\) are the spectral absorption and scattering cross sections, and the geometric cross section of a particle, respectively. \(C_{a\lambda}\) and \(C_{s\lambda}\) represent the apparent area that a particle presents to incident radiation along a path in relation to its ability to absorb or scatter radiation, respectively.

Depending on the particle size parameter \(x\), the efficiency factors and the scattering phase function of a single particle are obtained from geometric optics \((x \gg 1)\), Mie theory \((x \approx 1)\), or Rayleigh theory \((x \ll 1)\). Rayleigh scattering is not covered in this work since it is not applied in the analysis in the following chapters. An exhaustive explanation is given in the literature [35, 68].

### 2.4.1 Mie scattering theory

Mie scattering theory, developed by Gustav Mie [49], derives the properties of the electromagnetic field from electromagnetic theory for the case when a plane spectral wave is incident on a spherical surface across which the complex refractive index changes abruptly. The theory applies for arbitrary values of the complex refractive index of a particle \(m_2\) and the particle size parameter \(x\). The scattering and extinction efficiencies are given by [31]
\[ Q_{s\lambda} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n + 1) \left( |a_n|^2 + |b_n|^2 \right), \quad (2.43) \]
\[ Q_{e\lambda} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n + 1) \Re(a_n + b_n), \quad (2.44) \]
where \(a_n\) and \(b_n\) are the Mie scattering coefficients. They are complex functions of \(x\) and \(y = m_2/m_1\),
\[ a_n = \frac{\psi'_n(y) \psi_n(x) - m_2/m_1 \psi_n(y) \psi'_n(x)}{\psi'_n(y) \zeta_n(x) - m_2/m_1 \psi_n(y) \zeta'_n(x)}, \quad (2.45) \]
\[ b_n = \frac{m_2/m_1 \psi'_n(y) \psi_n(x) - \psi_n(y) \psi'_n(x)}{m_2/m_1 \psi'_n(y) \zeta_n(x) - \psi_n(y) \zeta'_n(x)}, \quad (2.46) \]
where derivatives are denoted by primes and \(m_1\) is the refractive index of the host medium. \(\psi_n\) and \(\zeta_n\) designate Riccati-Bessel functions, which can be related to Bessel and Hankel functions, \(J_n\) and \(H_n\), respectively,
\[ \psi_n(z) = \left( \frac{\pi z}{2} \right)^{\frac{1}{2}} J_{n+\frac{1}{2}}(z), \quad (2.47) \]
\[ \zeta_n(z) = \left( \frac{\pi z}{2} \right)^{\frac{1}{2}} H_{n+\frac{1}{2}}(z). \quad (2.48) \]
$z$ designates a non-dimensional spectral variable, either $x$ or $y$.

The scattering phase function for Mie scattering is expressed in terms of the elements $S_1$ and $S_2$ of the amplitude scattering matrix, and is given by

$$\Phi_\lambda(\theta) = \frac{|S_1|^2 + |S_2|^2}{4\pi \int_0^{2\pi} (|S_1|^2 + |S_2|^2) \, d\Omega}.$$  

(2.49)

$S_1$ and $S_2$ are functions of the scattering direction $\theta$ \cite{9,31},

$$S_1(\theta) = \sum_{n=1}^{\infty} \frac{2n + 1}{n(n + 1)} [a_n \pi_n(\cos \theta) + b_n \tau_n(\cos \theta)],$$  

(2.50)

$$S_2(\theta) = \sum_{n=1}^{\infty} \frac{2n + 1}{n(n + 1)} [b_n \pi_n(\cos \theta) + a_n \tau_n(\cos \theta)],$$  

(2.51)

with $\pi_n$ and $\tau_n$ being direction-dependent functions related to Legendre polynomials $P_n$ and are given by

$$\pi_n(\cos \theta) = \frac{dP_n(\cos \theta)}{d \cos \theta},$$  

(2.52)

$$\tau_n(\cos \theta) = \cos \theta \, \pi_n(\cos \theta) - \sin^2 \theta \frac{d\pi_n(\cos \theta)}{d \cos \theta}.$$  

(2.53)

There are several computer programs available for computing the absorption and scattering efficiency factors and the amplitude functions for scattering. The most popular is the BHMIE subroutine written by Bohren and Huffman \cite{9}, which is also used in the simulations in this work (see §7 and §8.1).

An example discussion of the influence and treatment of highly anisotropic Mie scattering in radiative heat transfer was given by Modest and Azad \cite{56}. Exact solutions for temperature distributions and radiative flux were obtained for scattering functions expressed by Legendre polynomial series expansion and compared with linear anisotropic scattering approximation and linear anisotropic differential approximation. The results of the comparison show that the linear approximation describes radiative transfer well, as long as the phase function is relatively smooth and the backscattering is insignificant. In contrast, the linear anisotropic differential approximation resulted in better accuracy when backscattering was included.

### 2.4.2 Large opaque spheres

Mie theory can be applied over a whole range of particle diameters as described previously. However, the evaluation of the complex amplitude functions requires a large number of series terms for bigger particles. In the limit of large particles, geometrical optics delivers satisfactory relations for the efficiency factors and scattering
phase function. In this case, the extinction efficiency factor approaches the limit of 2,
\[ \lim_{x \to \infty} Q_{\beta \lambda} = 2, \] (2.54)
i.e. the effective extinction cross section is equal to doubled geometrical particle cross section. While the contribution of refraction and reflection to the extinction efficiency factor is equal to 1 (the effective cross section is equal to that of the particle), the additional influence of the particle on the light passing in the neighbourhood is due to diffraction, \( Q_{\beta \lambda, \text{diff}} = 1 \). The phase function for diffraction is given by [73]

\[ \Phi(\theta) = \frac{x^2}{\cos^2 \theta} \left[ \frac{2J_1(x \tan \theta)}{x \tan \theta} \right]^2. \] (2.55)

From this equation follows that radiation is diffracted mostly into the forward scattering direction within a narrow solid angle. Therefore, diffraction by large spheres can be neglected in heat transfer calculation, and the extinction efficiency factor reduces in this case to \( Q_{\beta \lambda} = 1 \).

There are two limiting cases in calculations of the radiative properties of large opaque spheres. In the first one, particles are treated as ideal specular reflectors. Assuming the incident intensity uniform across the particle, the scattering and absorption efficiency factors are given by [55, 73]

\[ Q_{s \lambda} = \rho_{s \lambda}, \] (2.56)
\[ Q_{a \lambda} = 1 - \rho_{s \lambda}, \] (2.57)

where \( \rho_{s \lambda} \) designates the hemispherical reflectivity of a specular reflector. The scattering phase function depends on the angle between the direction of incident intensity \( \hat{s} \) and the normal to the particle surface \( \hat{n}, (\pi - \theta)/2, \)

\[ \Phi(\theta) = \rho_{s \lambda} \frac{(\pi - \theta)}{\rho_{s \lambda}}. \] (2.58)

The expressions for scattering and absorption efficiency factors, Equations (2.56) and (2.57), also apply for large diffusely reflecting spheres, but the hemispherical reflectivity \( \rho_{s \lambda} \) is that of a diffuse reflector. In contrast, scattering phase function is different from that of a specularly reflecting sphere, and

\[ \Phi(\theta) = \frac{8}{3\pi} (\sin \theta - \theta \cos \theta). \] (2.59)

While radiation incident on a specular sphere is mostly scattered in the forward direction \( (\theta = 0) \), a diffuse sphere scatters mostly backwards \( (\theta = \pi) \).

### 2.5 Radiative properties of gas-particle mixtures

Radiative intensity in a gas-particle mixture is attenuated due to absorption by the gas and the particles, and scattering by the particles. The extinction coefficient of
a mixture, $\beta_\lambda$, accounts for the contribution of both phases [90],

$$\beta_\lambda = \beta_{\lambda,g}(1 - f_v) + \beta_{\lambda,p},$$  \hspace{1cm} (2.60)

where $\beta_\lambda$ and $\beta_{\lambda,p}$ are the extinction coefficients of the gas and the particles, respectively. In general, scattering by gas molecules can be calculated from Rayleigh theory, but its contribution is negligible compared to absorption by the gas and the particles and scattering by the particles [61]. Therefore, Equation (2.60) reduces to

$$\beta_\lambda = \kappa_{\lambda,g}(1 - f_v) + \beta_{\lambda,p}.$$  \hspace{1cm} (2.61)

$\kappa_{\lambda,g}$ is the absorption coefficient of the gas phase. It rapidly varies with wavelength, which leads to computational difficulties in radiative heat transfer of two-phase media if the full line-by-line spectral structure is used. Therefore, spectral models are employed in order to reduce the spectral resolution.

Since the scattering by the gas is negligible, the single scattering albedo of a mixture is defined as the ratio of the particle scattering coefficient $\sigma_{\epsilon,\lambda,p}$ to the total extinction coefficient $\beta_\lambda$,

$$\omega_\lambda = \frac{\sigma_{\epsilon,\lambda,p}}{\beta_\lambda} = \frac{\sigma_{\epsilon,\lambda,p}}{\kappa_{\lambda,g}(1 - f_v) + \beta_{\lambda,p}}.$$  \hspace{1cm} (2.62)

An introduction to numerical methods used in transient analysis of radiative heat transfer problems including the Monte Carlo method is given in the next chapter.
Chapter 3

Numerical methods

3.1 Introduction

A solution to a system of coupled equations describing mass and heat transfer in a chemical reacting system rarely exists in an analytical form. Most of the known solutions refer to rather simple problems that are certainly very useful in basic understanding of the physics of mass and heat transfer, but they are not directly relevant for practical applications. In most engineering problems, where complex geometries, transients, composition and material property variation occur, the solution is obtainable only if numerical methods are employed. The rapid development in computer technology over the last few decades has resulted in simultaneous development of approximate solution methods in the field of mass and heat transfer known as computational fluid dynamics (CFD). Discretisation techniques like the finite difference, finite volume and finite element methods, solution methods of discretised equations, and the analysis of numerical schemes establish the core of CFD [17, 26, 65]. The general computational fluid dynamics encompasses many sub-specialities. It covers a wide range of industrial and non-industrial applications, from aerodynamics of aircraft and vehicles, through chemical process engineering up to meteorology and biomedical engineering.

In a manner analogous to computational fluid dynamics, numerical methods used in radiative heat transfer calculations have been named as computational thermal radiation (CTR) [1]. The most frequently used methods of CTR are the method of spherical harmonics, the method of discrete ordinates, the zonal method, and the Monte Carlo method. A solution of the equation of radiative transfer is always coupled to at least a solution of the energy equation. Therefore, the methods of CTR are used in conjunction with space discretisation techniques and time integration schemes.

The following sections are devoted to numerical methods selected for modelling the transient radiative heat transfer within non-uniform, non-grey, absorbing, emitting and anisotropically scattering media. The Monte Carlo method, the finite volume method, and several time integration schemes are presented. Also included are an example of the parallel implementation of a transient simulation using the
Monte Carlo method, and the brief description of low-pass smoothing filters for improving the accuracy of the Monte Carlo method in one-dimensional problems.

3.2 Monte Carlo method for thermal radiation

In 1777, Georges Louis Leclerc Comte de Buffon described his well-known experiment that conceives the basic idea of Monte Carlo (MC) computation, namely the application of a random process for evaluation of certain quantities of interest. The experiment is known as 'Buffon's needle' [14] and was used by numerous investigators to estimate the number \( \pi \) in the past. The use of experiments with random numbers to evaluate mathematical expressions like definite integrals, systems of equations, or more complicated mathematical models is called a Monte Carlo simulation and is now an essential tool adopted in many research areas, such as theoretical chemistry, statistical physics, structural biology, statistics, econometrics, engineering, and computer sciences. Its systematic use started in the 1940s, when Stanislaw Ulam, John von Neumann, Nicholas Metropolis, Enrico Fermi and others developed a statistical sampling-based method for solving numerical problems of random neutron diffusion in fissile material in atomic bomb designs and for estimating eigenvalues of the Schrödinger equation [39]. The name 'Monte Carlo' was brought up by Metropolis. In the early 1950s, a dynamic Monte Carlo method based on the Markov chain was introduced by statistical physicists for the simulation of simple fluids. The further development of Monte Carlo methods has continued until now resulting in an immense variety of them. Therefore, there is no general Monte Carlo method but only the underlying idea of statistical sampling. Researchers in different scientific disciplines have developed specific Monte Carlo methods for application in their field of activities. Among all, Markov chain-based Monte Carlo methods have been recognised as the most powerful ones, which enable simulation of very complicated stochastic physical systems.

The basic idea behind Markov chain Monte Carlo methods is that the sampler produces desirable random samples from a target distribution by making a series of local changes to an arbitrary initial state. This series of local changes is also called a random walk. The term Markov chain describes a sequence of events \( X^{(1)}, X^{(2)}, \ldots, X^{(n+1)} \) that satisfy the Markov property [39],

\[
P(X^{(n+1)}|X^{(n)}, \ldots, X^{(0)}) = P(X^{(n+1)}|X^{(n)}).	ag{3.1}
\]

It states that the event \( X^{(n+1)} \) depends only on its nearest past \( X^{(n)} \). In other words, a Markov chain has a minimal memory or is characterised by its fast forgetfulness. For a random variable \( X \) taking real values \( x \in \mathbb{R} \), a target distribution can be described by a distribution function defined as

\[
F(x) = P(X \leq x) = \int_{-\infty}^{x} g(x^*) \, dx^*,
\]

(3.2)
where \( g(x) \) is the probability density function,

\[
g(x) = \frac{dF(x)}{dx} = \frac{f(x)}{\int_{-\infty}^{\infty} f(x) \, dx}.
\]  

\( f(x) \) is the frequency function of the continuous random variable \( X \). It is derived based on the physical interpretation of \( X \) in the simulated problem. Therefore, the values of the random variable generated by the sampler from the target distribution \( F(x) \) must satisfy \( f(x) \) in order to fulfil the physical constrains of the simulation. This can be achieved either by using the acceptance/rejection method or, more efficiently, by inverting the distribution function. The second approach is based on the fact that the random variable \( Y \) taking values

\[
y = F(x),
\]  

is continuous and uniformly distributed in the interval \((0, 1)\). Choosing a random number from a uniform distribution \((0,1)\), \( R^{(i)} \), \( i = 1, 2, \ldots, m \), and calculating the inverse distribution function,

\[
x^{(i)} = F^{-1} (R^{(i)}),
\]

one obtains a realisation \( x^{(i)} \) of the random variable \( X \). The distribution of \( x^{(i)} \) will converge to the target distribution \( F(x) \) as the total number of realisations \( m \) approaches infinity. In practice, a finite number of realisations is used, which leads to a deviation of the actual distribution from the target distribution \( F(x) \).

The procedure of generating random variables can be extended to \( n \) dimensions by introducing multidimensional frequency, density and distribution functions, and a vector of random variables \( \mathbf{X} = [X_1, X_2, \ldots, X_n] \) taking real values given by the vector \( \mathbf{x} = [x_1, x_2, \ldots, x_n] \in \mathbb{R}^n \), so that

\[
g(\mathbf{x}) = \frac{f(\mathbf{x})}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} f(\mathbf{x}) \, dx_1 \, dx_2 \ldots dx_n},
\]

\[
F(\mathbf{x}) = \int_{-\infty}^{x_1} \int_{-\infty}^{x_2} \cdots \int_{-\infty}^{x_n} g(\mathbf{x}^*) \, dx_1^* \, dx_2^* \ldots dx_n^*.
\]

In the case of independent random variables \( X_i, i = 1, 2, \ldots, n \), the frequency function can be factored into a product form

\[
f(\mathbf{x}) = \prod_{i=1}^{n} f_i(x_i),
\]
leading to

\[ g(x) = \prod_{i=1}^{n} g_i(x_i), \]  

(3.9)

and

\[ F(x) = \prod_{i=1}^{n} F_i(x_i). \]  

(3.10)

If random variables are dependent, the general form of the density function (3.6) must be applied. Random variables are then found sequentially using

\[ F_1(x_1) = \int_{-\infty}^{x_1} \cdots \int_{-\infty}^{x_2} \cdots \int_{-\infty}^{x_n} g_1(x_1, x_2, \ldots, x_n) \, dx_1 \, dx_2 \cdots dx_n, \]

\[ F_2(x_2) = \int_{-\infty}^{x_2} \cdots \int_{-\infty}^{x_2} g_2(x_1 = \text{fixed}, x_2^*, \ldots, x_n) \, dx_2^* \cdots dx_n, \]

\vdots

\[ F_n(x_n) = \int_{-\infty}^{x_n} g_n(x_1 = \text{fixed}, x_2 = \text{fixed}, \ldots, x_{n-1} = \text{fixed}, x_n^*) \, dx_n^*. \]  

(3.11)

The Markov chain Monte Carlo was first applied to radiative heat transfer by Fleck [18], Howell and Perlmutter [29, 30], and Taniguchi [80] in the 1960s. The method was rapidly developed due to its strengths such as treatment of very complex geometries, incorporation of non-uniform, spectral and directional radiative material properties, and reduced programming time. However, the time penalty in performing calculations due to large numbers of traced rays and availability of other methods were limiting factors in the popularisation of Monte Carlo. A renewed interest has been exhibited in connection to the progress in high-performance computing in recent years with the objective of reduced computational time for solving complex realistic problems. Also the variety of different variants of the method spread out resulting in a group of methods including some improved approaches of increased performance and compatibility with the other heat transfer solution methods [16].

In a Monte Carlo simulation a statistically significant number of rays is used to compute net heat flux or radiative flux divergence, net heat transfer rates, incident intensity, emissive power, or exchange factors. The histories of the rays are controlled based on the probabilistic description of the underlying physics and the rays are traced through the geometry of the analysed problem. The Monte Carlo methods for radiative transfer can be divided into two groups: (1) forward methods and (2) reverse methods. In the forward approach, a ray’s history starts at emission and ends at absorption while the power transferred from one region to another is determined. These methods can easily simulate very complex problems and they are reasonably efficient for problems where the whole radiation field is needed. To this group belong the collision-based method and the pathlength method [16].
3.2. Monte Carlo method for thermal radiation

In the collision-based Monte Carlo method, an energy bundle is emitted and it travels undisturbed until it is absorbed or scattered. In its basic variant without any enhancement, it typically offers poor performance, especially in scattering media. A simulation based on this method begins with setting up the number of rays involved in the ray tracing, and power carried by a single ray. One of the strategies for doing that assumes equal power of all rays throughout a Monte Carlo run. In this case, the total number of rays $n_{\text{rays}}$ is chosen arbitrarily. The power carried by a single ray is then calculated as the total power emitted by all surface and volume elements, $A_i$ and $V_j$ respectively, divided by the total number of rays,

$$g_{\text{ray}} = \frac{1}{n_{\text{rays}}} \left( \sum_i \int e\sigma T^4 \, dA + \sum_j \int 4\kappa_p \sigma T^4 \, dV \right), \tag{3.12}$$

where $\kappa_p$ is the Planck mean absorption coefficient,

$$\kappa_p = \frac{\int_0^\infty \kappa_\lambda E_{\lambda\mu} \, d\lambda}{\int_0^\infty E_{\lambda\mu} \, d\lambda}. \tag{3.13}$$

Numbers of rays launched from surface and volume elements are then obtained as

$$n_{e,i} = \text{nint} \left( \frac{1}{g_{\text{ray}}} \int_{A_i} e\sigma T^4 \, dA \right), \tag{3.14}$$

$$n_{e,j} = \text{nint} \left( \frac{1}{g_{\text{ray}}} \int_{V_j} 4\kappa_p \sigma T^4 \, dV \right), \tag{3.15}$$

where nint$(x)$ is a function returning an integer nearest to $x$, $|\text{nint}(x) - x| = \text{min}$. The radiative processes are then simulated based on the distribution functions. These relations for obtaining the wavelength, direction of emission and scattering, and the mean free path to attenuation are summarised in [47, 55, 73]. Some of them are derived in [23]. Assuming that the radiative properties and phenomena do not depend on the azimuthal angle $\phi$, the probability density function for surface emission into a medium with $n \approx 1$ is given by

$$g(\lambda, \theta) = \frac{\varepsilon'_\lambda(\lambda, \theta, T) I_{\delta\lambda}(\lambda, T) \cos \theta \sin \theta}{2\pi \int_0^{\pi/2} \int_0^\infty \int_0^\infty \varepsilon'_\lambda(\lambda, \theta, T) I_{\delta\lambda}(\lambda, T) \cos \theta \sin \theta \cos \varphi \, d\varphi \, d\theta \, d\lambda} \tag{3.16}$$

$$= \frac{\varepsilon'_\lambda(\lambda, \theta, T) I_{\delta\lambda}(\lambda, T) \cos \theta \sin \theta}{\varepsilon(T) \sigma T^4}. \tag{3.17}$$
Recalling the property of the distribution function and its inversion, Equations (3.4) and (3.5), relations for obtaining direction and wavelength of an emitted ray are then derived as

\[ R_\varphi = \frac{\varphi}{2\pi}, \] (3.18)

\[ R_\theta = \frac{2\pi}{\varepsilon(T) \sigma T^4} \int_0^\theta \int_0^\infty \varepsilon'_A(\lambda, \theta, T) I_{\lambda b}(\lambda) \sin \theta^* \cos \theta^* d\theta^* d\lambda, \] (3.19)

\[ R_\lambda = \frac{2\pi}{\varepsilon(T) \sigma T^4} \int_0^{\pi/2} \int_0^\lambda \varepsilon'_A(\lambda^*, \theta, T) I_{\lambda b}(\lambda^*, T) \cos \theta \sin \theta d\theta d\lambda^*, \] (3.20)

where the variables \( \varphi, \theta, \) and \( \lambda \) are assumed to be independent. Similarly, the probability density function for an isotropic emission from a medium volume element is given by

\[ g(\lambda, \theta) = \frac{I_{\lambda b}(\lambda, T) \kappa_\lambda \sin \theta}{\int_0^{2\pi} \int_0^\infty \int_0^\lambda I_{\lambda b}(\lambda, T) \kappa_\lambda \sin \theta d\varphi d\theta d\lambda}, \] (3.21)

integration of which yields

\[ R_\varphi = \frac{\varphi}{2\pi}, \] (3.22)

\[ R_\theta = \frac{1}{2} (1 - \cos \theta), \] (3.23)

\[ R_\lambda = \frac{1}{\kappa_\rho \sigma T^4} \int_0^\lambda \kappa_\lambda(\lambda^*, T) I_{\lambda b}(\lambda^*, T) d\lambda^*. \] (3.24)

Subsequently, the rays are traced until they collide with the medium or they leave the considered domain. Choosing a random number \( R_\omega \), the distance \( s \) to a collision is obtained from

\[ \ln R_\omega = -\int_0^s \beta_\lambda(s^*) ds^* = -\sum_k \int_{s_k} \beta_\lambda(s) ds, \] (3.25)

where the summation is carried out over volumes intersected by a ray. \( s_k \) is a path distance along which a ray travels within volume \( V_k \). At the collision location \( s \), the type of attenuation is determined by choosing another random number, \( R_\omega \), and comparing it to the scattering albedo \( \omega_\lambda \) taken at location \( s \),

\[ \begin{cases} R_\omega \leq \omega_\lambda(s) & \Rightarrow \text{scattering,} \\ R_\omega > \omega_\lambda(s) & \Rightarrow \text{absorption.} \end{cases} \] (3.26)
In case of absorption, a local counter of rays absorbed within volume \( V_j \), \( n_{a,j} \), is updated and the simulation proceeds by emitting the next ray. Otherwise, the scattering direction is calculated. For a medium in which scattering direction does not depend on the azimuthal angle \( \varphi \) the azimuthal and polar angles are obtained from

\[
R_\varphi = \frac{\varphi}{2\pi}, \quad (3.28)
\]

\[
R_\theta = \frac{1}{2} \int_0^{\pi} \Phi_\lambda(\theta^*) \sin \theta^* \, d\theta^*. \quad (3.29)
\]

During the tracing, a ray may fall onto an enclosing surface. The reflection takes place if

\[
R_\rho \leq \rho'_\lambda(\lambda, \theta_i), \quad (3.30)
\]

where \( \rho'_\lambda(\lambda, \theta_i) \) is the spectral directional-hemispherical reflectivity. The direction of a reflected ray is then obtained from

\[
R_\rho = \frac{\varphi}{2\pi}, \quad (3.31)
\]

\[
R_\theta = \frac{2\pi}{\rho'_\lambda(\lambda, \lambda_i)} \int_0^{\pi/2} \rho''_\lambda(\lambda, \theta_i, \theta) \cos \theta \sin \theta \, d\theta. \quad (3.32)
\]

If condition (3.30) is not satisfied, the ray is absorbed and a local counter of rays absorbed by surface element \( A_i \), \( n_{a,i} \), is updated. After all \( n_{\text{rays}} \) rays have been traced, the net radiative heat transfer rates for surface and volume elements are calculated by

\[
q_{r,i} = \int_{A_i} \mathbf{q}_r'' \cdot \mathbf{n} \, dA = n_{a,i} \, q_{\text{ray}} - \int_{A_i} \varepsilon \sigma T^4 \, dA, \quad (3.33)
\]

\[
q_{r,j} = \int_{V_j} \nabla \cdot \mathbf{q}_r'' \, dV = n_{a,j} \, q_{\text{ray}} - \int_{V_j} 4 \kappa \sigma T^4 \, dV. \quad (3.34)
\]

Since the collision-based method in which the power of a single ray is constant from emission to termination is computationally relatively inefficient, a modified approach called absorption suppression is often applied to allow a single ray to have more than one collision location. Unlike in the basic collision-based method, the condition for absorption or scattering (3.27) is not checked. Instead, the power of a ray is multiplied by the scattering albedo and the ray continues travelling in a new scattering direction, obtained from the relations (3.28) and (3.29). The remaining power \( q_{\text{ray}}(1 - \omega) \) is absorbed by the medium at the location determined by Equation (3.26). The ray’s history is terminated when the cut-off condition is satisfied,

\[
\frac{q_{\text{ray}}}{q_{\text{ray,0}}} \leq \varepsilon, \quad (3.35)
\]
where $q_{\text{ray}}$ and $q_{\text{ray,0}}$ are the actual and initial power of the ray, respectively, and $\varepsilon$ is a small positive number designating the allowable cut-off error, $\varepsilon \ll 1$.

A further performance increase is possible when employing the pathlength method by allowing each ray to contribute continuously to every region it traverses. The power of an individual ray decreases along the path due to absorption. For a purely absorbing medium, the actual power of a ray is

$$q_{\text{ray,new}} = q_{\text{ray}} \exp \left( - \int_0^s \kappa(s^*) \, ds^* \right).$$

(3.36)

The power supplied to a medium region is

$$q_a = q_{\text{ray}} \left[ 1 - \exp \left( - \int_0^s \kappa(s^*) \, ds^* \right) \right].$$

(3.37)

If scattering is included, the ray redirection or ray splitting strategies are adopted [16]. The ray redirection approach has two options. In the first one, the power of a ray is calculated from the above equation. The collision distance and scattering are treated in the same manner as in the collision-based method except that the condition (3.27) is used only to check if the ray’s direction is to be changed or not due to scattering. No absorption occurs at the collision location since it is already included by the pathwise absorption. In the second option of the ray redirection approach, only the distance between scattering events is calculated,

$$\ln R_s = - \int_0^s \sigma_{s\lambda}(s^*) \, ds^*.$$  

(3.38)

The condition (3.27) is not checked. Instead, the ray is automatically redirected in the scattering direction. This option offers high speed-up for highly absorbing media.

The ray splitting approach improves the performance of Monte Carlo by allowing the pathwise attenuation and by launching new rays representing the scattered photons. The pathwise attenuation accounts for a decrease of the ray power due to both absorption and scattering. The power remaining in a ray that travelled distance $s$ within medium region of constant extinction coefficient, is

$$q_{\text{ray,new}} = q_{\text{ray}} \exp(-\beta\lambda s).$$

(3.39)

The power supplied to a medium region is then

$$q_a = q_{\text{ray}}(1 - \omega\lambda)[1 - \exp(-\beta\lambda s)].$$

(3.40)

Similarly, the scattered power cast into a new, split ray is given by

$$q_s = q_{\text{ray}} \omega\lambda[1 - \exp(-\beta\lambda s)].$$

(3.41)
3.2. Monte Carlo method for thermal radiation

The new ray is launched at an average location along path $s$ [16],

$$s_s = \frac{\int_0^s s^* \exp(-\sigma_s s^*) ds^*}{\int_0^s \exp(-\sigma_s s^*) ds^*}$$

$$= \frac{1}{\sigma_s} \left[ 1 - \sigma_s s \left( \frac{\exp(-\sigma_s s)}{1 - \exp(-\sigma_s s)} \right) \right].$$

(3.42)  (3.43)

Its direction is determined by using equations (3.28) and (3.29).

Rays histories are terminated in all pathlength methods if the cut-off condition, equation (3.35), is met. However, this condition introduces a systematic truncation error, but it can be minimised by subsequent execution of the basic collision-based method.

A modified Monte Carlo method for reducing the computing time and improving the convergence stability of iterative calculations without loosing the advantages of the conventional Monte Carlo method was proposed by Kobiyama [34]. In this method, the energy correcting rays are used for correcting the radiative energy difference between two successive iterative cycles, and the property correcting rays are used for correcting the radiative properties. The number of rays is proportional to the difference in emissive energy between two successive iterative cycles. A simplified variant of this method, which only applies to problems with constant properties, was employed in the simulation of transient radiation heat transfer in compound honeycomb transparent insulation by Schweiger et al. [70].

Another group of methods are the backward Monte Carlo techniques, based on the principle of reciprocity [12], in which rays are launched at a termination point and tracked in the reverse direction while power emitted along the path and incident on the termination point is determined. In contrast to the forward methods, backward methods are efficient for problems in which the radiative intensity hits only a small spot and/or is incident from a small range of solid angles [54].

In a multi-phase medium, different amounts of radiative power are emitted and absorbed by gas and particle phases. Such a situation is typical for solid-gas or liquid-gas mixtures like sprays, where the energy balance is performed for each phase separately, resulting in their different temperatures. Emission of each phase is calculated according to its properties and temperature. If the spectral line-by-line calculations are applied for gas phase, the mean free path length to attenuation is computed from

$$\ln R_s = - \int_0^s (\kappa_{\lambda g} + \beta_{\lambda p}) dS^*.$$  

(3.44)

In the basic collision-based method, condition (3.27) is checked at the location of attenuation for the scattering albedo given by Equation (2.62). If absorption takes
place, another condition is checked in order to determine if absorption is by the gas or by the particles. This condition reads

\[
\begin{align*}
R_K & \leq \frac{\kappa_{\lambda,g}}{\kappa_{\lambda,g} + \kappa_{\lambda,p}} \Rightarrow \text{absorption by gas}, \\
R_K & > \frac{\kappa_{\lambda,g}}{\kappa_{\lambda,g} + \kappa_{\lambda,p}} \Rightarrow \text{absorption by particles}.
\end{align*}
\] (3.45)

However, line-by-line calculations are impractical since high spectral resolution must be accounted for. Therefore, band models are used, which leads to lower spectral resolution. Implementation of the Monte Carlo method using the narrow band model in a two-phase absorbing medium was described by Modest [53]. Random number relations for the absorption path are derived, showing a difference in the path length for rays emitted by solid and gas.

### 3.2.1 Accuracy considerations

The Monte Carlo method as a sampling-based statistical solution technique produces results that have statistical errors. A given sample of size \( n_{\text{rays}} \) is split into a number of sub-samples of equal size \( n_{\text{rays},i} \), \( i = 1, 2, \ldots, n \), leading to \( n \) partial Monte Carlo results \( x_i \), which can be viewed as results of an experimental measurement series. From the central limit theorem, random measurement errors often follow the Gauss distribution. The measured values oscillate around the population mean \( \mu_x \) and their scattering around \( \mu_x \) is characterised by the population standard deviation \( \sigma_x \). Since the number of measurements \( n \) is finite, the whole population is not known, \( \mu_x \) and \( \sigma_x \) are estimated by the sample mean \( \bar{x} \) and the sample standard deviation \( S_x \), given by

\[
\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i, \quad (3.46)
\]

\[
S_x = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}. \quad (3.47)
\]

A \( P\% \) confidence interval, i.e. an interval into which the population mean falls with probability \( P \), is given by

\[
\left( \bar{x} - t_{\nu,P\%} \frac{S_x}{\sqrt{n}} : \bar{x} + t_{\nu,P\%} \frac{S_x}{\sqrt{n}} \right), \quad (3.48)
\]

where \( t_{\nu,P\%} \) designates a \( P\% \)-quantile from the Student \( t \)-distribution for \( \nu = n - 1 \) degrees of freedom.

The influence of the sample size on the solution accuracy can also be demonstrated by performing Monte Carlo simulations for two different sample sizes \( n_{\text{rays},1} \)
and \( n_{\text{rays},2} \), respectively, and calculating the relative difference between the results as

\[
\varepsilon_x = \left| 1 - \frac{x_1}{x_2} \right|.
\]  

(3.49)

While the first method based on the finite statistics quantifies errors so that results of different simulations can be compared, the method based on the relative difference represents a qualitative assessment.

### 3.3 Finite volume method

Finite volume method consists in direct discretisation in a physical space of conservation equations in their integral form by dividing the solution domain into a finite number of small control volumes. The computational mesh is defined by volume (cell) boundaries in contrast to the finite difference method, where the mesh is defined by nodal points. The method takes the advantage of an arbitrarily shaped mesh, which is formed by triangular and quadrilateral cells in two dimensions, and by tetrahedrals and hexahedrals in three dimensions. In general, it is applied for space discretisation of all Navier-Stokes equations. Recently, the method has become more popular in the field of radiation heat transfer, where it is used for direct discretisation of the equation of radiative transfer. It can be regarded as a generalisation of the discrete ordinates method by applying the finite volume discretisation to solid angles.

In this work, the finite volume method is used only for spatial discretisation of mass and energy conservation equations for quasi-continuous media, i.e. discontinuous media with physical properties averaged over a control volume. In order to illustrate the method without adding too much complexity at this time, it is applied to the energy equation of a single-component medium. The energy equation in integral form is given by [26]

\[
\frac{\partial}{\partial t} \int_V \rho U \, dV = - \int_A \left( q'' - \sigma \cdot v \right) \cdot \hat{n} \, dA + \int_V \left( q'' + \rho f_e \cdot v \right) \, dV, 
\]  

(3.50)

where \( U = u + v^2/2 \) is the total energy per unit mass, and \( u \) is the internal energy per unit mass. \( q'' \) is the total heat flux vector through a volume’s boundary \( A \), representing the sum of convective, conductive and radiative heat fluxes,

\[
q'' = \rho U v - k \nabla T + q_r''.
\]  

(3.51)

\( \sigma \) and \( f_e \) are the viscous stress tensor and the external force vector, respectively. For a medium at rest and without local volumetric heat sources \( q'' \), Equation (3.50) reduces to

\[
\frac{\partial}{\partial t} \int_V \rho u \, dV = \int_A \left( k \nabla T - q_r'' \right) \cdot \hat{n} \, dA.
\]  

(3.52)
The above equation can be rewritten as

\[
\frac{\partial}{\partial t} (\rho u V) = \int_A k \nabla T \cdot \hat{\mathbf{n}} \, dA - \int_V \nabla \cdot \mathbf{q}_r \, dV.
\]  

(3.53)

For small volume \( V \), which is constant in time, density can be assumed as constant over \( V \). The following approximations are introduced:

\[
\frac{\partial}{\partial t}(\rho u V) \approx \left( \frac{\partial \rho}{\partial t} \bar{u} + \rho \frac{\partial \bar{u}}{\partial t} \right) V, \tag{3.54}
\]

\[
\int_A k \nabla T \cdot \hat{\mathbf{n}} \, dA \approx \sum_i k \frac{\partial T}{\partial n_i} A_i. \tag{3.55}
\]

The volume integral from the divergence of the radiative flux is given by Equation (2.36). For instance, it can be approximately calculated by the Monte Carlo method as described in the previous section. The final form of the space-discretised equation reads

\[
\frac{dT}{dt} = \frac{1}{\rho c_v} \left[ \frac{1}{V} \left( \sum_i k \frac{\partial T}{\partial n_i} A_i + q_t \right) - \frac{\partial \rho}{\partial t} \bar{u} \right]. \tag{3.56}
\]

For a small time step interval \( \Delta t = t_{n+1} - t_n \) and a weak dependence of the density on state variables, the density can be assumed constant within \( \Delta t \). Integration over \( \Delta t \) leads to

\[
T^{n+1} = T^n + \int_{t_n}^{t_{n+1}} \frac{1}{\rho V c_v} \left( \sum_i k \frac{\partial T}{\partial n_i} A_i + q_t \right) dt. \tag{3.57}
\]

The integral on the right-hand side is computed by numerical schemes of time integration described in the next section.

### 3.4 Time integration schemes

Finding a solution to a time dependent problem requires, as seen in the previous section, a stepwise time integration of a function, whose complicated form often makes application of analytical methods impossible. Therefore, integration is carried out by employing numerical methods for resolution of unsteady problems called time integration schemes. In general, an initial value problem is considered [17]. It can be written as

\[
\frac{d\phi(t)}{dt} = f(t, \phi(t)), \quad \phi(t_0) = \phi^0. \tag{3.58}
\]

The solution \( \phi \) at time \( t_{n+1} \) is constructed by stepwise integration of Equation (3.58) over time step intervals \( \Delta t \),

\[
\int_{t_n}^{t_{n+1}} \frac{d\phi}{dt} \, dt = \phi^{n+1} - \phi^n = \int_{t_n}^{t_{n+1}} f(t, \phi(t)) \, dt, \tag{3.59}
\]
where the current initial condition \( \phi^n \) is the solution from the previous time step. The integral is calculated by approximate methods. The most popular are two level, predictor-corrector, multi-point, and Runge-Kutta schemes. General description of methods for solving the initial value problems, and in particular, used for integration in time, can be found in [17, 26, 79]. In this work, the following schemes are considered:

- explicit Euler,
  \[ \phi^{n+1} = \phi^n + f(t_n, \phi^n) \Delta t, \]  
  \( (3.60) \)

- implicit Euler,
  \[ \phi^{n+1} = \phi^n + f(t_{n+1}, \phi^{n+1}) \Delta t, \]  
  \( (3.61) \)

- Crank-Nicolson,
  \[ \phi^{n+1} = \phi^n + \frac{1}{2} \left[ f(t_n, \phi^n) + f(t_{n+1}, \phi^{n+1}) \right] \Delta t, \]  
  \( (3.62) \)

- second order Runge-Kutta,
  \[ \phi^{*n+1} = \phi^n + f(t_n, \phi^n) \frac{\Delta t}{2}, \]  
  \( (3.63) \)
  \[ \phi^{n+1} = \phi^n + f \left( t_{n+\frac{1}{2}}, \phi^{*n+\frac{1}{2}} \right) \Delta t, \]  
  \( (3.64) \)

- fourth order Runge-Kutta,
  \[ \phi^{*n+\frac{1}{2}} = \phi^n + f(t_n, \phi^n) \frac{\Delta t}{2}, \]  
  \( (3.65) \)
  \[ \phi^{**n+\frac{1}{2}} = \phi^n + f \left( t_{n+\frac{1}{2}}, \phi^{*n+\frac{1}{2}} \right) \frac{\Delta t}{2}, \]  
  \( (3.66) \)
  \[ \phi^{*n+1} = \phi^n + f \left( t_{n+\frac{1}{2}}, \phi^{*n+\frac{1}{2}} \right) \Delta t, \]  
  \( (3.67) \)
  \[ \phi^{n+1} = \phi^n + \left[ f(t_n, \phi^n) + 2f \left( t_{n+\frac{1}{2}}, \phi^{*n+\frac{1}{2}} \right) \right] \]  
  \[ + 2f \left( t_{n+\frac{1}{2}}, \phi^{**n+\frac{1}{2}} \right) + f \left( t_{n+1}, \phi^{*n+1} \right) \right] \frac{\Delta t}{6}. \]  
  \( (3.68) \)

The explicit Euler and both Runge-Kutta schemes are self-starting. They only require the initial condition \( \phi^0 \). The implicit Euler and Crank-Nicolson schemes require, in addition, value at level \( n + 1 \), which is found iteratively. For problems involving thermal radiation, function \( f \) contains the radiative heat rate \( q_r \), which is calculated at each time level and at every iteration. This leads to large computational times when the radiative term is obtained by the Monte Carlo method, but such a procedure can be applied in a straightforward manner to problems involving time-dependent radiative properties.
3.5 Parallel computing

The Monte Carlo method for radiative heat transfer requires in general large computational time. A large number of rays must be traced to achieve acceptable accuracy of the solution, especially in a multi-mode heat transfer analysis. Additional time requirements arise when MC is repeated within an iterative or transient solution and/or a high resolution of the spatial grid is used. The computational time can be reduced by applying an efficient MC approach, leading to improved accuracy for a smaller number of total rays. On the other hand, high-performance computing strategies such as parallelisation and algorithm optimisation help to shorten the execution time.

The use of high-performance computing methods in computational radiative transfer has steadily grown in recent years, which is coincident with the advancement in scientific computing in general. High-performance computing includes two categories: vector and parallel processing. The first one, vector processing, is based on the decomposition of a computation into operations that are performed on succeeding elements of a vector or matrix. The output of an operation is the input to the next operation. This allows computations for a new element to be launched before the processing of the previous element is completed. Unlike the vector processing, the parallel approach consists in performing operations or a group of operations by different processing units simultaneously. An efficient parallel implementation depends on the parallel programming approach and hardware architecture being used. Different parallel architectures like SPMD, SIMD, MIMD, shared and distributed memory are discussed in [16, 67]. The SPMD (single program multiple data) approach together with a domain decomposition paradigm discussed below, seems to be the simplest approach for parallelisation of a serial application. In SPMD, a program or its parts are run on different processing nodes instead of a single instruction, which contrasts to the case of the SIMD (single instruction multiple data) architecture. MIMD (multiple instruction multiple data) is characterised by performing different instructions sets on different data sets on each node. Shared memory systems consist of processing units that operate on the same data located in the shared memory. If separate memory is assigned to each processing node, it is called distributed memory architecture and is used in distributed computational environments like computer clusters. A critical issue in such systems is the efficient communication and data transfer between the nodes. Different message passing protocols like MPI (Message-Passing Interface) or PVM (Parallel Virtual Machine) are in common use today.

Among the three main parallelisation paradigms—domain decomposition, farming, and pipeling [16]—domain decomposition is the simplest one that can be easily used for parallelisation of Monte Carlo simulations. It involves distributing data to the various processor nodes and performing similar tasks on them. Other names for this paradigm are data parallelism and array processing, originating from the fact that arrays of data or calculations in loops are often split to each node. The Monte Carlo ray tracing for radiative heat transfer features many different forms of
3.6. Smoothing filters

Another possibility for improving accuracy of Monte Carlo solution is the application of low-pass filters to smooth noisy data. Terms Savitzky–Golay, least-squares, and digital smoothing polynomial filters refer to the same averaging procedure originally applied to smooth data in time domain, but they can be applied by analogy to smooth any equidistant one-dimensional data. Noisy values of a quantity $x$ are replaced by filtered ones, $x^f$, obtained as [67]

$$
x^f_i = \sum_{n=-n_L}^{n_R} c_n x_{i+n}, \quad (3.69)
$$

where $n_L$ is the number of points taken to the left of data point $i$, and $n_R$ is number of points taken to the right. The coefficients $c_n$ are derived by fitting a polynomial...
Figure 3.1: Example of a parallelisation concept for Monte Carlo based on MPI, applied to a transient simulation.
of degree $m$ in $i$ to the values $f_{-n_L}, \ldots, f_{n_R}$ with minimising the bias introduced by the filter [67]. In the simplest form, $m = 0$, the filtering procedure is called moving window averaging and it does not introduce any bias into results if the underlying function is constant or linear. In general, the low-pass filter will improve the quality of the Monte Carlo results if the spatial variation of the underlying function is much smaller than spatial noise level in the raw MC results.
Chapter 4

Transient analysis of a grey isotropic medium

The goal of this chapter is to conduct a series of numerical tests with the Monte Carlo method combined with several time integration schemes for the purpose of demonstrating the feasibility of the method to treat transient radiative heat transfer problems, and, of showing the qualitative interrelation between the accuracy of the Monte Carlo method, time integration schemes, and the combination of these numerical techniques. The accuracy of Monte Carlo combined with time integration schemes is determined by solving for the temperature distribution within a plane layer of a grey isotropic participating medium, and comparing the results with those obtained using a semi-analytical method.

A one-dimensional plane layer of a non-isothermal, absorbing, emitting, and isotropically scattering grey medium is considered (Figure 4.1). The medium is contained within black, plane boundaries at constant temperature $T_b$ and its initial temperature is $T_0$. The physical properties are listed in Table 4.1 and are assumed arbitrary and constant. Neglecting convection, conduction, pressure work, and internal heat generation, the general energy equation for a one-component medium (3.50) reduces to

$$pc_v \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q}_r,$$

where $\mathbf{q}_r$ is the radiative heat flux vector across the medium. Two approaches for finding the divergence of $\mathbf{q}_r$ are considered: (1) the semi-analytical method; and (2) the Monte Carlo method. The finite volume technique is employed in both approaches for spatial discretisation of Equation (4.1). In particular, for a one-dimensional geometry divided into a large number of sub-layers, each of the same thickness and at uniform temperature,

$$T_j^{n+1} = T_j^n + \int_{t_n}^{t_{n+1}} \frac{1}{\rho c_v \Delta z} \int_{z_{j-1}}^{z_j} \left(-\frac{\partial q_{r,z}}{\partial z}\right) \, dz \, dt,$$

where $j$ denotes a sub-layer of thickness $\Delta z = z_j - z_{j-1}$ and $\Delta t = t_{n+1} - t_n$ is the
4.1 The semi-analytical method

For an emitting, absorbing, and isotropically scattering plane medium, the radiative flux divergence derived analytically from the equation of radiative transfer can be written as \[ \frac{d q_r''}{dz} = 4 \frac{\kappa}{\omega} [\sigma T^4(z, t) - \pi S(z, t)]. \]

The source function can be expressed analytically as

\[ S(z, t) = (1 - \omega) \frac{\sigma T^4(z, t)}{\pi} \]

\[ + \frac{\omega}{2} \left\{ \frac{\sigma T^4_b}{\pi} [E_2(\tau) + E_2(\tau_L - \tau)] + \frac{\tau_L}{\tau} \left[ S(\tau^*, t) E_1(|\tau^* - \tau|) \right] \right\}, \]

where \( \tau = \tau(z) \) and \( \tau_L = \tau(L) \) are the optical thickness at \( z \) and \( L \), respectively, and \( E_n \) are the exponential integral functions \([11, 73]\). Inserting (4.3) into (4.2) and further assuming that the flux divergence and field variables are constant over each sub-layer, an expression for the temperature in each sub-layer is derived \([71, 72]\) as

\[ T^{n+1} = T^n + \frac{4 \kappa}{\rho c_v \omega} \int_{t_n}^{t_{n+1}} [\pi S(z, t) - \sigma T^4(z, t)] dt, \]

where spatial discretisation in sub-layers is omitted in the notation for simplicity. The temperature distribution is obtained using Equation (4.5), where the integral is computed using selected time integration schemes presented in §3.4: explicit Euler, implicit Euler, Crank-Nicolson, second-order Runge-Kutta, and fourth-order Runge-Kutta.

4.2 The Monte Carlo method

The integral of the divergence of the radiative flux over a sub-layer, shown in the right-hand side of Equation (4.2), represents the net radiative power absorbed by
that sub-layer, i.e. the difference between absorbed and emitted radiative power (see Equation (2.36)),

\[ q_{r,j} = \int_{z_{j-1}}^{z_j} \left( -\frac{\partial q_{r,z}''}{\partial z} \right) dz = q_a - q_e. \]  

(4.6)

In the case of a one-dimensional grey medium, Equation (3.34), used in the collision-based Monte Carlo method, which is implemented here, takes the form

\[ q_{r,j} = n_{a,j} q_{ray} - \int_{z_{j-1}}^{z_j} 4\kappa\sigma T^4 dV. \]  

(4.7)

Distribution functions for the direction of a ray emitted within a sub-layer are given by Equations (3.23) and (3.24). Since the medium is grey, there is no need to assign a wavelength to the emitted ray. The distance to a collision is found from a simplified form of Equation (3.26), which reads

\[ s = -\frac{1}{\beta} \ln R_s. \]  

(4.8)

Finally, the scattering direction is determined by using Equations (3.28) and (3.29). For the considered problem, the latter equation simplifies to

\[ R_\theta = \frac{1}{2} (1 - \cos \theta). \]  

(4.9)

Inserting Equation (4.6) into Equation (4.2) yields

\[ T^{n+1} = T^n + \frac{1}{\rho c_v \Delta z} \int_{t_n}^{t_{n+1}} (q_a - q_e) dt. \]  

(4.10)

At the boundaries, the diffuse fluxes emitted into the medium are

\[ q_{e,b_1}'' = -q_{e,b_2}'' = \epsilon_b \sigma T_b^4. \]  

(4.11)

Temperatures, and consequently, the total power emitted vary with time. In contrast, the total number of rays for each MC iteration is set constant with time. Thus, the power carried by each ray is calculated at each MC iteration as the ratio of the total power emitted to the total number of rays. The temperature distribution is obtained using Equation (4.10), where the integral is computed using the different time integration schemes presented in §3.4.
4.3 Results

The solution was obtained by the Monte Carlo method for samples containing $n_{\text{rays}} = 10^4, 10^5, \text{ and } 10^6$ rays, combined with the aforementioned time schemes for time steps $\Delta t = 2 \cdot 10^{-3}, 4 \cdot 10^{-3}, \text{ and } 8 \cdot 10^{-3}s$, with and without the smoothing filter. In addition, the semi-analytical method was applied using the fourth-order Runge-Kutta time integration scheme for $\Delta t = 10^{-3}s$, yielding the most accurate solution, referred to as the 'reference' solution. Common baseline parameters are listed in Table 4.1. Since for this specific example material properties are assumed constant with time, results are presented in a non-dimensional form

$$\tilde{z} = \frac{z}{L}, \quad (4.12)$$
$$\tilde{t} = \frac{4\sigma T_0^3}{\rho c_v L} t, \quad (4.13)$$
$$\tilde{T} = \frac{T}{T_0}. \quad (4.14)$$

Table 4.1: Baseline parameters used in the simulation of a grey isotropic medium

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_v$</td>
<td>720</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$L$</td>
<td>0.1</td>
<td>m</td>
</tr>
<tr>
<td>$L/\Delta z$</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>$T_0$</td>
<td>1000</td>
<td>K</td>
</tr>
<tr>
<td>$T_b$</td>
<td>300</td>
<td>K</td>
</tr>
<tr>
<td>$\epsilon_b$</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>10.7</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>9.3</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>2250</td>
<td>kg m$^{-3}$</td>
</tr>
</tbody>
</table>

Figure 4.2 shows the temperature profiles for the reference solution and for the filtered/unfiltered Monte Carlo results using $n_{\text{rays}} = 10^5$ with the fourth-order Runge-Kutta integration scheme. The unfiltered results are indicated by the dots scattered around the reference solution. Scattering increases as steady state is approached because for this particular problem the ratio of the absorbed to emitted power increases with time and the statistical Monte Carlo error originates mostly from $q_a$. The temperature profile for the filtered results coincides well with the reference curve.

The accuracy of the Monte Carlo method combined with time integration schemes is determined by calculating the error in the temperature profile based on the average relative difference between the actual and the reference solution,
Table 4.2: Parameters for the MC method

<table>
<thead>
<tr>
<th>Case</th>
<th>$n_{\text{rays}}$</th>
<th>$\Delta t$</th>
<th>Time integration scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$10^5$</td>
<td>0.28, 0.56, 1.12</td>
<td>explicit Euler</td>
</tr>
<tr>
<td>2</td>
<td>$10^5$</td>
<td>0.28, 0.56, 1.12</td>
<td>second-order Runge–Kutta</td>
</tr>
<tr>
<td>3</td>
<td>$10^5$</td>
<td>0.28, 0.56, 1.12</td>
<td>fourth-order Runge–Kutta</td>
</tr>
<tr>
<td>4</td>
<td>$10^4$, $10^5$, $10^6$</td>
<td>0.56</td>
<td>explicit Euler</td>
</tr>
<tr>
<td>5</td>
<td>$10^4$, $10^5$, $10^6$</td>
<td>0.56</td>
<td>second-order Runge–Kutta</td>
</tr>
<tr>
<td>6</td>
<td>$10^4$, $10^5$, $10^6$</td>
<td>0.56</td>
<td>fourth-order Runge–Kutta</td>
</tr>
</tbody>
</table>

according to

$$
\varepsilon_T(t) = \frac{1}{L} \int_0^L \left| 1 - \frac{T(z,t)}{T_{\text{ref}}(z,t)} \right| \, dz,
$$

(4.15)

where $T_{\text{ref}}$ denotes the temperature distribution obtained for the reference (semi-analytical) solution and $T$ the one obtained for the MC solution. This error is caused by the approximation in the time and space discretisation due to a finite time and space intervals, and by the statistical approximation due to a finite sample of rays. Space grid refinement was carried out until the error due to space discretisation could be neglected resulting in a space grid resolution $L/\Delta z = 250$. Figure 4.3 shows the error in the filtered MC solution, calculated by Equation (4.15), as a function of time for the cases listed in Table 4.2.

Obviously, the accuracy is improved with shorter time step intervals, larger samples of rays, and with the use of a filter. The explicit Euler scheme exhibited the best stability with longer time steps and minimum computational time. However, its first order accuracy leads to an unacceptable error in the early transient phase of about 20% for $n_{\text{rays}} = 10^5$ and $\Delta t = 1.12$. As expected, the fourth-order Runge–Kutta scheme gives the highest accuracy, with an error of less than 1% for $n_{\text{rays}} \geq 10^5$ and $\Delta t \leq 1.12$. Increasing the sample of rays by an order of magnitude decreases the error roughly by half an order of magnitude. The introduction of filters further improves the accuracy such that the error for $n_{\text{rays}} = 10^5$ and without filter is comparable to the one for $n_{\text{rays}} = 10^4$ and with filter. For the implicit Euler or the Crank-Nicolson schemes, the MC method does not converge for chosen range of time steps and sample sizes due to stochastic oscillations higher than the cut-off condition of iterative cycles. For the second-order or the fourth order Runge-Kutta schemes with $\Delta t \geq 1.12$, $n_{\text{rays}} \leq 10^4$ and without low-pass filter, the Monte Carlo method does not converge either.

The presented analysis demonstrates that the accuracy of the Monte Carlo method significantly influences the stability of the time integration process. However, no quantitative relations are derived for the purpose of the stability analysis. One of the major difficulties relies in the fact that there is no explicit expression for the net radiative power $q_r$ obtained by the Monte Carlo method. Even though, more general conclusions may be drawn after an additional test series for different values
Figure 4.2: Temperature profiles calculated by the ‘reference’ semi-analytical method and by the filtered and unfiltered MC method using $n_{\text{rays}} = 10^5$ and the fourth-order Runge–Kutta time integration scheme.

Figure 4.3: Error of the MC method (cases are listed in Table 4.2).
of the scattering albedo and optical thickness, but this topic is not further covered here in favour of moving to more complex physical problems involving thermal radiation in reacting media, presented in the next chapters.

As long as the procedure combining the Monte Carlo method with numerical time integration is followed, the generalisation of the solution method to problems involving time-dependent radiative properties is straightforward and only requires the additional computation of these properties at each time level. In Chapters 7 and 8, the filtering procedure and the Monte Carlo parallelisation technique applied to a transient simulation are adapted to model the transient behaviour of non-grey and anisotropically scattering media with an improved solution quality and shortened computational time. The explicit Euler scheme is chosen as a basic time integration technique in the following chapters due to its best stability and lowest implementation effort.
Chapter 5

Model chemical reactions

This chapter describes model chemical reactions used in the transient radiative heat transfer analyses of chemically reacting media, presented later in this work. Kinetic parameters and rate equations are given for the thermal decomposition of calcium carbonate and steam gasification of coal. Both chemical reactions have great significance in industrial applications, and, as endothermic processes, are attractive for the solar thermal applications.

5.1 Thermal decomposition of calcium carbonate

The basic chemistry of the calcination process, detailed in a number of references [10, 25, 62], can be described by the reaction

\[ \text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g). \]  

(5.1)

It proceeds endothermically above 1200 K at atmospheric pressure. Its enthalpy change, when the reactants are initially at 298 K and the products are at 1200 K, is 270 kJ mol\(^{-1}\). The significance of the reaction (5.1) relies in its wide range of industrial applications. Calcium oxide is widely used in construction and building, iron and steelmaking processes, water and sewage treatment, agriculture and the food industry, and fine chemicals production.

The reaction takes place on a definite boundary between the calcium carbonate core and the layer of porous lime formed outside it. The boundary moves towards the centre of the particle as the reaction progresses. The reaction rate was found to be controlled by the transfer of heat to the boundary and by the diffusion of CO\(_2\) away from it [25].

The reaction kinetics for CaCO\(_3\) powder with particle size in the 1–5 μm range is well described by the contracting area rate law, which proved universally applicable [21]. It reads

\[ \frac{dX}{dt} = k(1 - X)^{0.5}, \]  

(5.2)
where $X$ is the reaction extent, defined as

$$X = 1 - \frac{n_{CaCO_3}}{n_{0,CaCO_3}}.$$  

(5.3)

The temperature dependency of the reaction rate constant $k$ is determined by imposing an Arrhenius-type equation,

$$k = k_0 \exp \left( \frac{E_a}{RT} \right).$$  

(5.4)

The rate of weight loss of the CaCO$_3$ powder was studied by thermogravimetric dynamic measurements. The apparent activation energy and frequency factor obtained by linear regression are $E_a = 156.8 \text{ kJ mol}^{-1}$ and $k_0 = 7.24 \cdot 10^4 \text{s}^{-1}$, respectively [77]. The kinetic parameters were also found for samples with particle size in the 2–3 mm range. Thermogravimetric investigations were performed with the Carrara limestone [48]. The measurements were conducted with 400 mg samples under ideal conditions for different gaseous atmospheres (pure air; and a mixture of N$_2$ with varying CO$_2$ content) at a heating rate of 10 K min$^{-1}$ and air mass flow 100 ml min$^{-1}$. As expected, the results changed when the carrier gas was enriched with CO$_2$. The results for the dilute case, i.e. no CO$_2$ in the gas phase, are shown in Figure 5.1. The kinetic parameters in the Arrhenius equation were determined again by fitting the data to the rate equation (5.2). The apparent activation energy and the pre-exponential factor obtained by linear regression are $E_a = 187.3 \text{ kJ mol}^{-1}$ and $k_0 = 6.45 \cdot 10^5 \text{s}^{-1}$, respectively.
5.2 Coal gasification under direct irradiation

It is known that, additionally to the composition of the gaseous atmosphere, the sample weight, the shape of the crucibles, the heating rate, etc., influence the kinetic parameters [46, 69]. As a consequence, discrepancies between experimental results and those obtained from modelling using kinetic parameters from a single thermogravimetric measurement are to be expected. Furthermore, the rate of the decomposition reaction under direct irradiation is expected to vary from that one in thermogravimetric measurements due to substantially different heat and mass transfer conditions.

The chemical approach to the interpretation of the exponential dependence of the rate of thermal decomposition of solids on temperature has been transferred from the kinetics of homogeneous reactions without appropriate theoretical validation [42]. Thus, the kinetic parameters in the Arrhenius equation (5.4) have lost their original physical meaning. As an alternative, the physical approach based on the Hertz–Langmuir prediction of the proportional dependence of the evaporation rate on the equilibrium partial pressure of the vapour, which depends exponentially on temperature, has been developed and applied to the quantitative interpretation of some important features of crystolysis reactions and identification of decomposition mechanisms for several classes of solids [42, 43, 44, 45].

5.2 Coal gasification under direct irradiation

Another chemical reaction considered in this work is the steam gasification of coal.\(^1\) It is a complex process, but the overall chemical conversion for a complete reaction can be represented by the simplified net reaction

\[
C_1H_xO_y + (1 - y) H_2O = \left(\frac{x}{2} + 1 - y\right) H_2 + CO,
\]

where \(x\) and \(y\) are the elemental molar ratios of H/C and O/C in coal, respectively, e.g. \(x = 0.43, y = 0.03\) for anthracite; \(x = 0.81, y = 0.23\) for lignite. The chemical product is synthesis gas (syngas), whose quality depends on \(x\) and \(y\). The coal gasification reaction is of great importance for energy technology because of the overall efficiency improvement of the electricity generation and reduction of pollutants emission when the synthesis gas instead of solid coal is used as a fuel. A further application is the synthesis of various chemicals such as ammonia and methanol. The thermodynamics aspects of the solar coal gasification have been previously examined by v. Zedtwitz and Steinfeld [91].

The kinetic modelling is based on the analysis of elementary reaction mechanisms describing reversible adsorption/desorption processes and irreversible surface chemistry, derived by Müller et al. [60]. Assuming plug flow conditions and pseudo first-order reactions, a set of simplified rate laws is formulated to describe the for-

\(^1\)This section contains material developed by R. Müller within the framework of his master's thesis [59, 60].
Chapter 5. Model chemical reactions

Figure 5.2: Arrhenius plots for the thermal gasification of coal under direct irradiation: (a) $K_1\alpha$, (b) $K_2\alpha$, and (f) $K_3$.

The reaction rate of gaseous species $i$ for heterogeneous surface reaction is defined as

$$ r_i'' = \frac{1}{A} \frac{dn_i}{dt} = \frac{1}{m_C a} \frac{dn_i}{dt}, $$

where $A$ is the active surface area and $a$ the mass specific active surface area that includes pores. The reaction rates are normalised to the mass of coal by multiplying
Table 5.1: Reaction kinetics parameters for the Arrhenius rate law [60]

<table>
<thead>
<tr>
<th>$E_{a,l}/(kJ \ mol^{-1})$</th>
<th>Pre-exponential factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1a$</td>
<td>163.8</td>
</tr>
<tr>
<td>$K_2a$</td>
<td>-405.5</td>
</tr>
<tr>
<td>$K_3$</td>
<td>-480.7</td>
</tr>
</tbody>
</table>

Equations (5.6)–(5.9) by $a$,

\[
    r_i = \frac{a}{A} \frac{dn_i}{dt} = \frac{1}{m_C} \frac{dn_i}{dt}. \tag{5.11}
\]

The partial pressures are calculated assuming ideal gases,

\[
    p_i = \frac{\dot{n}_i}{\sum_j \dot{n}_j}. \tag{5.12}
\]

The system of four coupled differential equations (5.6)–(5.9) was solved numerically by iterating on the values of $K_i$, $i = 1, 2, 3$, to minimise the difference between theoretically calculated and experimentally measured molar flow rates of products. The experimental data was collected using a fluidised bed reactor of coal particles in steam, directly exposed to concentrated thermal radiation [60]. The temperature dependence of each $K_i$ is determined by imposing an Arrhenius-type rate law,

\[
    K_i = K_{i,0} \exp \left( \frac{-E_{a,i}}{RT} \right). \tag{5.13}
\]

The results are shown in Figure 5.2. The apparent activation energies and corresponding pre-exponential factors are listed in Table 5.1. Since the $K_i$ represent complex reaction mechanisms rather than elementary steps, negative values are possible. Finally, the rate of decomposition of coal particles is obtained by mass balance on carbon,

\[
    r_C = -r_{CO} - r_{CO_2}. \tag{5.14}
\]
Chapter 6

Packed bed of large reacting particles

The present chapter describes experimental investigations with calcium carbonate particles conducted at ETH's high-flux solar simulator and a three-dimensional transient heat transfer model that links conduction, convection, and radiation heat transfer to the chemical kinetics. The thermal decomposition of calcium carbonate, which is selected here as a model chemical reaction, is described in §5.1. The model is formulated using wavelength and chemical composition dependent material properties assuming the Rosseland diffusion approximation for the internal radiative transport. Monte Carlo ray tracing is employed to obtain the radiative flux distribution at the boundaries. The unsteady energy equation is solved by finite volume technique and by explicit Euler time integration scheme. The model is validated by comparing the computed temperature and reaction extent variation with time to the values experimentally measured.\footnote{This chapter contains material partially developed by M. Gächter within the framework of his semester thesis [20].} It is an example of an approximate treatment of the radiative heat transfer in reacting media. More sophisticated problems, to which the methodology introduced in Chapter 3 and §4.2 is applied, are analysed in Chapters 7 and 8.

6.1 Direct irradiation experimental set-up

The high-flux solar simulator provides a rapid external source of intense thermal radiation, mostly in the visible and IR spectrum [28]. It consists of a high-pressure argon arc enclosed in a quartz envelope of 27 mm diameter, 1.5 mm thickness and 200 mm length. The maximum electrical power input to the tungsten-made electrodes is, according to specifications, 200 kW DC under a maximum electrical current of 700 A. The arc envelope is internally cooled by using a swirling film of de-ionised water that rapidly flows between the plasma arc and the quartz lamp tube. The source is close-coupled to precision optical reflectors to produce an intense beam of concentrated radiant energy. The focusing mirrors are horizontal-axis troughs of elliptical cross section having a vertical major axis, and are positioned with one of
the linear foci coinciding with the arc. The focal plane of the solar simulator is thus defined as the horizontal plane perpendicular to the ellipse's major axis containing the second linear focus. The elliptical mirrors are truncated 9.2 cm above the focal plane to permit external access, so that the reflected beam-down radiation is confined within an angular range of half-angle 45°. With this arrangement, power fluxes exceeding 4500 kW m\(^{-2}\) are attained at the focal plane. Power, power fluxes, and temperature can be adjusted to meet the specific requirements by simply varying the electrical input power to the arc electrodes. Power flux intensities are measured optically with an absolute point radiometer, with an estimated error of ±6.5%.\(^2\)

The experimental set-up is shown in Figure 6.1. A 100 mm-length, 20 mm-width and 3.7 mm-height prism made of CaCO\(_3\) particles was positioned on top of a 200 mm-length, 148 mm-width and 17 mm-depth refractory SiC plate, and mounted at the focal plane of the solar simulator. Thermocouples of type K were used to measure temperatures of the plate and plate-sample interface at various locations, as indicated in Figure 6.1. Their exact location is listed in Table 6.1. Samples were irradiated at constant power fluxes during controlled intervals of time, weighed before and after each run to determine their mass loss, and finally completely calcined in an electrical furnace after each run to verify their degree of calcination.

---

\(^2\)See Appendix A for the description of the calibration procedure of the solar simulator.
Table 6.1: Location of temperature measurements points (see Figure 6.1)

<table>
<thead>
<tr>
<th>Measurement point</th>
<th>x/mm</th>
<th>y/mm</th>
<th>z/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{p_1}$</td>
<td>50</td>
<td>0</td>
<td>3.7</td>
</tr>
<tr>
<td>$T_{p_2}$</td>
<td>0</td>
<td>0</td>
<td>3.7</td>
</tr>
<tr>
<td>$T_{p_3}$</td>
<td>0</td>
<td>10</td>
<td>3.7</td>
</tr>
<tr>
<td>$T_{p_4}$</td>
<td>0</td>
<td>74</td>
<td>12.2</td>
</tr>
<tr>
<td>$T_{p_5}$</td>
<td>0</td>
<td>74</td>
<td>20.7</td>
</tr>
</tbody>
</table>

6.2 Heat transfer model

The system domain is defined as the sum of two sub-systems: the CaCO$_3$-prism sample plus the plate, as indicated in Figure 6.1. Thus, the system is bounded by 11 planes. The general energy conservation law for a differential solid applied to each sub-system is given by

$$\frac{\partial U}{\partial t} = -\nabla \cdot \mathbf{q}'' + q''', \quad (6.1)$$

where $U$ is the internal energy per unit volume, $\mathbf{q}''$ is the heat flux vector, and $q'''$ is the heat sink/source per unit volume. For the sample, $U = \rho_{\text{CaCO}_3} u_{\text{CaCO}_3} + \rho_{\text{CaO}} u_{\text{CaO}}$, and for the plate, $U = \rho_{\text{SiC}} u_{\text{SiC}}$, $u$ being the specific internal energy. The boundary conditions for the sample are:

- at the upper surface of the sample

$$-(1 - p)k_{c,s} \frac{\partial T_s}{\partial n} \bigg|_{w} - pkr \frac{\partial T_a}{\partial n} \bigg|_{w} = q'' + q_{cv} - q_a'', \quad (6.2)$$

- at the sample-plate interface

$$-(1 - p)k_{c,s} \frac{\partial T_s}{\partial n} \bigg|_{w} - pkr \frac{\partial T_s}{\partial n} \bigg|_{w} = q''_{\text{total,int}}, \quad (6.3)$$

- at all other free surfaces of the sample

$$-(1 - p)k_{c,s} \frac{\partial T_s}{\partial n} \bigg|_{w} - pkr \frac{\partial T_s}{\partial n} \bigg|_{w} = q_e'' + q_{cv}'', \quad (6.4)$$

where $q_e''$, $q_{cv}''$, and $q_a''$ are the heat fluxes by emission, natural convection and absorption, respectively. $p$ designates the sample's porosity.

The boundary conditions for the plate are

- at the upper free surface of the plate

$$-k_{c,p} \frac{\partial T_p}{\partial n} \bigg|_{w} = q_e'' + q_{cv}'' - q_a'', \quad (6.5)$$
at the plate-sample interface

\[ k_{c,p} \frac{\partial T_p}{\partial n} \bigg|_w = q''_{\text{total,int}} + q''_r, \quad (6.6) \]

at all other free surfaces of the plate

\[ -k_{c,p} \frac{\partial T_p}{\partial n} \bigg|_w = q''_e + q''_{cv}. \quad (6.7) \]

where \( q''_{\text{total,int}} \) and \( q''_r \) are the total heat flux between the sample and plate at their interface and the heat flux transmitted through the sample, respectively.

The set of boundary and initial conditions is closed by setting the free stream temperature around the system \( T_\infty \), and the initial temperature within the system \( T_0 \).

We now proceed to the derivation of the heat fluxes by radiation, convection, and conduction for each sub-system. The local distribution of the radiative heat flux in the focal plane of the solar simulator was modelled by Monte Carlo ray tracing [66]. The spectral distribution is assumed equivalent to Planck’s blackbody distribution at 5780 K, which corresponds to an approximation of the solar spectrum. Radiation incident on the upper surface of the sample undergoes absorption, reflection, and transmission. Thus, for the sample

\[ q''_{\text{in}} = q''_a + q''_{\text{refl}} + q''_r, \quad (6.8) \]

\[ q''_a = q''_{\text{in}} (\epsilon_{\lambda_1-\lambda_2} F_{0-\lambda_1} T_{\text{source}} + \epsilon_{\lambda_2-\lambda_3} F_{\lambda_2} T_{\text{source}} - \lambda_3 T_{\text{source}} + \ldots + \epsilon_{\lambda_n-\infty} F_{\lambda_n} T_{\text{source}} - \infty), \quad (6.9) \]

where the grey band approximation of the hemispherical spectral emissivity has been employed. Similarly, for the plate, neglecting transmission,

\[ q''_{\text{in}} = q''_a + q''_{\text{refl}}, \quad (6.10) \]

\[ q''_a = q''_{\text{in}} (\epsilon_{\lambda_1-\lambda_2} F_{0-\lambda_1} T_{\text{source}} + \epsilon_{\lambda_2-\lambda_3} F_{\lambda_2-\lambda_3} T_{\text{source}} - \lambda_3 T_{\text{source}} + \ldots + \epsilon_{\lambda_n-\infty} F_{\lambda_n} T_{\text{source}} - \infty), \quad (6.11) \]

The radiative flux emitted by the surface at \( T \) is

\[ q''_e = \sigma T^4 (\epsilon_{0-\lambda_1} F_{0-\lambda_1} T + \epsilon_{\lambda_1-\lambda_2} F_{\lambda_1} T - \lambda_2 T + \ldots + \epsilon_{\lambda_n-\infty} F_{\lambda_n} T - \infty). \quad (6.12) \]

Inside the sample, the total heat flux has two components,

\[ q''_{\text{total}} = (1 - p) q''_c + p q''_r, \quad (6.13) \]

where \( q''_c \) is the portion transferred by conduction, \( q''_r \) is the one transferred by radiation. Using Fourier’s law, the conductive heat transfer through the sample is given by

\[ q''_c = -k_{c,\text{r}} \nabla T. \quad (6.14) \]
The radiative heat transfer inside the porous sample is determined assuming the Rosseland diffusion approximation for an optically thick medium [73], and

\[ q''_r = -k_r \nabla T, \quad (6.16) \]

where \( k_r \) is calculated using the grey band approximation by

\[
k_r = -\frac{4}{3} \sigma T^3 \left\{ \frac{1}{K_{0-\lambda_1}} \left[ 4F_{0-\lambda_1}T + \frac{15}{\pi^4} \frac{\zeta_1^3}{e^{\zeta_1^3} - 1} \right] + \frac{1}{K_{\lambda_1-\lambda_2}} \left[ 4F_{\lambda_1-\lambda_2}T - \frac{15}{\pi^4} \left( \frac{\zeta_2^3}{e^{\zeta_2^3} - 1} - \frac{\zeta_1^3}{e^{\zeta_1^3} - 1} \right) \right] \right. \\
+ \left. \frac{1}{K_{\lambda_n-\infty}} \left[ 4F_{\lambda_n-\infty} - \frac{15}{\pi^4} \frac{\zeta_n^3}{e^{\zeta_n^3} - 1} \right] \right\}, \quad (6.17)
\]

with \( \zeta = C_2/\lambda T \).

Similarly, the total heat flux between the sample and plate at their interface is

\[ q''_{\text{total, int}} = (1 - p_{\text{int}})q''_{\text{int}} + p_{\text{int}}q''_{r, \text{int}}, \quad (6.18) \]

where \( p_{\text{int}} \) stands for the sample porosity at the interface zone, which is higher than the average porosity of the sample due to the particles' spherical shape. The convection heat transferred at the sample-plate interface is

\[ q''_{\text{int}} = h_{\text{int}} (T_{s,w} - T_{p,w}). \quad (6.19) \]

The portion transferred by radiation through the pores at the sample-plate interface is

\[
q''_{r, \text{int}} = \frac{F_{0-\lambda_1}T_{s,w}T_{s,w}^4}{1} - \frac{F_{0-\lambda_1}T_{p,w}T_{p,w}^4}{1} - 1 \\
+ \frac{F_{\lambda_1-\lambda_2}T_{s,w}T_{s,w}^4}{1} - \frac{F_{\lambda_1-\lambda_2}T_{p,w}T_{p,w}^4}{1} - 1 \\
+ \ldots + \frac{F_{\lambda_n-\infty}T_{s,w}T_{s,w}^4}{1} - \frac{F_{\lambda_n-\infty}T_{p,w}T_{p,w}^4}{1} - 1, \quad (6.20)
\]

where \( T_{s,w} \) and \( T_{p,w} \) are the temperatures at the boundaries of the two materials. Computation of natural convection at the exposed surfaces of both sample and plate has been carried out using the following correlations for natural convection at flat surfaces [32]:

- for top surfaces \( (L = A/P) \)
  \[
  \overline{N}_L = 2.52, \quad \text{for } Ra_L < 10^4, \quad (6.21)
  \overline{N}_L = 0.54 Ra_L^{1/2}, \quad \text{for } 10^4 \leq Ra_L < 10^7, \quad (6.22)
  \overline{N}_L = 0.15 Ra_L^{1/2}, \quad \text{for } 10^7 \leq Ra_L < 10^{11}, \quad (6.23)
  \]
6.3. Methodology

The finite volume method was employed for a discretised domain. Integration of Equation (6.1) over the finite volume \( V_j \) and time interval \( \Delta t = t_{n+1} - t_n \) yields

\[
\int_{t_n}^{t_{n+1}} \int_{V_j} \frac{\partial U}{\partial t} \, dV \, dt = \int_{t_n}^{t_{n+1}} \int_{V_j} \nabla \cdot q'' \, dV \, dt + \int_{V_j} q''' \, dV \, dt. \tag{6.29}
\]

For \( V_j \) small and \( \Delta t \) short, \( \rho \) and \( c_v \) are constant. Moreover, for a solid \( c_v \approx c_p \). Substituting all terms in their discretised form and solving for \( T \), yields

\[
T_j^{n+1} = T_j^n + \frac{\Delta t}{\rho_j^n c_p j} \left( \sum_{l_j} q'' \bigg|_{l_j} \cdot A_{lj} + q_j^n \right), \tag{6.30}
\]

where \( l_j \) and \( A_{lj} \) designate a face of cell \( j \) and its surface, respectively. \( q_j^n \) is the heat sink given by Equation (6.28). For the structured hexahedral mesh employed

- for the bottom surface of the plate \( (L = A/P) \)
  \[
  \tilde{Nu}_L = 4.8, \quad \text{for } Ra_L < 10^5, \tag{6.24}
  \]
  \[
  \tilde{Nu}_L = 0.27 Ra_L^{\frac{1}{4}}, \quad \text{for } 10^5 \leq Ra_L < 10^{10}, \tag{6.25}
  \]

- for vertical surfaces \( (L = H) \)
  \[
  \tilde{Nu}_L = \left\{ 0.825 + \frac{0.387 Ra_L^{\frac{1}{4}}}{1 + \left( \frac{0.492}{Pr} \right)^{\frac{1}{8}}} \right\}^2, \tag{6.26}
  \]

with properties of air evaluated at the average boundary layer temperature. The convective flux is then obtained from

\[
q'' = \frac{\tilde{Nu} k_{c, \text{air}}}{L} (T_w - T_\infty). \tag{6.27}
\]

Finally, the energy sink due to chemistry in the sample is given by

\[
q_{ch} = \Delta H_f^{\circ} \frac{dn_{\text{CaCO}_3}}{dt} = -\Delta H_f^{\circ} \frac{dX}{dt} n_{0, \text{CaCO}_3}, \tag{6.28}
\]

where \( \Delta H_f^{\circ} \) and \( X \) are the standard reaction enthalpy and the extent of the calcination reaction, respectively. The rate equation and the kinetic parameters \( E_a \) and \( k_0 \) of the calcination reaction for particle size range 2–3 mm are given in Chapter 5. \( q_{ch} \) is set to zero in the plate.
Chapter 6. Packed bed of large reacting particles

here, \( l \) takes the values \( t, b, e, w, n, s \), which mean top, bottom, east, west, north, and south as typical in the finite volume method. The heat fluxes through cell faces may be of radiative, convective, or conductive in nature. They are evaluated at each time step \( n \) using Equations (6.8)-(6.27). The solution begins by setting the initial conditions in the whole domain,

\[
T_s = T_0, \\
T_p = T_0. 
\]

(6.31)

(6.32)

The new temperature field is then computed using Equation (6.30). The temperature at the boundaries are calculated as a function of the already computed heat fluxes and temperatures using Equations (6.2)-(6.7). For example, the temperature at \( t \)-face of cell \( j \) laying directly at the top surface of the sample is calculated using

\[
T_{t_j}^{n+1} = T_{t_j}^n + \frac{\Delta z}{2 k_{t,j}^n} q''_{t_j}^n, 
\]

(6.33)

where

\[
k_{t,j}^n = (1 - p) k_{c,j}^n + pk_{r,j}^n, 
\]

(6.34)

and the net heat flux through the top face of cell \( j \) at time step \( n \) is

\[
q''_{t_j}^n = q_{cv,t_j}^n + q_{e,t_j}^n + q_{a,t_j}^n. 
\]

(6.35)

Since the material properties of the sample and the plate are functions of temperature, they are also evaluated at each time step. Further, the material properties of the sample are functions of its composition, which in turn changes with time. Thus, the \( \rho, c_p, k, \) and \( \epsilon \) of cell \( j \) at time step \( n \) are, respectively,

\[
\rho_j^n = \frac{n_{CaCO_3,j} M_{CaCO_3} + \left( n_{0, CaCO_3,j} - n_{CaCO_3,j} \right) M_{CaO}}{V_j}, 
\]

(6.36)

\[
c_{p,j}^n = \frac{n_{CaCO_3,j} C_{p, CaCO_3,j} + \left( n_{0, CaCO_3,j} - n_{CaCO_3,j} \right) C_{p, CaO,j}}{\rho_j^n V_j}, 
\]

(6.37)

\[
k_{c,j}^n = \frac{k_{CaCO_3,j} n_{CaCO_3,j} M_{CaCO_3} + k_{CaO,j} \left( n_{0, CaCO_3,j} - n_{CaCO_3,j} \right) M_{CaO}}{\rho_j^n V_j}, 
\]

(6.38)

\[
\epsilon_{\lambda,j}^n = \begin{cases} 
\left[ \frac{n_{CaCO_3,j} - n_{0, CaCO_3,j}}{n_{0, CaCO_3,j} X_\epsilon} \right] \epsilon_{\lambda, CaCO_3} \\
\left( \frac{n_{0, CaCO_3,j} - n_{CaCO_3,j}}{n_{0, CaCO_3,j} X_\epsilon} \right) \epsilon_{\lambda, CaO}, & \text{for } X < X_\epsilon, \\
\epsilon_{\lambda, CaO}, & \text{for } X \geq X_\epsilon.
\end{cases} 
\]

(6.39)
### Table 6.2: Baseline parameters used in the calculation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{p,CaCO_3}$</td>
<td>$104.52 + 21.92 \cdot 10^{-3}T - 2.59 \cdot 10^6T^{-2}$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$C_{p,p,CaO}$</td>
<td>$50.42 + 4.18 \cdot 10^{-3}T - 0.85 \cdot 10^6T^{-2}$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$C_{p,p,SiC}$</td>
<td>$10.997 \ln T - 30.213$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$E_a$</td>
<td>$187.3 \cdot 10^3$</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$g$</td>
<td>$0.5$</td>
<td>–</td>
</tr>
<tr>
<td>$k_0$</td>
<td>$4 \cdot 10^5$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$k_{c,CaCO_3}$</td>
<td>$2.5$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$k_{c,CaO}$</td>
<td>$0.8$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$k_{c,SiC}$</td>
<td>$10$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$m_{\theta,CaCO_3}$</td>
<td>$10^{-2}$</td>
<td>kg</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$0.44$</td>
<td>–</td>
</tr>
<tr>
<td>$\rho_{int}$</td>
<td>$0.55$</td>
<td>–</td>
</tr>
<tr>
<td>$t$</td>
<td>$1800$</td>
<td>s</td>
</tr>
<tr>
<td>$X_c$</td>
<td>$0.657$</td>
<td>–</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$336$</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>$2 \cdot 10^{-2}$</td>
<td>s</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>$5 \cdot 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta y$</td>
<td>$4 \cdot 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta z$</td>
<td>$1.23 \cdot 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>$\epsilon_{\lambda,CaCO_3}$</td>
<td>$0.16$ for $\lambda \leq \lambda_c$, $0.84$ for $\lambda &gt; \lambda_c$</td>
<td>–</td>
</tr>
<tr>
<td>$\epsilon_{\lambda,CaO}$</td>
<td>$0.38$ for $\lambda \leq \lambda_c$, $0.62$ for $\lambda &gt; \lambda_c$</td>
<td>–</td>
</tr>
<tr>
<td>$\epsilon_{SiC}$</td>
<td>$0.92$</td>
<td>–</td>
</tr>
<tr>
<td>$\lambda_c$</td>
<td>$2.4 \cdot 10^{-6}$</td>
<td>m</td>
</tr>
<tr>
<td>$\rho_{SiC}$</td>
<td>$2700$</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>$5 \cdot 10^{-2}$</td>
<td>–</td>
</tr>
</tbody>
</table>

The extinction coefficient $\beta$ is evaluated for attenuation by large diffuse spheres as (see §2.4.2)

$$\beta = \kappa + \sigma_s = \pi R_p^2 N_p,$$  \hspace{1cm} (6.40)

where $N_p$ is the number of particles of radius $R_p$ per unit volume. As it can be seen in the above equation, $\beta$ does not depend on physical properties of particle's material. Since $N_p$ and $R_p$ remain constant during the reaction, the number of particles is given by

$$N_p = \frac{3(1 - p)}{4\pi R_p^2}.$$  \hspace{1cm} (6.41)

Substituting in Equation (6.40),

$$\beta = \frac{3(1 - p)}{4R_p}. \hspace{1cm} (6.42)$$
measured x-direction 200 A
measured x-direction 300 A
measured y-direction 200 A
measured y-direction 300 A

Figure 6.2: Flux distribution along the x- and y-axis at the focal plane of the high-flux solar simulator for arc currents 200 and 300 A: optically measured values (data points) and calculated curves using Monte-Carlo ray-tracing.

For a mean particle radius $R_p = 1.25 \times 10^{-3}$ m and a sample porosity $p = 0.44$, $\beta = 336$ m$^{-1}$. For the calculation of radiative and conductive fluxes across the cell boundaries, the mean $k_c$ and $k_r$ between adjacent cells are taken as

$$k_{c,j+\frac{1}{2}}^n = \frac{k_{c,j}^n + k_{c,j+1}^n}{2}, \quad (6.43)$$

$$k_{r,j+\frac{1}{2}}^n = \frac{k_{r,j}^n + k_{r,j+1}^n}{2}. \quad (6.44)$$

6.4 Theoretical and experimental results

Table 6.2 on page 53 shows the baseline parameters used in the calculation. Experimental runs were performed with arc currents of 200 and 300 A. The measured and calculated power flux distributions at the focal plane, along the x and y directions, are shown in Figure 6.2. The Monte Carlo numerical results fit well to the measured values. A slight deviation and asymmetry lie within the error of the measurements. The uncertainty in the Monte Carlo results was calculated by splitting the sample of rays into $n = 10$ sub-samples as discussed in §3.2.1. The maximal absolute uncertainty in the calculated radiative flux at the focal plane was found at $x = -1.75$ and $y = 0$ cm, $q''_r = 675.54 \pm 1.85$ kW m$^{-2}$ ($P = 95\%$, $\nu = 9$), whereas the maximal relative uncertainty was found at $x = -8.75$ and $y = -6$ cm as equal to 2.45%.

Figure 6.3 shows the extent of the chemical reaction as a function of time, measured and calculated. For the case with 200 A, the computed curve for the reaction progress agrees well with the measured one, but differ by 25% at the beginning and 14% at $X = 0.5$, where the reaction rate peaks. For the case with 300 A, the predicted curve agrees well with the single measurement. Table 6.3 lists the relative
6.4. Theoretical and experimental results

Figure 6.3: Overall extent of the reaction as a function of time for arc currents 200 and 300 A: measured values (data points) and calculated curves.

Table 6.3: Relative uncertainty in the measurements of reaction extent $X_{ov}$ ($P = 95\%$, $\nu = 2$) and relative difference between calculated and measured values as a function of time for the case with 200 A

| $t$/s | Uncertainty/% | $|1 - (x_{cal}/x_{meas})|$/% |
|-------|----------------|-----------------------------|
| 300   | 72.61          | 24.57                       |
| 600   | 12.53          | 13.89                       |
| 900   | 1.42           | 3.20                        |
| 1200  | 5.80           | 1.12                        |
| 1500  | 10.90          | 0.37                        |
| 1800  | 7.67           | 0.57                        |

Figure 6.4: Time-dependent relative heat losses from the system (sample plate) to the environment due to reflection, emission, and natural convection. Also indicated is the absorbed radiative power.

Table 6.4: Relative difference $|1 - T_{cal}/T_{meas}|$, in $\%$, between measured and calculated temperatures at various locations (see Table 6.1 and Figure 6.1) as a function of the calculated reaction extent for the case with 200 A

<table>
<thead>
<tr>
<th>$t$/s</th>
<th>$X_{ov,meas}$</th>
<th>$T_{P1}$</th>
<th>$T_{P2}$</th>
<th>$T_{P3}$</th>
<th>$T_{P4}$</th>
<th>$T_{P5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.07</td>
<td>1.01</td>
<td>0.52</td>
<td>3.04</td>
<td>7.73</td>
<td>5.01</td>
</tr>
<tr>
<td>600</td>
<td>0.51</td>
<td>0.15</td>
<td>2.05</td>
<td>1.93</td>
<td>4.61</td>
<td>1.84</td>
</tr>
<tr>
<td>1500</td>
<td>0.99</td>
<td>0.86</td>
<td>1.08</td>
<td>1.96</td>
<td>4.82</td>
<td>2.17</td>
</tr>
<tr>
<td>1800</td>
<td>0.99</td>
<td>1.02</td>
<td>0.86</td>
<td>2.13</td>
<td>5.20</td>
<td>2.20</td>
</tr>
</tbody>
</table>
Figure 6.5: Calculated and measured variation of temperatures with time for (a) \( T_{p_1} \), (b) \( T_{p_2} \), (c) \( T_{p_3} \), (d) \( T_{p_4} \), and (e) \( T_{p_5} \).
uncertainty in the measurements and the relative difference between calculated and measured values as a function of time for the case with 200 A. The calculated and measured variation of temperatures with time at different plate locations are shown in Figure 6.5 for cases with arc currents 200 and 300 A. In general, the agreement is reasonably good and Table 6.4 shows the relative difference between calculated and measured values at $X_{\text{ov,meas}} = 0.07, 0.51,$ and $0.99$ for the case with 200 A. The differences are believed to be mainly the result of discrepancies between the real material properties ($C_p, k,$ and $\epsilon$) of the actual experimental system and those employed in the modelled system that were extracted from the literature [8, 82, 83, 84]. Furthermore, the spectrum of the emitted radiation by the solar simulator differs from that of a blackbody at 5780 K, which was applied in the model. Moreover, the diffusion approximation is strictly valid only for optically thick media ($\tau \gg 1$), and the values of the optical thickness related to $\Delta x$, $\Delta y$, and $\Delta z$ are, respectively, 1.68, 1.34, and 0.41. As discussed in §5, kinetic parameters taken originally from thermogravimetric measurements lead to further discrepancies between the experimental and theoretical results. Hence, the model parameters were modified, which resulted in better agreement of the results. The pre-exponential coefficient, originally equal to $6.45 \cdot 10^5 \text{s}^{-1}$, was reduced to $4 \cdot 10^5 \text{s}^{-1}$. This can be partially justified by the fact that the original value was measured in the absence of CO$_2$ in the streaming gas under forced convection conditions, which was in the favour of the chemical reaction. On the contrary, the removal of CO$_2$ from the sample in the solar simulator experiments was only due to natural convection and under atmospheric conditions. Finally, the heating rate was different in thermogravimetric and solar experiments.

A sensitivity analysis revealed that the strongest temperature variation was observed when varying either the emissivities of both materials or the distribution of the incoming flux.

As far as heat losses from the system (sample + plate) to the environment are concerned, Figure 6.4 shows the calculated time-dependent percentage of the incident power lost either by radiation (both emission and reflection) and by natural convection. As expected, the radiative losses are dominant and about six times higher than the convective ones.

6.5 Summary

In this chapter, a three-dimensional model that links thermal radiation, conduction, and natural convection heat transfer to the chemical reaction is applied for a packed bed of calcium carbonate particles undergoing thermal decomposition under direct irradiation. The model uses the Monte Carlo ray tracing technique for determining the radiative flux at boundaries and the finite volume method and the explicit Euler scheme for solving the unsteady energy equation including the volumetric heat sink due to the chemical reaction. The internal radiative flux is obtained based on the Rosseland diffusion approximation for optically thick media. This model enables one to treat non-isothermal non-grey chemical systems involving optically thick media
with a time dependent chemical composition.
Chapter 7

Suspension of small reacting particles

A suspension of small particles directly exposed to concentrated thermal radiation and undergoing chemical transformation is analysed in this chapter. The system domain is depicted schematically in Figure 7.1. The particle suspension is modelled as a non-isothermal, non-grey, absorbing, emitting, and anisotropically scattering layer surrounded by black plane boundaries at 0 K (non-participating surroundings). Each particle is assumed isothermal (a good approximation for \( \text{Bi}_c = \sigma T^3 e d_p / k \ll 1 \)), spherical (a generally good assumption for most irregularly shaped and randomly oriented particles), and having independent scattering (as justified by referring to independent/dependent scattering regime map, as given by Tien et al. [81]—see Figure 2.1 on page 12—for the range of particle volume fractions and size parameters used in this study). For simplification, the gas phase is assumed to be a non-participating medium. For the purpose of better elucidating the physical phenomena involved in the pure interaction of radiation with the chemical reacting particles, convection and conduction are omitted from consideration. Two cases are examined: (1) non-shrinking particles, i.e., particle diameter remains constant with time; and (2) shrinking particles, i.e., particle diameter decreases with time. In both cases the composition of each particle varies with time as the reaction progresses. The first
case is typical for heterogeneous reactions in which a solid reactant decomposes into solid and gaseous products. The reaction may be formulated as

$$A(s) \rightarrow B(s) + C(g).$$

(7.1)

To this group belongs the reaction of the thermal decomposition of calcium carbonate, given by Equation (5.1). The latter case is typical for reactions in which a solid decomposes into gaseous products only,

$$A(s) \rightarrow B(g) + C(g).$$

(7.2)

An example of a chemical reaction of this type is the thermal decomposition of zinc oxide [58]. The model of shrinking particles also applies to the reaction of steam coal gasification, described §5.2 and further analysed in Chapter 8.

In this chapter, the influence of the particle models on thermal behaviour of the irradiated suspension is investigated. For the purpose of comparing the models, the physical properties of species A, B, and C, and the rate equation of the decomposition reaction are taken the same in both cases as those of the calcium carbonate decomposition with the kinetic parameters for particles in the 1–5 μm range, given in §5.1.

### 7.1 Radiative properties

Absorption and scattering efficiency factors and the phase function for Mie scattering were calculated by applying the Fortran subroutine BHMIE [9] for a given size parameter $x = \pi d/\lambda$ and complex refractive index $m_\lambda = n_\lambda + ik_\lambda$ (see §2.4.1). Since incident and emitted radiation in the presented model is confined mostly in the visible and infrared spectra, the statistically active range of particle size parameters falls within $0.3 < x < 40$. The complex refractive index of pure calcium carbonate, $m_\lambda$, was extracted from literature [63] and its real and imaginary parts are shown
as a function of wavelength in Figure 7.2. Pure CaCO$_3$ is transparent in the wavelength range 0.2–6.25 μm, $k_{0.2-6.25\mu m} = 0$, but the value of $k_{0.2-6.25\mu m}$ was increased to account for possible mineral impurities such as MgO, SiO$_2$, and Al$_2$O$_3$ [62]. The effect of varying $k_{0.2-6.25\mu m}$ is examined in the following analysis. For simplification, the influence of the reaction progress on the complex refractive index of particle material is omitted from analysis. The absorption and scattering coefficients were calculated by using Equations (2.39) and (2.40).

7.2 Mass and energy conservation

7.2.1 Case 1—non-shrinking particles

At a given time $t$, a particle consists of a mixture of solids A and B, but, according to Equation (7.1), the total number of moles is conserved,

$$n_p = n_{0,A} = n_A + n_B.$$ (7.3)

Making use of the contracting geometry rate law, given by Equation (5.2), and applied here as the model rate equation, the decomposition rate of solid A is

$$r_A = \frac{dn_A}{dt} = -n_{A,0} k \left( \frac{n_A}{n_{A,0}} \right)^{0.5}.$$ (7.4)

Its integration yields the actual amount of A at time $t$,

$$n_A = n_{A,0} + \int_{t_0}^{t} r_A dt.$$ (7.5)

For a solid particle under constant pressure, the energy balance may be expressed as enthalpy balance. Neglecting conduction and convection heat transfer,

$$\frac{d(n_A h_A + n_B h_B)}{dt} = q_r - r_C h_C,$$ (7.6)

where $q_r$ is the net radiative power supplied to the particle. Assuming each particle being isothermal, the expression for the particle temperature is derived,

$$T_p = T_{p,0} + \int_{t_0}^{t} \frac{(q_r - r_A h_A - r_B h_B - r_C h_C)}{C_p,A n_A + C_p,B n_B} dt.$$ (7.7)

7.2.2 Case 2—shrinking particles

The gaseous product B is assumed to be removed from the system as soon as it is produced. Thus, according to Equation (7.2),

$$n_p = n_A = n_{A,0} - n_B.$$ (7.8)
The particle diameter at time $t$ is

$$d_p = \left[ \frac{6M_A n_A}{\pi \rho_A} \right]^{\frac{1}{3}}. \quad (7.9)$$

Applying energy conservation and accounting for the enthalpy removed from the system by products B and C,

$$\frac{d(n_A h_A)}{dt} = q_r - r_B h_B - r_C h_C, \quad (7.10)$$

which leads to the expression for the particle temperature,

$$T_p = T_{p,0} + \int_{t_0}^{t} \frac{(q_r - r_A h_A - r_B h_B - r_C h_C)}{C_{p,A} n_A} \, dt. \quad (7.11)$$

The initial conditions for both cases are:

- for the mass conservation equation

$$n_p(t = 0) = n_{0,A} = \rho_A V_p, \quad (7.12)$$

$$d_p(t = 0) = d_0, \quad (7.13)$$

- for the energy conservation equation

$$T_p(t = 0) = T_0. \quad (7.14)$$

The mass and energy conservation equations do not explicitly require boundary conditions since convection and conduction heat transfer are omitted from consideration. However, evaluation of $q_r$, which is an essential part of the conservation of energy, requires that the spectral and directional characteristics of incident radiative flux be specified at the boundaries. This is achieved implicitly by specifying the temperature and radiation properties of the surroundings (0 K, black), and explicitly by defining any additional fluxes at the boundaries. The boundary conditions for both cases are:

$$T_{\text{surr}} = 0, \quad (7.15)$$

$$\epsilon_{\text{surr}} = 1, \quad (7.16)$$

$$q^\prime\prime_{\text{in,b}}(0, t) = q_{\text{in,b1}} \hat{k}, \quad (7.17)$$

$$q^\prime\prime_{\text{in,b}}(L, t) = 0. \quad (7.18)$$

The incident collimated flux $q_{\text{in,b1}}$ has the spectral distribution of a blackbody at temperature $5780$ K—to simulate concentrated solar power—and is perpendicular to the boundary.
7.3 Numerical solution

The one-dimensional suspension was treated as a quasi-continuous medium, divided into a number of homogeneous sub-layers \( V_j \). The explicit Euler scheme was used to discretise the time integrals of mass and energy conservation equations. The temperature, composition, and properties of the particle suspension are assumed to be constant over each sub-layer. In both cases (1) and (2), the mole number of A in sub-layer \( j \) at time step \( n+1 \) is, in discretised form,

\[
n_A|^{n+1}_j = n_A|^{n}_j + r_A|^{n}_j \Delta t.
\]  

The discretised equation for temperature of sub-layer \( j \) takes the form:

- for case (1), from Equation (7.7),

\[
T_j^{n+1} = T_j^n + \left( \frac{q_t - r_A h_A - r_B h_B - r_C h_C}{C_{p,A} n_A + C_{p,B} n_B} \right)^n_j \Delta t,
\]  

- for case (2), from Equation (7.11),

\[
T_j^{n+1} = T_j^n + \left( \frac{q_t - r_A h_A - r_B h_B - r_C h_C}{C_{p,A} n_A} \right)^n_j \Delta t.
\]

The net radiative power to the finite volume \( V_j \) at time step \( n \), \( q_r|^{n}_j \), is calculated by the forward collision-based Monte Carlo method (see §3.2).

### Table 7.1: Baseline parameters used in the calculation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{p,A} )</td>
<td>( 104.52 + 21.92 \cdot 10^{-3} T - 2.59 \cdot 10^6 T^{-2} )</td>
<td>J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>( C_{p,B} )</td>
<td>( 50.42 + 4.18 \cdot 10^{-3} T - 0.85 \cdot 10^6 T^{-2} )</td>
<td>J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>( C_{p,C} )</td>
<td>( 51.13 + 4.37 \cdot 10^{-3} T - 1.47 \cdot 10^6 T^{-2} )</td>
<td>J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>( d_0 )</td>
<td>( 5 \cdot 10^{-6} )</td>
<td>m</td>
</tr>
<tr>
<td>( f_{v,0} )</td>
<td>( 10^{-5} )</td>
<td>–</td>
</tr>
<tr>
<td>( L )</td>
<td>0.1</td>
<td>m</td>
</tr>
<tr>
<td>( L/\Delta z )</td>
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<td>–</td>
</tr>
<tr>
<td>( n_{rays} )</td>
<td>( 2 \cdot 10^6 )</td>
<td>–</td>
</tr>
<tr>
<td>( g_{in,b1} )</td>
<td>( 10^6 )</td>
<td>W m(^{-2})</td>
</tr>
<tr>
<td>( T_0 )</td>
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<td>K</td>
</tr>
<tr>
<td>( T_{surr} )</td>
<td>0</td>
<td>K</td>
</tr>
<tr>
<td>( T_{source} )</td>
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<td>K</td>
</tr>
<tr>
<td>( \Delta t )</td>
<td>( 10^{-3} ) for case (1)</td>
<td>s</td>
</tr>
<tr>
<td>( 2.5 \cdot 10^{-4} ) for case (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \rho_A )</td>
<td>2500</td>
<td>kg m(^{-3})</td>
</tr>
</tbody>
</table>
7.4 Results

Baseline parameters are listed in Table 7.1 and are used for each run unless stated otherwise. The total simulation time for the reaction was set to 3s.

Calculated temperatures are shown in Figure 7.3. The transient variation of the temperature at the first sub-layer, directly exposed to the external radiation source ($z/L = 1.67 \cdot 10^2$), is shown in Figure 7.3a for both cases. This layer is heated to above 1550 K in less than 0.5 s. After this heating phase, the temperature for case (1) further increases monotonically because of less energy consumption by the endothermic reaction as the reaction rate decreases with time. It reaches 1593 K after 3 s. In contrast, for case (2), the temperature peaks at 1582 K after 0.73 s and then decreases as a result of the decreasing absorption coefficient, which in turn depends on the ratio of volume fraction to particle diameter, as discussed in the following analysis. Additionally, the profile for case (2) reveals an oscillatory character due to oscillations in the absorption coefficient. Temperature profiles across the layer at $t = 0, 0.1, 1, 2, \text{ and } 3$ s are shown in Figure 7.3b. For case (2), the temperature distribution becomes more uniform with time because of the decreasing optical thickness as the particles shrink. The maximal temperature across the layer was obtained at $z/L = 0.58$ for case (1) at $t = 0.1, 1, 2, \text{ and } 3$ s.

Predicted reaction extents defined as $X = 1 - n_A/n_{0,A}$ are shown in Figure 7.4. Figure 7.4a shows the overall reaction extent, integrated over the entire layer, as a function of time for both cases. It reaches 95% and 77% after 3 s for cases (1) and (2), respectively. Obviously, case (2) results in a lower reaction rate because of the less efficient absorption as the medium becomes optically thinner. Figure 7.4b shows the reaction extent profile across the layer at $t = 0, 1, 2, \text{ and } 3$ s for both cases. In case (2), the reaction peaks at $z/L = 0.58$ due to the highest temperature at this location. The reaction extent in case (2) exhibits oscillations across the layer because of the spatial oscillations in the temperature.

The influence of the imaginary part of the complex refractive index in the wavelength interval $0.2-6.25 \mu m$ and of the particle volume fraction $f_v$ on the total reaction extent is summarised in Table 7.2. $X_{ov}$ increases with increasing $k_{0.2-6.25 \mu m}$. In addition, the temperature gradient across the layer significantly increases with increasing $f_v$, which results in more inhomogeneous reaction extent across the layer.

Table 7.2: Overall reaction extent $X_{ov}$ in % for case (1) at $t = 3$ s and for different values of $k_{0.2-6.25 \mu m}$ and $f_v$

<table>
<thead>
<tr>
<th>$f_v$</th>
<th>$10^{-4}$</th>
<th>$4 \cdot 10^{-4}$</th>
<th>$5 \cdot 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-5}$</td>
<td>0.3</td>
<td>76</td>
<td>95</td>
</tr>
<tr>
<td>$5 \cdot 10^{-5}$</td>
<td>33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$7.5 \cdot 10^{-5}$</td>
<td>66</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 7.3: (a) Transient variation of temperature of the first sub-layer. (b) Temperature profiles across the layer at $t = 0, 0.1, 1, 2$ and $3\,s$. Case (1): non-shrinking particles; case (2): shrinking particles.

Figure 7.4: (a) Overall reaction extent $X_{ov}$ as a function of time. (b) Reaction extent $X$ across the layer at $t = 0, 1, 2$, and $3\,s$. Case (1): non-shrinking particles; case (2): shrinking particles.
Chapter 7. Suspension of small reacting particles

Figure 7.5: Absorption and scattering efficiency factors at $\lambda = 0.5 \mu m$ as a function of particle diameter.

Figure 7.6: Absorption and scattering coefficients as a function of time for the first sub-layer at $\lambda = 0.5$ and $1.85 \mu m$.

Figure 7.7: Scattering phase function for the first sub-layer at $t = 0$ and $3 s$, and at $\lambda = 0.5$ and $1.85 \mu m$.

Figure 7.8: Transient variation of the overall reflectance $R$, absorptance $A$, and transmittance $T$ for the suspension of shrinking particles.
7.4. Results

The effect that shrinking particles have on the optical thickness of the layer can also be observed in Figures 7.5 and 7.6. Absorption and scattering efficiency factors at $\lambda = 0.5\,\mu m$ are shown in Figure 7.5 as a function of the particle diameter. While $Q_{a,\lambda}$ increases with increasing diameter, $Q_{s,\lambda}$ remains approximately constant. Both factors reveal the oscillatory character of the Mie theory, which would be averaged in a polydispersion [9, 52].

Absorption and scattering coefficients are shown in Figure 7.6 for the first sub-layer. Curves are plotted for two wavelengths: 0.5 and 1.85 $\mu m$, which correspond to the peaks of the Planck’s spectral emissive power at 5780 K and 1570 K, respectively, simulating the temperature of the external radiation source (solar) and of reactor walls. Both coefficients decrease with time due to the decreasing ratio of the volume fraction to diameter as the particles shrink. Furthermore, the decreasing time-averaged absorption efficiency factor enhances the decrease in the time-averaged absorption coefficient.

The time-dependent size parameter also results in a time-dependent scattering phase function, shown in Figure 7.7 for the first sub-layer at $t = 0$ and 3 s. Scattering is predominantly forward, but back-scattering is enhanced with increasing time and wavelength.

Finally, for case (2), the transient behaviour of the overall reflectance, absorptance, and transmittance of the particle suspension is shown in Figure 7.8. Transmittance—initially at 0.92—increases by 5% after 3 s. Reflectance and absorptance—initially at 0.06 and 0.02, respectively,—decrease after 3 s by 50 and 73%, respectively.

7.4.1 Error estimation

The error in the temperature and reaction extent caused by the time discretisation and by the statistical character of the Monte Carlo method was assessed for case (1) by varying the time step ($\Delta t = 10^{-3}$ and $5 \cdot 10^{-4}$ s) and the number of rays ($n_{\text{rays}} = 2 \cdot 10^6$ and $10^7$). The relative differences in the temperature and reaction extent were calculated by (see §3.2.1)

$$
\varepsilon_T(z, t) = \left| 1 - \frac{T(z, t)}{T_{\text{ref}}(z, t)} \right| \cdot 100\%,
$$

(7.22)

$$
\varepsilon_X(z, t) = \left| \frac{X(z, t) - X_{\text{ref}}(z, t)}{1 - X_{\text{ref}}(z, t)} \right| \cdot 100\%,
$$

(7.23)

where the subscript ‘ref’ denotes the reference case with baseline parameters. The maximal relative difference in the temperature was $\varepsilon_T = 0.18\%$ (at $z/L = 9.83 \cdot 10^{-1}$ and $t = 5 \cdot 10^{-3}$ s) when varying $\Delta t$, and $\varepsilon_T = 0.14\%$ (at $z/L = 1.67 \cdot 10^{-2}$ and $t = 10^{-3}$ s) when varying $n_{\text{rays}}$. The maximal relative difference in the reaction extent was $\varepsilon_X = 2\%$ (at $z/L = 5.17 \cdot 10^{-1}$ and $t = 3$ s) when varying $\Delta t$, and $\varepsilon_X = 1.23\%$ (at $z/L = 5.17 \cdot 10^{-1}$ and $t = 3$ s) when varying $n_{\text{rays}}$. 
7.5 Summary

In this chapter, the methodology for solving a general unsteady radiative heat transfer problem including spectral and directional variation of radiative properties, introduced in §4.2 for a grey and isotropic medium, has been applied to a suspension of reacting particles. The models for non-shrinking and shrinking particles were compared in terms of the temperature, reaction extent, and optical properties of the suspension. The comparison of the two cases shows that radiation absorption is superior in the non-shrinking particle case resulting in higher attained temperatures and a higher reaction rate. In the shrinking particle case, radiative properties vary strongly with time as the reaction progresses due to their strong dependence on the size parameter. The reaction rate is lower because of the less efficient absorption as the size parameter decreases and the medium become optically thinner.

The time-dependent particle size has a significant influence on the unsteady radiative heat transfer within a monodispersion, and therefore, on its transient characteristics. The results show the necessity of taking this effect into consideration in order to correctly predict the conditions under which a solar chemical reaction is conducted. Examples of such chemical reactions include the thermal decomposition of zinc oxide and the thermal gasification of coal.
Chapter 8

Application to coal gasification

The shrinking particle model developed in the previous chapter for small reacting particles is now applied to both small and large coal particles undergoing endothermic gasification. Radiative properties are predicted from the Mie scattering theory and from the laws of geometric optics for the small and large particles, respectively. In addition to the methodology based on the quasi-continuous modelling, an alternative approach employing a direct ray tracing of randomly located spheres is presented.

The general model constraints are very similar to those made for the suspension of reacting particles described in the previous chapter. The suspension is submerged in non-participating surroundings (0 K, black). Monodispersed particles are isothermal and have independent scattering. The host medium is assumed to be non-participating. Convection and conduction heat transfer are omitted from the analysis.

The kinetics of the steam coal gasification reaction under direct irradiation is described in Chapter 5. The reaction rates for the involved species (H₂O, H₂, CO, and CO₂) are given by Equations (5.6)–(5.9). The time-dependent particle size due to the gasification process has an impact on both the radiative properties and the active surface area of a particle.

8.1 Mie-scattering particles

The radiative properties of the particle suspension are obtained in this case as described in §7.1 except that the complex refractive index $m_\lambda$ is taken for propane soot [13]. Its real and imaginary parts were interpolated linearly and are plotted as a function of wavelength in Figure 8.1.

8.1.1 Mass and energy conservation equations

The rate of decomposition of coal particles, given by Equation (5.14), is

$$r_C = -r_{CO} - r_{CO_2}. \quad (8.1)$$
The actual number of carbon moles is obtained by integrating the rate equation,

\[ n_C = n_{0,C} + \int_{t_0}^{t} m_C r_C \, dt, \quad (8.2) \]

and the actual diameter of a spherical particle at time \( t \)—compare Equation (7.9)—is

\[ d_p = \left( \frac{6 M_C n_C}{\pi \rho_C} \right)^{\frac{1}{3}}. \quad (8.3) \]

Applying energy conservation and accounting for the enthalpy change of \( C \) in the solid phase and of \( H_2, H_2O, CO \) and \( CO_2 \) in the gas phase,

\[ \frac{d(n_C h_C)}{dt} = q_r - m_C (r_{H_2} h_{H_2} + r_{H_2O} h_{H_2O} + r_{CO} h_{CO} + r_{CO_2} h_{CO_2}), \quad (8.4) \]

where \( q_r \) is the net radiative power supplied to the particle. For an isothermal particle, the expression for the particle temperature is derived as

\[ T_p = T_{p,0} + \int_{t_0}^{t} \left( q_r - m_C \sum_i r_i h_i \right) \frac{dt}{C_{p,C} n_C}. \quad (8.5) \]

where \( i = H_2, H_2O, CO \) and \( CO_2 \). The initial conditions for the mass conservation equation are the initial composition and diameter of every particle,

\[ n_p(t = 0) = n_{C,0} = \frac{\rho_C V_{p,0}}{M_C}, \quad (8.6) \]

\[ d_p(t = 0) = d_0. \quad (8.7) \]

The initial condition for the energy conservation equation is the initial temperature of every particle,

\[ T_p(t = 0) = T_0. \quad (8.8) \]
8.1. Mie-scattering particles

Table 8.1: Baseline parameters used for the coal particle suspension

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p,c$</td>
<td>$0.11 + 38.94 \cdot 10^{-3} T - 0.15 \cdot 10^6 T^{-2}$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$C_p,co$</td>
<td>$30.96 + 2.44 \cdot 10^{-3} T - 0.28 \cdot 10^6 T^{-2}$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$C_p,co_2$</td>
<td>$51.31 + 4.37 \cdot 10^{-3} T - 1.47 \cdot 10^6 T^{-2}$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$G_{p,co_2}$</td>
<td>$26.88 + 3.59 \cdot 10^{-3} T + 0.11 \cdot 10^6 T^{-2}$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$C_p,H_2$</td>
<td>$50.42 + 4.18 \cdot 10^{-3} T - 0.85 \cdot 10^6 T^{-2}$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$C_{p,H_2O}$</td>
<td>$2.5 \cdot 10^{-6}, 5 \cdot 10^{-6}$ and $7.5 \cdot 10^{-6}$</td>
<td>m</td>
</tr>
<tr>
<td>$f_{v,0}$</td>
<td>$10^{-5}$</td>
<td>–</td>
</tr>
<tr>
<td>$L$</td>
<td>0.1</td>
<td>m</td>
</tr>
<tr>
<td>$L/\Delta z$</td>
<td>30</td>
<td>–</td>
</tr>
<tr>
<td>$n_{rays}$</td>
<td>$2 \cdot 10^6$</td>
<td>–</td>
</tr>
<tr>
<td>$q_{b_1}$</td>
<td>$2 \cdot 10^6$</td>
<td>W m$^{-2}$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>$3 \cdot 10^{-4}$ for $d_0 &gt; 2.5 \cdot 10^{-6}$ m</td>
<td>s</td>
</tr>
<tr>
<td>$T_0$</td>
<td>298.15</td>
<td>K</td>
</tr>
<tr>
<td>$T_b$</td>
<td>0</td>
<td>K</td>
</tr>
<tr>
<td>$T_{source}$</td>
<td>5780</td>
<td>K</td>
</tr>
<tr>
<td>$\rho_C$</td>
<td>815</td>
<td>kg m$^{-3}$</td>
</tr>
</tbody>
</table>

The boundary conditions for the evaluation of $q_r$ for an externally irradiated plane medium surrounded by black and cold boundaries, are given by Equations (7.15)–(7.18)

$$T_{surr} = 0,$$  \hspace{1cm} (8.9)

$$\epsilon_{surr} = 1,$$  \hspace{1cm} (8.10)

$$q''_{in,b}(0, t) = q_{in,b_1} \hat{k},$$  \hspace{1cm} (8.11)

$$q''_{in,b}(L, t) = 0.$$  \hspace{1cm} (8.12)

The incident collimated flux $q''_{b_1}$ has the spectral distribution of a blackbody at temperature 5780 K and is perpendicular to the boundary.

8.1.2 Numerical solution

The numerical solution employed here follows that one described in §7.3. The discretised equations for the actual number of carbon moles and temperature, Equa-
tions (8.2) and (8.5) respectively, of sub-layer j at time step $n + 1$ are

$$
\begin{align*}
n_{C,j}^{n+1} &= n_{C,j}^{n} + (mC_r_{C})_{j}^{n} \Delta t, \\
T_{j}^{n+1} &= T_{j}^{n} + \left[ \frac{(q_{i} - mC \sum_{i} r_{i}h_{i})}{C_{p,j}n_{C}} \right]_{j}^{n} \Delta t.
\end{align*}
$$

The net radiative power $q_{i}$ to each elemental volume $V_{j}$ is calculated at every time step $n$ by the Monte Carlo ray tracing.

### 8.1.3 Results

A set of numerical simulations was conducted for parameters listed in Table 8.1. The total simulated reaction time was 5 s. Figure 8.2 shows the temperatures obtained. The variation of the temperature of the first sub-layer, which is directly exposed to the incoming flux, with time is shown in Figure 8.2a for three values of the initial particle diameter: 2.5, 5, and 7.5 μm. For all three cases, this first sub-layer is rapidly heated and reaches peak temperature levels of 1910, 1826, and 1802 K within 0.005, 0.01, and 0.012 s, respectively. Afterwards, the temperature decreases slightly as a result of two competing phenomena: less heat absorption due to decreasing absorption coefficient, as it will be shown in the following discussion, and less heat consumption by the endothermic reaction due to decreasing reaction rate. The temperature distribution across the suspension after various reaction times is shown in Figure 8.2b. While after 0.003 s the highest temperature was obtained in the first sub-layer, the peak switched to the sixth sub-layer after 0.009 s. The temperature profile becomes more uniform with time as the optical thickness of the medium decreases.

The reaction extent for the coal gasification reaction is defined as $X = 1 - \frac{n_{C}}{n_{C,0}}$. The overall reaction extent $X_{ov}$ is shown in Figure 8.3a as a function of time for various initial particle diameters. Figure 8.3b shows the local reaction extent $X$ as a function of location for various reaction times. The fastest conversion occurs for $d_{0} = 2.5 \mu m$ because of the corresponding higher temperatures (as seen in Figure 8.2a). After 5 seconds, the reaction extent reaches 83, 72, and 69% for the three initial particle diameters 2.5, 5, and 7.5 μm, respectively. Figure 8.3b indicates that the reaction extent for $d_{0} = 5 \mu m$ is maximum at the sixth sub-layer ($z/L = 0.183$), where it reaches 77% after 5 s, because of the highest temperature at this location.

The radiation properties of the suspension are shown in Figures 8.4–8.8. Figure 8.4 shows the absorption and scattering efficiency factors as a function of the particle diameter for $\lambda = 0.5$ and 1.8 μm, which correspond to the peaks of the blackbody spectral emissive power at 5780 (solar radiation) and 1600 K (typical reactor wall temperature). For particle sizes in the range $10^{-6}$–$10^{-5} \text{m}$, the absorption efficiency factor decreases with particle diameter while the scattering efficiency factor remains constant. The curves cross each other, implying that $\omega > 0.5$ for $d_{0} > 1.3 \cdot 10^{-6} \text{m}$.
8.1. Mie-scattering particles

Figure 8.2: Variation of the temperature for a suspension of coal particles undergoing steam gasification. (a) Temperature variation of temperature for the first sub-layer—exposed directly to the external radiative flux—for particles of initially $d_0 = 2.5$, 5, and 7.5 μm. (b) Temperature profiles across the layer for particles of initially $d_0 = 5$ μm, at $t = 0, 0.003, 0.009, \text{ and } 5$ s.

Figure 8.3: Variation of the extent of the reaction for a suspension of coal particles undergoing steam gasification. (a) Overall reaction extent as a function of time for particles of initially $d_0 = 2.5, 5, \text{ and } 7.5$ μm. (b) Local reaction extent profiles across the layer for particles of initially $d_0 = 5$ μm, at $t = 0, 2, \text{ and } 5$ s.
and $2.5 \cdot 10^{-6}$ m at $\lambda = 0.5$ and $1.8 \mu$m, respectively. Thus, radiation in the visible and near IR spectrum (shown only for $\lambda = 0.5$ and $1.8 \mu$m) incident on a cloud of particles greater than $2.5 \cdot 10^{-6}$ m is more likely to be scattered than absorbed, but the opposite is true as the particles shrink below $1.3 \cdot 10^{-6}$ m. Both efficiencies are higher at $\lambda = 1.8 \mu$m than at $\lambda = 0.5 \mu$m, and the medium becomes optically thicker for longer wavelengths.

The variation of the absorption and scattering coefficients with time is shown for the first sub-layer in Figures 8.5a and 8.5b, respectively. Curves are plotted for two radiation wavelengths $\lambda = 0.5$ and $1.8 \mu$m, and for three initial particle diameters, $d_0 = 2.5$, 2.5, and 7.5 $\mu$m. Both coefficients are higher for smaller initial particle diameters and decrease monotonically with time as the particle shrink due exclusively to the decrease in the ratio of volume fraction to particle diameter, because, as seen in Figure 8.4, the corresponding efficiencies increase or remain approximately constant with shrinking particles (see Equations (2.39) and (2.40)). As far as the effect of the spectrum is concerned, both coefficients increase with longer wavelength (shown only for $\lambda = 0.5$ and $1.8 \mu$m), consistent with the results of Figure 8.4.

The scattering phase function $\Phi_\lambda$ is shown in Figure 8.6 as a function of the polar angle $\theta$ measured from the direction of incident ray ($\Phi_\lambda$ is independent of the azimuthal angle for spherical particles) for the first sub-layer at $t = 0$ and 5 s. Curves are plotted for two radiation wavelengths: $\lambda = 0.5 \mu$m (Figure 8.6a), and $1.8 \mu$m (Figure 8.6b). At all times, scattering is predominantly in the forward direction and an order of magnitude higher for $0.5 \mu$m than for $1.8 \mu$m radiation. Backscattering remains almost unchanged with time. The oscillatory character of the phase function can be observed especially at the shorter wavelength. From the point of view of energy transfer to a chemical reactor, the dominant forward scattering is a desired property because of the deeper penetration of the incident solar radiation and lesser radiation losses.

The transient radiative behaviour of the whole slab can in part be examined
8.1. Mie-scattering particles

Figure 8.5: Variation of the absorption (a) and scattering (b) coefficients with time for the first sub-layer of a suspension of coal particles undergoing steam-gasification, for radiation at $\lambda = 0.5$ and $1.8 \, \mu m$, and for initial particle diameters $d_0 = 2.5$, 5, and $7.5 \, \mu m$.

Figure 8.6: Scattering phase function for the first sub-layer at $t = 0$ and 5 s, and for radiation at $\lambda = 0.5 \, \mu m$ (a) and at $\lambda = 1.8 \, \mu m$ (b).
in Figure 8.7, where its spectral optical thickness, Equation (2.30), is plotted as a function of time at $\lambda = 0.5$ and $1.8 \mu m$, and for $d_0 = 2.5$, 5, and $7.5 \mu m$. As expected from the values of absorption and scattering coefficients, the medium becomes optically thinner as the particle shrink. This effect is more pronounced for smaller initial particles because these offer higher $f_v/d$ ratio and, consequently, attain higher temperatures and gasification rates. As observed already in Figure 8.5 for the first sub-layer, the whole medium becomes thicker at longer wavelengths.

Finally, the attenuation characteristics of the whole slab are shown in Figure 8.8, where the variation of the overall reflectance $R$, absorptance $A$, and transmittance $T$ of the slab with time are plotted for three initial particle diameters, $d_0 = 2.5$, 5, and $7.5 \mu m$. Obviously, $R + A + T = 1$. Transmission of incident radiation is dominant. The portion of absorbed radiation decreases logarithmically with time as the particle shrink and the medium becomes optically thinner. For example, for $d_0 = 5 \mu m$, it amounts initially to 27% and decreases to 13% after 5 seconds. The reflectance is more than one order of magnitude smaller. In practice, the reactor’s walls absorb, reflect, and re-emit the transmitted incident solar radiation.

### 8.1.4 Error estimation

The errors in the temperature and reaction extent caused by the time discretisation and by the statistical character of the Monte Carlo method were assessed by varying the time step ($\Delta t = 3 \cdot 10^{-4}$ and $1.5 \cdot 10^{-4} s$) and the number of rays ($n_{rays} = 2 \cdot 10^6$ and $10^7$). The relative differences in the temperature and reaction extent were calculated by using Equations (7.22) and (7.23). The maximal relative difference in the temperature was $\varepsilon_T = 2.55\%$ (at $z/L = 1.67 \cdot 10^{-2}$ and $t = 3 \cdot 10^{-3} s$) when varying time step, and $\varepsilon_T = 0.5\%$ (at $z/L = 1.67 \cdot 10^{-2}$ and $t = 4.233 s$) when varying number of rays. The maximal relative difference in the reaction extent was $\varepsilon_X = 9.22 \cdot 10^{-2}\%$ (at $z/L = 2.83 \cdot 10^{-1}$ and $t = 5 s$) when varying time step, and $\varepsilon_X = 0.7\%$ (at $z/L = 1.5 \cdot 10^{-1}$ and $t = 5 s$) when varying number of rays.
8.2 Large specular particles

A suspension of large specular and opaque coal particles is examined in this section by employing two modelling approaches: (1) quasi-continuous modelling of a heterogeneous medium; and (2) direct, or discontinuous, modelling of randomly located spheres.\(^1\)

The first approach follows the methodology applied to the problem in the previous section except that the radiative properties of the medium are obtained by using the laws of geometric optics. In the second approach, every particle is considered as a separate system that is randomly located in a limited three-dimensional space.

In both approaches, emission, absorption and reflection from particle's surface are included, while diffraction effects are neglected. The specular directional-hemispherical reflectivity of the particle surface for the unpolarised incident radiation, \(\rho_{\alpha}\), is obtained from Equation (2.22) for the complex refractive index \(m\) of propane soot, whose real and imaginary parts are shown in Figure 8.1 as a function of wavelength. \(\rho_{\alpha}\) is depicted in Figure 8.9 as a function of the incidence angle \(\theta\) at \(\lambda = 0.5\) and 1.8\,\mu m. The scattering and absorption efficiency factors, and the scattering phase function, needed in approach (1), are calculated by use of Equations (2.56), (2.57), and (2.58), respectively. Figure 8.10 shows the scattering phase function as a function of the scattering direction \(\theta_s\) at \(\lambda = 0.5\) and 1.8\,\mu m. The radiative intensity is predominantly scattered into the forward direction and this effect is more pronounced at the shorter wavelength.

\(^1\)The direct model was developed by A. Z'Graggen in the framework of his master's thesis [92].
Chapter 8. Application to coal gasification

8.2.1 Methodology

While the numerical solution in approach (1) is based on the subdivision of the quasi-continuous medium into a number of uniform sub-layers and the mass and energy equations are applied to the whole sub-layers, the mass and energy equations for individual particles are used in approach (2). Assuming an isothermal particle, the radiative power emitted from its surface is given by

\[ q_e = \pi d_p^2 c \sigma T_p^4, \]  

where \( d_p \) is the particle diameter and

\[ \epsilon = \frac{2\pi}{\sigma T_p^4} \int_0^{\pi/2} \int_0^{\infty} \epsilon' \lambda(\lambda, T_p) \cos \theta \sin \theta \, d\lambda \, d\theta, \]  

is the total hemispherical emissivity of particle's surface. The numerical solution in approach (2) is applied to a suspension volume of finite dimensions \( L_x, L_y, \) and \( L_z \), selected from the infinite slab. In this approach, the random locations of particles are obtained by calculating the co-ordinates of their centre points as

\[ x_j = \frac{d_0}{2} + (L_x - d_0) R_x, \]  

\[ y_j = \frac{d_0}{2} + (L_y - d_0) R_y, \]  

\[ z_j = \frac{d_0}{2} + (L_z - d_0) R_z, \]  

Figure 8.9: Spectral directional-hemispherical reflectivity of a particle surface at \( \lambda = 0.5 \) and 1.8 \( \mu \)m, and for complex refractive index of propane soot.

Figure 8.10: Scattering phase function of a specularly reflecting particle at \( \lambda = 0.5 \) and 1.8 \( \mu \)m.
8.2. Large specular particles

Table 8.2: Specific simulation parameters for the suspension of large coal particles

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_0$</td>
<td>$5 \cdot 10^{-4}$</td>
<td>m</td>
</tr>
<tr>
<td>$f_{c,0}$</td>
<td>$10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$L_x, L_y^2$</td>
<td>0.025</td>
<td>m</td>
</tr>
<tr>
<td>$L_z$</td>
<td>0.1</td>
<td>m</td>
</tr>
<tr>
<td>$n_{rays}$</td>
<td>$10^6$</td>
<td></td>
</tr>
<tr>
<td>$q_{b,i}$</td>
<td>$2.5 \cdot 10^6$</td>
<td>W m$^{-2}$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>$5 \cdot 10^{-3}$ for approach (1)</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>$1 \cdot 10^{-4}$ for approach (2)</td>
<td></td>
</tr>
</tbody>
</table>

where $R_x, R_y$, and $R_z$ are random numbers chosen from a uniform distribution $(0,1)$. The developed algorithm tests the placement of particles in order to eliminate their overlapping. Particles near boundaries of the selected volume $L_xL_yL_z$ are not truncated by them, which leads to a lower particle volume fraction near the boundaries. Rays that leave the volume by crossing the boundaries perpendicular to $x$- and $y$-axis enter the domain on the opposite side at a corresponding location being the projection of the exit point, while the propagation direction remains unchanged.

In order to compare results obtained by both modelling approaches, the temperatures and reaction extents obtained in approach (2) are averaged over corresponding sub-layers in approach (1),

$$T_j^n = \frac{1}{n_{p,j}} \sum_{k=1}^{n_{p,j}} T_k^n,$$

$$X_j^n = 1 - \frac{\sum_{k=1}^{n_{p,j}} n_{0,C,k}^{p}}{\sum_{k=1}^{n_{p,j}} n_{0,C,k}}. \tag{8.21}$$

where $n_{p,j}$ is the number of particles in a sub-layer $j$. $T_k$ and $X_k$ are the temperature and the reaction extent taken for a single particle, respectively. A particle is considered to be inside the $j$-th sub-layer if the $z$-co-ordinate of its centre point meets the condition

$$j - 1 \leq \frac{z_k}{\Delta z_k} < j. \tag{8.22}$$

In contrast to the Monte Carlo implementation used in approach (1), which consists in tracing rays through a quasi-continuous medium and which is the same as applied in Chapter 7 and §8.1, the ray tracing algorithm employed in approach (2) directly accounts for the interactions between a ray and a particle surface.

$^2$Used only for approach (2).

$^3$n$_{rays}$ refers to one sub-sample in both approaches.
8.2.2 Results

Table 8.2 contains the common parameters for both modelling approaches. Only parameters different from those in Table 8.1 are indicated. The total simulation time was 10 s. In approach (1), the ray sample was split into $n$ sub-samples and the mean values of temperature and reaction extent were calculated for every sub-layer,

$$T_j^n = \frac{1}{n} \sum_{i=1}^{n} T_{i,j}^n,$$  \hspace{1cm} (8.23)

$$X_j^n = \frac{1}{n} \sum_{i=1}^{n} X_{i,j}^n,$$  \hspace{1cm} (8.24)

where $T_{i,j}$ and $X_{i,j}$ designate partial solutions in temperature and reaction extent calculated for different sets of random numbers, but for the same total number of rays. In approach (2), a complete 10-second simulation was carried out for only one sub-sample.

Mean temperature profiles for approach (1) and temperature profiles for one sub-sample for approach (2) across the suspension at $t = 0.01$, 0.1, 1, and 10 s are shown in Figure 8.11. For approach (1), the temperature rises in less than 0.5 s to above 1740 K and 1670 K in the first ($z/L_z = 1.67 \cdot 10^{-2}$), directly exposed to external flux, and last sub-layer ($z/L_z = 9.83 \cdot 10^{-1}$), respectively. Subsequently, it increases after 10 s to 1768 K and 1753 K, respectively, as a result of a faster decrease of the heat consumption by the endothermic reaction than of the heat absorption due to shrinking particles.

Figure 8.12a shows the overall reaction extent for the suspension. In approach (1), it reaches 88% after 10 s. The reaction extent across the layer at $t = 2$, 5, and 10 s is shown in Figure 8.12b. The maximal reaction extent after 10 s (91%) is obtained at the first sub-layer due to the highest temperature at this location. The minimal reaction extent after 10 s (83%) is obtained, as expected, at the last sub-layer.
Finally, the transient behaviour of the whole suspension is reflected in the values of the time-dependent overall reflectance, absorptance and transmittance, shown in Figure 8.13. Reflectance and absorptance, initially equal to 0.01 and 0.23, decrease by 67% and 74% of their initial values after 10s, respectively. Transmittance, initially at 0.75, increase after 10s by 23% of its initial value.

The results obtained for the single sub-sample in approach (2) generally exhibit similar trends to those obtained in approach (1), especially for overall quantities such as the overall reflectance, absorptance, and transmittance. For this single sub-sample, the temperatures are systematically lower than the mean temperatures obtained in approach (1), resulting in lower reaction rates.

### 8.2.3 Accuracy considerations

The statistical uncertainty in the temperature and reaction extent was estimated for approach (1) for the complete simulation time of 10s. The largest confidence interval ($P = 95\%$, $\nu = 9$) in the temperature was $1488.65 \pm 2.19\, K$ (at $z/L_z = 9.83 \cdot 10^{-1}$ and $t = 0.34\, s$), and in the reaction extent $(707.87 \pm 1.11) \cdot 10^{-3}$ (at $z/L_z = 1.67 \cdot 10^{-2}$ and $t = 5.675\, s$).

The errors in the temperature and reaction extent caused by the time discretisation were assessed for approach (1) by varying the time step ($\Delta t = 5 \cdot 10^{-3}$ and $2.5 \cdot 10^{-3}\, s$). The relative difference $\varepsilon_T$ in the mean temperature and reaction extent obtained for $n$ sub-samples were calculated by using Equations (7.22) and (7.23).

The maximal relative difference in the mean temperature was $\varepsilon_T = 1.08\%$ (at $z/L_z = 1.67 \cdot 10^{-2}$ and $t = 2.5 \cdot 10^{-2}\, s$). The maximal relative difference in the mean reaction extent extent was $\varepsilon_X = 1.47\%$ (at $z/L_z = 8.17 \cdot 10^{-1}$ and $t = 0.135\, s$). The
largest confidence interval in the temperature and reaction extent for the solution with the reduced time step ($\Delta t = 2.5 \cdot 10^{-3}$) was $1433.06 \pm 2.05 \, K$ (at $z/L_z = 9.83 \cdot 10^{-1}$ and $t = 0.3175 \, s$), and $(708.05 \pm 1.03) \cdot 10^{-3}$ (at $z/L_z = 1.67 \cdot 10^{-2}$ and $t = 5.6825 \, s$), respectively.

The accuracy for approach (2) was assessed only for the total simulation time reduced to $0.2 \, s$ because of the large computational effort in this case. At $t = 0.2 \, s$, the largest confidence interval in the temperature across the suspension was $1138.03 \pm 45.14 \, K$ at $z/L_z = 6.5 \cdot 10^{-1}$, significantly exceeding the size of the confidence interval obtained in approach (1). This higher uncertainty in approach (2) results from the stochastic character of the ray tracing procedure and, in addition, from the stochastic character of the procedure for generating the particle locations. The high geometric resolution in approach (2) is the reason for large uncertainty of the ray tracing procedure itself.

At $t = 0.2 \, s$, the maximal relative difference between the mean temperatures obtained for both approaches was $\varepsilon_T = 3.6\%$ at $z/L_z = 6.5 \times 10^{-1}$, corresponding to the absolute difference of $42 \, K$. This difference is smaller than the sum of the uncertainties at this particular location, but it exceeds this sum at some other locations.

### 8.3 Summary

The shrinking particle model has been applied to coal particles undergoing endothermic gasification. Two ranges of particle size parameters that imply application either of the Mie scattering theory or of the geometric optics for the prediction of radiative properties are considered. It is shown that the time-decreasing particle size leads to the decreasing temperature of small coal particles because absorption of the radiative heat decreases faster than the heat consumption by the chemical reaction. The opposite is observed for large coal particles, for which the temperature increases...
with time.

Two modelling approaches for the suspension of the large coal particles have been presented and compared. The quasi-continuous approach is proved to be more efficient and accurate, but it delivers results averaged over control volumes. In contrast, the direct approach gives detailed information about every particle in the suspension, but at a cost of very long computational time and with large statistical errors, making it impractical for modelling solid-gas reacting flows.
An emerging application field of transient radiative heat transfer in chemical reacting systems is solar thermochemistry. The direct irradiation of the chemical reactants provides efficient energy transfer to the reaction site, bypassing the limitations imposed by indirect heat transfer through reactor walls. Modelling such directly irradiated solar chemical reactors is crucial for anticipating the consequences of a given design decision on the reactor's performance. A solution to the realistic coupled radiation-chemistry problems is possible only if numerical methods are employed.

Radiative heat transfer problems involving time-dependent directional and spectral radiative properties, anisotropic scattering and irregular geometries are typical for high temperature heterogeneous reacting systems. Only a transient model of a reacting system may give enough insight into the process and its complexity, so that correct prediction of the conditions under which a chemical reaction is conducted is possible in order to optimally match the rate of the reaction to the rate of the radiative heat transfer. There is no example of previous modelling work applied to solar thermochemistry that incorporates transient analysis of a directly-irradiated reacting medium in which the influence of the reaction progress on the time variation of the radiative properties is taken into account.

In this work, two methodologies are proposed to treat the unsteady radiative heat transfer. The first one makes use of the Rosseland diffusion approximation and, therefore, is limited to optically thick media. In the second methodology, the Monte Carlo method is employed to obtain the distribution of the radiative source. Both methodologies are based on the finite volume method for space discretisation of the mass and energy equations, and on the time integration schemes for time discretisation. Combination of the Monte Carlo method with time integration schemes preserves the robustness and relatively easy implementation of the method, demonstrated extensively for steady-state conditions in numerous works. As long as the procedure combining the Monte Carlo method with numerical time integration is followed, a solution to unsteady radiative heat transfer problems involving the mutual coupling between temperature, composition, material properties and rate of chemical reaction within non-gray, non-uniform, and anisotropically scattering media with arbitrary values of the optical thickness and scattering albedo may be
found.

However, the full ray tracing run at every discrete time step makes the well-known disadvantages of the Monte Carlo method especially noticeable, of which the most important is the long computational time. Moreover, in contrast to the numerical methods for conduction and convection heat transfer, the relatively low accuracy of the Monte Carlo method further decreases with increasing grid resolution influencing the compatibility of the method with methods for other heat transfer modes. The statistical fluctuations in the distribution of the radiative source prevent implicit schemes of time integration to converge. Furthermore, volumetric temperature-dependent heat sources in chemical systems are sensitive to small temperature differences. The stochastic errors lead to local under- or over-prediction of the chemical conversion. In order to improve the accuracy of the Monte Carlo method and to shorten the computational time, a low-pass smoothing filter and parallel computational techniques are proposed.

A transient analysis of reacting media is carried out in order to demonstrate the applicability of the selected methods and to show the importance of transient effects for practical applications. A three-dimensional model that links thermal radiation, conduction and natural convection heat transfer to the chemical reaction is applied for a packed bed of calcium carbonate particles undergoing thermal decomposition under direct irradiation. The model uses the Monte Carlo ray tracing technique for determining the radiative flux at boundaries and the Rosseland diffusion approximation for obtaining the internal radiative flux. This model enables one to treat a non-isothermal non-grey chemical system involving optically thick media with a time dependent chemical composition. The computed temperature field and overall reaction extent are in good agreement with the experimentally measured values obtained with directly irradiated samples of limestone.

Another group of models concerns one-dimensional suspensions of particles undergoing chemical reaction. A model of a suspension of small reacting particles having radiative properties predicted from Mie theory and undergoing a decomposition reaction is formulated for non-shrinking and shrinking particles. The comparison of the two cases shows that radiation absorption is superior in the non-shrinking particle case resulting in higher attained temperatures and a higher reaction rate. In the shrinking particle case, radiative properties vary strongly with time as the reaction progresses due to their strong dependence on the particle size parameter. The reaction rate is lower because of the less efficient absorption as the size parameter decreases and the medium becomes optically thinner. Varying the imaginary part of the complex refractive index \( k \) and the particle volume fraction \( f_v \) in the non-shrinking particle case revealed that the overall reaction extent increases with increasing \( k \) and \( f_v \) due to the increasing layer absorptance. However, the optical thickness of the layer, and therefore, the temperature gradient across the layer increase faster with increasing \( f_v \) than with increasing \( k \), which results in more inhomogeneous reaction extent across the layer in this case. The comparison shows the necessity of taking into consideration the effect of time-dependent particle size in order to avoid an over-prediction of the reaction conversion. Examples of chemical
reactions to which this conclusion applies include the thermal decomposition of zinc oxide and the thermal gasification of coal.

Simulation of a suspension of Mie-scattering coal particles undergoing shrinking due to the gasification reaction showed that radiation in the visible and near infrared spectrum incident on the particles greater than 2.5 μm is more likely to be forward scattered than absorbed, but the opposite is true as the particles shrink below 1.3 μm. Similarly as in the previous problem, particle shrinking resulted in temperature decrease with time as a result of two competing phenomena: lesser heat absorption due to the decreasing absorption coefficient, which in turn depends on the ratio of the volume fraction to particle diameter, and lesser heat consumption by the endothermic reaction. The opposite trend, namely increasing temperature with time, was observed for a suspension of large coal particles, whose radiative properties were predicted from the geometric optics. Shrinking of the particles resulted in this case in a faster decrease of the heat consumption by the chemical reaction than of the heat absorption due to decreasing absorption coefficient. A quasi-continuous modelling approach is proved to be more efficient and accurate when the volume-averaged composition and temperatures are of interest. On the other hand, the direct, or discontinuous, modelling approach gives detailed information about every particle in the suspension, but at a cost of very long computational time and with large statistical errors, making it impractical for simulations of solar reactors.

The models presented can be applied for solving transient radiative heat transfer problems involving high-temperature solid-gas thermochemical reactions with changing radiative properties due to changing composition, particle size, and temperature dependence as is typical for combustion, decomposition, cracking, and gasification processes. If the transient effects are accounted for, the temperatures, reaction rates, and residence time requirements for a particular solar thermochemical reaction are predicted more precisely and, therefore, the assessment of the expected performance of a chemical reactor is more accurate than in the case when only the steady-state conditions are considered.

A further development of the models presented is needed in order to account for more realistic conditions encountered in chemical reactors. It includes implementation of three-dimensional unstructured tetra- and hexahedral meshes with a possibility of grid coarsening, implementation of more efficient Monte Carlo approaches such as the pathlength methods, application of spectral models for gas radiation, introduction of conduction and convection heat transfer modes, and, finally, employment of different particle size distributions and particle tracking algorithms.

An important issue is the experimental validation of the radiation models. Particle cloud models can be validated by using ultrasonic particle technology, which enables one to keep small particles in a ‘frozen’ state in space, while they are externally irradiated. In this way, overall layer reflectance and transmittance, and the overall reaction extent can be investigated and compared with the numerical results. Another possibility, which requires the advancement of the models, is the creation of a laminar flow of a fluid loaded with particles exposed to an external radiation source.
In all models presented, most of the material data were extracted from the literature. For use in practical applications, the assumed values or functions for properties of specific materials should be verified by experimental techniques.
Appendix A

Calibration of the solar simulator

Experimental work at the sun simulator is crucial for proper validation of numerical models. For a reliable evaluation of experimental results, the incident radiative flux at the focal plane must be precisely known. The properties of the simulator change with time as a result of the ageing process of the arc lamp and reflectors. In this chapter, the calibration of ETH's solar simulator conducted in conjunction with the experiments presented in §6 is described. The presented values were only a selective and provisional control and no conclusions about the ageing process of the simulator were drawn—for this purpose a series of calibration measurements should be conducted systematically.

A.1 Measurement set-up

A series of measurements with the Kendall radiometer was carried out for various arc currents and positions of the measurement point. Vertically set up with its opening \((A = 5.998 \text{ mm}^2)\) at the top, the radiometer was precisely positioned \((x, y\) co-ordinates\) at a desired measurement location at the focal plane of the solar simulator. Radiative flux passing through the opening was measured according to the thermocolumn principle and the corresponding voltage was displayed by the digital voltmeter. Based on this value, the radiative flux was calculated by using several device-specific constants. This procedure was repeated for varying \(x\) and \(y\) co-ordinates to obtain flux profiles along the \(x\)- and \(y\)-axis at the focal plane. Subsequently, the procedure was repeated for several values of the arc current.

A.2 Results

The radiative flux was calculated based on the measured voltage using the formula

\[
q_r'' = \alpha U,
\]  

(A.1)

where \(\alpha = 8.78 \times 10^7 \text{ W m}^{-2} \text{ V}^{-1}\) is the conversion factor. Tables A.1–A.3 show the radiative flux distributions along the \(x\)- and \(y\)-axis at the focal plane of the solar
simulator for arc currents 150, 200, and 300 A. Flux distribution along the y-axis for arc current 300 A is shown in Table A.4. Finally, values of the radiative flux at $x = 0$ and $y = 0$ for various arc currents are given in Table A.5.

### A.3 Accuracy considerations

The values given in Tables A.1–A.5 contain errors due to the limited accuracy of the measurement device and procedure. The error of the measurement device is dominated by the error of the radiometer ($\pm 1\%$), whereas the error of the control unit is much lower ($\pm 0.05\%$). The errors associated with the measurement procedure are due to

- finite area of the radiometer opening,
- limited accuracy of the positioning system,
- errors in the measured arc current.

Uncertainty in the measured flux was calculated for the value measured at $x = 0$ and $y = 0$ and for arc currents $I = 200$ and 300 A. For the case $I = 200$ A, the confidence interval for $\nu = n - 1 = 2$ degrees of freedom and confidence probability $P = 95\%$ was $q''_r = 1170.08 \text{ kW m}^{-2} \pm 75.28 \text{ kW m}^{-2}$, resulting in the relative error equal to 6.43%. For the case $I = 300$ A, the confidence interval for $\nu = 1$ degree of freedom and confidence probability $P = 95\%$ was $q''_r = 682.65 \text{ kW m}^{-2} \pm 183.9 \text{ kW m}^{-2}$, resulting in the relative error equal to 27%. However, the only two measured values led to the very high t-quantile equal to 12.7. Therefore, the error for the case $I = 200$ A was alternatively assessed by calculating the difference between the two measured values as equal to 28.96 kW m$^{-2}$, resulting in the relative difference related to the lower value of the measured flux equal to 4.33%.
### Table A.1: Radiative flux, in kW m\(^{-2}\), along the x- and y-axis for arc current \(I = 150\) A.

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### Table A.2: Radiative flux, in kW m\(^{-2}\), along the x- and y-axis for arc current \(I = 200\) A.

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### Table A.3: Radiative flux, in kW m\(^{-2}\), along the x- and y-axis for arc current \(I = 300\) A.

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### Table A.4: Radiative flux, in kW m\(^{-2}\), along the y-axis for arc current \(I = 300\, \text{A}\).

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<th>(x/\text{mm})</th>
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<th>(I/\text{A})</th>
<th>(q_r''/(\text{kW m}^{-2}))</th>
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### Table A.5: Radiative flux, in kW m\(^{-2}\), at \(x = 0\) and \(y = 0\) for various arc currents.

<table>
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<tr>
<th>(x/\text{mm})</th>
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<th>(I/\text{A})</th>
<th>(q_r''/(\text{kW m}^{-2}))</th>
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Bibliography


Curriculum vitae

Name: Wojciech Sławomir Lipiński
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