Detailed Population Balance Modelling of Titanium Dioxide Nanoparticle Synthesis



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Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this thesis are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This thesis is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the acknowledgements, text and appendices. This thesis contains fewer than 65,000 words including appendices, bibliography, footnotes, tables and equations and has fewer than 150 figures. The work was performed at the University of Cambridge and the Cambridge Centre for Advanced Research and Education in Singapore between May 2015 and August 2019.

Some of the work in this thesis has been published:

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This thesis develops and applies a new detailed population balance model to study the aerosol synthesis of titanium dioxide nanoparticles. It begins by exploring whether the morphological data captured by a existing detailed particle model can be used in a milling model to relate particle morphology and ultimately the particle synthesis conditions to the behaviour of particles in the milling process. The study identifies limitations in the existing particle model and informs the development of a new detailed particle model.

A new, detailed, geometrical particle model is introduced that tracks the size and position of individual primary particles and their relationship with neighbouring primaries in an aggregate. The particle model forms part of a detailed population balance model that can describe the morphological evolution of aggregate particles under inception, coagulation, growth, sintering and coalescence, while resolving the neck radius, free surface area and volume of each individual primary, as well as the fractal-like structure of each aggregate. The model removes the need to assume a fractal dimension and prefactor when calculating the particle gyration and collision diameters, and permits the visualisation of particles. The process sub-models are tested and the convergence behaviour is investigated for a simple batch reactor test case. The synthesis of TiO₂ aggregates from TTIP precursor in a lab-scale hot wall reactor is simulated.

A two-step simulation methodology is presented to apply the model to a stagnation flame. The methodology extends an existing two-step method, where a detailed population balance model is applied as a post-processing step to flame profiles obtained from a fully-coupled simulation with gas-phase chemistry, flow dynamics and a simple particle model. The new methodology addresses a previously unidentified issue in employing the post-processing step to simulate flames with steep temperature gradients. A corrective sample volume scaling term is introduced to account for the effect of thermophoresis.

Finally, the new detailed particle model and methodology are used to simulate the synthesis of titanium dioxide nano-aggregates in a stagnation flame. Model predictions are evaluated against experimental results by comparing experimental measurements from transmission electron microscopy (TEM) data with identical, simulated quantities. A parametric sensitivity study is performed to investigate key model parameters.

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List of symbols

Upper-case Roman

Α	Rate prefactor [process specific]
A_i	Free surface area of primary p_i [m ²]
A _n	Neck area [m ²]
A _{pr}	Projected area [m ²]
B_{ij}	Auxiliary sintering variable, Eq. (4.33) [m ²]
C_i	Concentration of species $i [mol m^{-3}]$
Ci	Inlet concentration $[mol m^{-3}]$
Co	Outlet concentration $[mol m^{-3}]$
$C_{\rm v0}$	Equilibrium vacancy concentration
С	Aggregate particle connectivity matrix
C_{ij}	Connectivity matrix element [-]/common surface area of p_i and p_j [m ²]
CVp	Coefficient of variation of the primary particle diameter
CV _a	Coefficient of variation of the aggregate projected spherical equivalent diameter
D_{f}	Fractal dimension
$D_{ m v}$	Vacancy diffusion coefficient $[m^2 s^{-1}]$
$D_{p,1}$	Brownian diffusion coefficient of a TiO ₂ monomer $[m^2 s^{-1}]$
Ε	Type space
Ea	Activation energy [Jmol ⁻¹]
F_d	Flame distance from stagnation surface [m]
F_{v}	Volume fraction

G	Point (coordinates)
Н	Spherical cap height [m]
Ι	Total number of gas-phase chemical species
I_P	Confidence interval with confidence level P
J	Total number of time steps
K	Coagulation kernel [m ³ s ⁻¹]
Ŕ	Majorant coagulation kernel [m ³ s ⁻¹]
Kn	Knudsen number
L	Number of repeat simulation runs
М	Index set of linear processes
M_r	Particle number moment of order $r [m^{-3}]$
$\dot{M_r}$	r^{th} moment source term $[m^{-3}s^{-1}]$
$M_{\rm TiO_2}$	Molar mass of TiO_2 [kg mol ⁻¹]
Ν	Number of aggregate/stochastic particles
N_{A}	Avogadro constant [mol ⁻¹]
0	Origin
Р	Probability
P_q	Aggregate particle with index q
Q	State of the system/particle ensemble
R	Ideal gas constant $[J \mod^{-1} K^{-1}]$
R	Radius [m]
R	Particle process rate [process specific]
Ŕ	Majorant rate [process specific]
R_{ij}	Rate of breakage of neck between p_i and p_j [s ⁻¹]
R	Rotation matrix
S	Surface area [m ²]
$S_{ m sph}$	Surface area of volume equivalent sphere [m ²]
S_{v}	Surface area per unit volume $[m^2 m^{-3}]$

Т	Temperature [K]
Ts	Stagnation surface temperature [K]
U	Uniform random variate
V	Volume
V _{smpl}	Simulation sample volume [m ³]
$ar{W}$	Average molar mass $[kg mol^{-1}]$
X	Poisson distributed random variate
Lower-case	Roman
a	Neck radius [m]
a_P	Critical value of the standard normal distribution for confidence level P
CP	Half-width confidence interval for confidence level P
d	Particle diameter [m]
\bar{d}	Ensemble mean particle diameter [m]
$\langle d angle$	Median particle diameter [m]
$d_{{ m Ti}({ m OH})_4}$	Diameter of a Ti(OH) ₄ molecule [m]
d_{TiO_2}	Diameter of a TiO ₂ molecule [m]
d_{a}	Aggregate projected spherical equivalent diameter [m]
d _{p,crit}	Critical sintering diameter [m]
d_{ij}	Primary centre to centre separation [m]
$e_{\rm r}(t)$	Relative error at time t

e _{tot} Tot	al relative error
----------------------	-------------------

j (i g) i i operio i g (properio) specific	$f(P_q)$	Property of particle P_q [property specific]
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f_{α}	Fraction	of aggregates	with	circular	projection
					1 5

- $g_m(P_r)$ Particle resulting from process *m* acting on P_r
- *k* Rate constant [process specific]
- $k_{\rm B}$ Boltzmann constant [m² kg s⁻² K⁻¹]
- *k*_f Fractal pre-factor

т

Particle mass [kg]

$m_{\rm Ti(OH)_4}$	Mass of a Ti(OH) ₄ molecule [kg]
$m_{\rm TiO_2}$	Mass of a TiO ₂ molecule [kg]
n	Particle number density [m ⁻³]
n	Temperature exponent
$n_{\rm f}$	Number of TEM frames
<i>n</i> _p	Number of primary particles in an aggregate
$\bar{n}_{ m p}$	Ensemble mean number of primary particles per aggregate
р	Pressure [Pa]
p_i	Primary particle with index <i>i</i>
r	Radius [m]
r _i	Radius of primary p_i [m]
S _{ij}	Sintering level of the neck between primaries p_i and p_j
<i>s</i> _{avg}	Mean sintering level of an aggregate particle
<u>s</u>	Ensemble mean sintering level
t	Time [s]
t^*	Dimensionless time
t _{res}	Reactor residence time [s]
и	Convective velocity $[ms^{-1}]$
v _{TiO2}	Volume of one unit of TiO ₂ [m ³]
v _T	Thermophoretic velocity [ms ⁻¹]
Vi	Volume of primary p_i [m ³]
x	General particle type
\mathbf{x}_i	Centre of mass coordinates of primary p_i [m]
<i>x</i> , <i>y</i> , <i>z</i>	Spatial coordinates [m]
<i>x</i> _{<i>ij</i>}	Distance from the centre of p_i to the neck with p_j [m]
Z.	Spatial displacement [m]
Upper-case	Greek

Δ**d** Spatial translation [m]

$\Delta t_{\rm s}$	Splitting time step [s]
Δ_T	Temperature perturbation [K]
Δ_z	Spatial perturbation [m]
Γ	Rate of gas-phase expansion per unit volume $[s^{-1}]$
Ω	Vacancy volume [m ³]
Lower-case	Greek
α	Milling rate exponent
$\alpha(P_q)$	Ratio of particle projected diameter of gyration to projected spherical equivalent diameter
$\alpha_{\rm crit}$	Critical sintering exponent
α_{T}	Thermal accommodation factor
β	Growth rate constant [process specific]
$\delta_{ m gb}$	Grain boundary thickness [m]
ε	Collision enhancement factor
η_i	Composition of primary particle p_i
$\eta_{ m TiO_2}$	TiO ₂ composition
γ	Surface free energy [J m ⁻²]
γin	Inception efficiency
$\gamma_{ m sg}$	Surface growth efficiency
к	Sintering constant [sm ⁻⁴]
λ	Mean (Poisson distribution)
λ	Mean free path [m]
μ	Viscosity $[kgm^{-1}s^{-1}]$
μ_1	Empirical mean
μ_2	Variance
μ_r	Reduced moment of order r
v_i	Order of reaction with respect to gas-phase species <i>i</i>
ϕ	Azimuthal angle

ϕ	Equivalence ratio
ρ	Density of the gas-phase $[kgm^{-3}]$
$ ho_{{ m TiO}_2}$	Density of TiO ₂ [kg m ⁻³]
σ	Surface smoothing factor
τ	Non-dimensionalised time
τ	Waiting time [s]
$ au_{ m s}$	Characteristic sintering time [s]
θ	Characteristic sintering time (new particle model) [s]
θ	Polar angle
ξ_l	General macroscopic quantity of the system measured for run l
ζ	High precision solution to a general macroscopic quantity

Subscripts

0	Initial
2D	Two-dimensional
avg	Aggregate particle average
b	Bounding sphere
c	Collision
cap	Spherical cap
cg	Coagulation
cond	Condensation
crit	Critical
eff	Effective
f	Final
g	Gyration
i	Gas-phase chemical species index
i, j, k, l, m	Primary particle index
inc	Inception
l	Run number

xxiv

m	Mobility
т	Particle process index
max	Maximum
min	Minimum
р	Primary particle
part	Aggregate particle
q, r, s	Aggregate particle index
r	Moment order
S	Sintering
sg	Surface growth
sph	Sphere
tot	Total

Superscripts

exp	Experimental
fm	Free-molecular
sf	Slip-flow
sim	Simulation
tr	Transition

Acronyms / Abbreviations

BCCA	Ballistic Cluster-Cluster Aggregation
CFD	Computational Fluid Dynamics
CPU	Central Processing Unit
CV	Coefficient of Variation
DEM	Discrete Element Modelling
DLCA	Diffusion Limited Cluster Aggregation
DMA	Differential Mobility Analyser
DSA	Direct Simulation Algorithm
DSMC	Direct Simulation Monte-Carlo

GM	Geometric Mean
GSD	Geometric Standard Deviation
KMC-ARS	Kinetic Monte-Carlo Aromatic Site
LHS	Left Hand Side
LPDA	Linear Process Deferment Algorithm
MD	Molecular Dynamics
MoMIC	Method of Moments with Interpolative Closure
ODE	Ordinary Differential Equation
PAH	Polycyclic Aromatic Hydrocarbon
PBE	Population Balance Equation
PBM	Population Balance Model
PPSD	Primary Particle Size Distribution
PSD	Particle Size Distribution
RHS	Right Hand Side
SD	Standard Deviation
SMPS	Scanning Mobility Particle Sizer
TEM	Transmission Electron Microscopy
TTIP	Titanium Tetraisopropoxide

XRD X-Ray Diffraction

Chapter 1

Introduction

1.1 Motivation

Titanium dioxide (titania, TiO_2) particles are an important industrial product, most commonly used as a white pigment in a wide range application including paints, plastics, paper and cosmetics. Other important applications include solar cells, optical coatings, in heterogeneous catalysis and as a photocatalyst [39, 53], used, for example, in the photolysis of water [52] and in water purification [123].

The production capacity of titania pigment was estimated at 7.66 million tonnes globally in 2018 [12] via two principal methods: the wet-phase sulphate process and the gas-phase chloride process. Aerosol, or flame synthesis has been identified as an attractive alternative to the older, wet-phase process due to advantages in waste management at the production stage and easier collection of particles [140]. The oxidation of titanium tetrachloride (TiCl₄) in a flame or oxygen plasma is a key route for the industrial manufacture of TiO₂ particles. Another route, more typically used in lab-scale studies, is the hydrolysis or thermal decomposition of titanium tetraisopropoxide (TTIP, Ti(OC₃H₇)₄).

The functionality of titanium dioxide particles is strongly dependent on the size, morphology and crystalline phase of the particles. The pigmentary properties are dependent on the refractive index and crystal size. Titania in the rutile form has a very high refractive index resulting in greater opacity. The crystal size needs to be carefully controlled to optimise its light scattering properties and maximise its effectiveness as a pigment [22, 53]; hence, control of the particle size distribution is important in the production process. However, despite its commercial importance, a comprehensive understanding of the formation of TiO_2 and the mechanisms that control the particle properties is still lacking. Optimisation of the industrial process remains largely empirical. Modelling studies, combined with experiments, provide a way to understand the complex processes involved in the formation and growth of titanium dioxide particles. A comprehensive understanding of these mechanisms provides a means to optimise and tailor particle properties. The mechanism of particle formation can be considered to consist of gas-phase chemistry interacting with a particle population. This thesis will focus on modelling the particle population using numerical methods. The principal goal is to develop a detailed population balance model that is able to capture the morphological evolution of particles and to develop the necessary methods to simulate particle synthesis under experimental conditions. This thesis aims to develop a model framework that can be used to test hypotheses and improve our understanding of the processes governing the size, morphology and crystalline phase of particles.

1.2 Novel aspects of this thesis

Novel developments in this thesis include:

- The development of particle breakage models that utilise structural information captured by a detailed particle model and the application of these breakage models to simulate the post-synthesis milling of titanium dioxide particles. The breakage models are used to relate the behaviour of particles during milling to their morphology developed under different reactor conditions.
- The development of a new geometrical particle model that tracks the size and position of individual primary particles and their relationship with neighbouring primaries. The particle model is part of a detailed population balance model that can describe the morphological evolution of aggregate particles under inception, coagulation, growth, sintering and coalescence processes. The new geometrical particle model has several advantages:
 - It removes the need to make an assumption about the particle fractal dimension and prefactor. The radius of gyration and collision diameter of an aggregate particle can be directly calculated.
 - The model resolves the neck radius, free surface area and volume of each individual primary particle.
 - The morphology of aggregate particles is resolved throughout a simulation and can be visualised, for example, in TEM-style images for comparison with experimental data.

- The new particle model is combined with a detailed chemical mechanism for the decomposition of TTIP. Particle inception and growth processes are treated as collision limited reactions of gas-phase species. This avoids the need to make the assumptions made in previous studies about the relative rates of inception and growth for a single step decomposition model of TTIP.
- A post-processing methodology for detailed simulations of particle formation in laminar flames is extended to stagnation flames by addressing a previously unidentified issue in applying the methodology to systems with steep temperature gradients. A correction is introduced to the post-processing step to account for the significant effect of thermophoresis on the simulated particle number density moments.
- Detailed particle model simulation results are evaluated against experimental data by comparing experimental measurements with identical, simulated quantities, for example, the projected area spherical equivalent diameter obtained from TEM image analysis.

1.3 Structure of this thesis

The next chapter covers related work and introduces the model framework and numerical methods that are used in this thesis. Chapter 3 begins by looking at a pre-existing detailed particle model and evaluating the quality of structural data it captures. Breakage models are developed that utilise this structural information and the work attempts to relate the morphology of titanium dioxide particles to their milling behaviour. The chapter concludes by reviewing the particle model and suggests areas for development.

A new detailed particle model is introduced in Chapter 4 with the aim of addressing the limitations identified in Chapter 3. A mathematical description of the population balance model is given along with the model algorithms. The process sub-models are tested and the convergence behaviour is investigated for a simple batch reactor test case. Finally, the synthesis of TiO₂ aggregates from TTIP precursor in a lab-scale hot-wall reactor is simulated.

Chapter 5 extends a two-step simulation methodology used to apply a detailed population balance model as a post-process to flame simulations. The work identifies a previously unaddressed issue in employing the methodology to simulate flames with strong temperature gradients, such as a stagnation flame. A thermophoretic correction is introduced in the second simulation step to account for the significant effect of thermophoresis near the stagnation surface. The new methodology is evaluated by comparison with results from an established, fully-coupled method. Chapter 6 combines the new detailed particle model and the newly developed methodology with a detailed chemical mechanism for the thermal decomposition of TTIP to simulate the synthesis of titanium dioxide nano-aggregates in a stagnation flame. Model predictions are evaluated against experimental results by comparing experimental measurements from transmission electron microscopy (TEM) data with identical, simulated quantities. Finally, a parametric sensitivity study is performed to investigate important model parameters. Chapter 7 concludes this thesis with a critical review, and suggestions for further work and improvements to the model.

Chapter 2

Background

This chapter is divided into two sections. The first presents an overview of the relevant literature, while the second describes the pre-existing particle model framework and numerical methods that are used in this thesis.

2.1 Related work

This section begins with a review of the literature concerning the kinetics of titania formation and proposed chemical mechanisms for the two main chemical precursors. A short introduction to the experimental aspects of studying titania nanoparticle synthesis precedes a discussion of nanoparticle morphology and processes affecting particle structure. The section concludes with a review of the population balance modelling literature.

2.1.1 Kinetics of titanium dioxide formation

The two main precursors used in the aerosol synthesis of titanium dioxide particles are titanium tetrachloride (TiCl₄) and titanium tetraisopropoxide (Ti(OC₃H₇)₄, TTIP). Particles can be synthesised by the oxidation or hydrolysis of TiCl₄, or the thermal decomposition or hydrolysis of TTIP. The oxidation of TiCl₄ and thermal decomposition of TTIP are discussed here.

Oxidation of TiCl₄

An important route for the industrial production of pigmentary titania is the chloride process involving the gas-phase oxidation of $TiCl_4$. Impure TiO_2 is first chlorinated to produce $TiCl_4$, which is then purified before undergoing oxidation at high temperature (above 1500 K) in a pure oxygen plasma or flame to produce titania nanoparticles. Finally, the particles may be

subjected to after-treatments such as milling to achieve the desired properties for the final product [53]. Research into titania nanoparticle formation is focussed on the oxidation process:

$$TiCl_4 + O_2 \longrightarrow TiO_2 + 2Cl_2$$

A number of investigations have sought to improve our understanding of the reaction kinetics. Ghoshtagore [58] used a hot-wire experiment to investigate the surface reaction of TiCl₄ with a TiO₂ film at 673–1120 K. The investigation concluded that the reaction proceeds by an Eley-Rideal mechanism with atomic oxygen as the chemisorbed species and molecular TiCl₄ colliding on the surface from the gas phase. Pratsinis et al. [141] studied the global kinetics of TiCl₄ oxidation in a hot wall reactor at 973–1273 K. The overall reaction was found to be first-order in TiCl₄ and approximately zero-order in O₂ up to ten-fold excess O₂. Pratsinis and Spicer [142] attempted to quantify the relative rates of the gas-phase oxidation of TiCl₄ and the reaction on the particle surface using reported rates for the overall reaction [141] and surface reaction [58]. Surface growth was found to have a significant effect on the particle diameter.

West et al. [183, 184] proposed a detailed thermodynamically consistent gas-phase kinetic model to describe the oxidation of TiCl₄. Subsequent investigations presented an updated mechanism [185] and considered the role of aluminium trichloride additives [159] and hydro-carbon species [170]. A comparison of the particle inception behaviour of the mechanisms from Pratsinis and Spicer [142] and West et al. [185] was performed by Mehta et al. [118]. They showed that the choice of model caused inception to occur at different locations in simulations of a turbulent flame. This is consistent with other studies [4, 158]. Mehta et al. [117] later proposed a reduced version of the detailed mechanism [185] to facilitate the simulation of TiCl₄ oxidation in turbulent methane flames.

Shirley et al. [158] performed a theoretical investigation of the adsorption of TiCl₄ on the [110] surface of rutile TiO₂. Their findings were consistent with an Eley-Rideal surface growth mechanism. The rate parameters of the surface reaction and choice of inception model were observed to strongly affect simulations of the experiment of Pratsinis et al. [141]. The experimental data could be reproduced by simulations using the gas-phase chemistry from West et al. [185] with an inception model based on the collision of any two Ti_xO_yCl_z species ($x, y, z \ge 1$). Several surface growth models were proposed based on a combination of the calculated activation energies and fitting to the experiment of Pratsinis et al. [141].

Decomposition of TTIP

The second, commonly used precursor, titanium tetraisopropoxide, is typically seen in laboratory investigations because it is less corrosive and easier to handle than TiCl₄. Okuyama et al. [135] performed hot-wall reactor studies at 400–600°C and proposed a first-order reaction rate with the following decomposition pathway

$$\mathrm{Ti}(\mathrm{OC}_{3}\mathrm{H}_{7})_{4} \longrightarrow \mathrm{Ti}\mathrm{O}_{2} + 4\mathrm{C}_{3}\mathrm{H}_{6} + 2\mathrm{H}_{2}\mathrm{O}.$$

This has been supported by more recent studies [92, 178]. Many attempts at modelling high temperature TiO_2 formation from TTIP assume a one-step thermal decomposition of TTIP [131, 153]. Tsantilis et al. [172] combined the one-step reaction with a first-order surface reaction [11] to model TiO₂ formation in a premixed flat flame. A similar reaction model has also been used in other studies [108, 195, 200].

An experimental and computational study by Shmakov et al. [160] identified intermediate species in the decomposition of TTIP in a $H_2/O_2/Ar$ flame and took the first steps in developing a detailed chemical mechanism describing both hydrolysis and thermolysis reactions. Buerger et al. [23, 24] later developed a systematically derived and thermodynamically consistent kinetic mechanism of TTIP decomposition. The work identified three main reaction pathways with Ti(OH)₄ as the final decomposition product. However, more recent experimental and computational work by Ershov et al. [47] suggests that the mechanism proposed by Buerger et al. [23] is incomplete and identified another important pathway.

2.1.2 Aerosol synthesis of titanium dioxide

Tubular hot wall reactor experiments are a popular technique for studying the aerosol synthesis of titania nanoparticles: from understanding the chemical reaction kinetics [135, 141, 178] and sintering kinetics [34, 153] to investigating the relationship between reaction conditions and particle size, morphology and crystal phase [3, 131, 132]. The simplicity of the reactor geometry makes the set-up ideal for modelling studies. For determining reaction rate, the concentration of TiCl₄ is typically measured using infra-red absorption spectroscopy. A variety of techniques are used to characterise the properties of particles including differential mobility analysers (DMA) and scanning mobility particle sizers (SMPS) to measure the electrical mobility size of aggregates. The morphology of aggregates and primary particle size is usually obtained by analysing transmission electron microscopy (TEM) images and the crystal phase of particles is characterised by X-ray diffraction (XRD).

Combustion synthesis of metal oxide nanoparticles in flame experiments has also received widespread attention due to potential applications in the manufacture of functional nanomaterials [103, 157], for example, by the direct deposition of titania nanoparticles onto a substrate in a stagnation flame set-up [133, 168]. Flame aerosol synthesis has been used to synthesise and study ultra-fine titania particles. The technique has been shown to achieve highly tunable particle properties by controlling experimental conditions, including the particle size distribution [169, 197] and crystal phase content [87, 109, 119]. Experimental investigations have also synthesised metastable phases of titania in flames [109, 145].

2.1.3 Particle morphology and particulate processes

The structure of particles is important in our understanding of their evolution during synthesis, for example, the effect of surface shielding on the growth rate [7] and the impact of a fractal-like structure on the collision cross-section of particles [202]. Furthermore, morphology has a significant effect on the functional properties of nanoparticles, such as their mechanical and transport properties [38, 165], and light scattering [48, 164].

Evolution of fractal-like aggregates

Flame made nanoparticle aggregates are generally observed to have fractal-like properties [75, 93, 113]. The particle radius of gyration r_g follows a power law scaling with the number of constituent primary particles n_p [107]

$$n_{\rm p} = k_{\rm f} \left(\frac{r_{\rm g}}{r_{\rm p,avg}}\right)^{D_{\rm f}},\tag{2.1}$$

where D_f is the fractal dimension, k_f is the fractal prefactor and $\bar{r_p}$ is the average primary radius. Early computational efforts (a comprehensive review of the early work on fractal aggregates is presented by Meakin [116]) used Monte-Carlo methods to generate fractal structures from monodisperse spherical primary particles, both on and off lattice, and studied the effect of spatial dimensionality and aggregation model on the fractal scaling relations. The main mechanisms of interest to the study of aerosol synthesis are ballistic cluster-cluster aggregation (BCCA) [81] in the free molecular regime and diffusion limited cluster aggregation (DLCA) [82] in the continuum regime. Recent work has also investigated the effect of primary particle polydispersity on the fractal properties of aggregates. Eggersdorfer and Pratsinis [42] found that primary polydispersity has a significant effect on estimates of the fractal prefactor and to a lesser extent the fractal dimension. These results are consistent with a study by Goudeli et al. [63], who also showed that aggregates composed of polydisperse primaries attain the same asymptotic fractal dimension as monodisperse collections of primaries but for a significantly larger number of primaries.

In addition to coagulation, sintering and surface growth processes are also important in determining particle morphology and fractal properties [2, 21, 151]. The sphericity of a particle is governed by the competition between aggregation and rounding processes; namely, sintering and surface growth. Mitchell and Frenklach [124, 125] modelled a single sterically resolved collector particle immersed in an environment of primary particles and surface growth species to investigate the transition from coalescent soot growth to aggregate formation. The work showed the dependence of morphology on the rates of surface growth and nucleation, and demonstrated that aggregation is strongly linked to nucleation – contrary to commonly made assumptions. Further investigations into the evolution of fractal morphology under coagulation and surface growth have been performed by extending the collector-particle model [126] and by discrete element modelling (DEM) [85, 86].

Discrete element modelling is an important technique for studying the morphological evolution of complex aggregates under specific processes because it allows for the incorporation of a very high level of physical detail. Pratsinis and co-workers have performed a number of detailed studies of particle process dynamics, including sintering [40, 41], coagulation [63, 64], coagulation with surface growth [85, 86] and coagulation with sintering [62]. Such studies prove useful in testing commonly made modelling assumptions, for example, the assumption of a constant fractal dimension and the relationship between mobility diameter and radius of gyration [86]. Simple functional relationships for particle properties can be obtained from detailed DEM studies for use in population balance models [63].

Sintering kinetics of titania

Surface area reduction is the main driving force behind sintering. Early stage sintering is usually described in terms of the evolution of the neck radius between two particles [36, 56, 70]. Koch and Friedlander [89] obtained the commonly used expression for the late stage decay in excess surface area from the expression for the neck size obtained by Hiram and Nir [70]. The phenomenological model of Koch and Friedlander [89] lends itself well to use in modelling studies, the simplest of which consider the surface area and volume of an aggregate [172, 188], and also to fitting a characteristic sintering time to experimental data [34, 153] due to the relationship between the surface area and measured mobility diameter [148].

A number of studies have attempted to obtain the sintering kinetics from experimental data [34, 153, 187]. Seto et al. [153] performed an experimental investigation into the sintering of titania aggregates and compared characteristic sintering times obtained from surface diffusion, grain boundary diffusion and volume diffusion models in the literature. The best agreement

with experimental data was observed for the surface diffusion based model of Kobata et al. [88], which is often used in modelling studies on titania [172, 185, 188, 189].

Molecular dynamics (MD) simulations have also been used to investigate the sintering of titania nanoparticles. Collins et al. [37] identified three stages of sintering – contact, locking and fusion – and determined that sintering takes place largely by surface diffusion. This is consistent with results from other MD studies [25, 91]. Buesser et al. [25] performed MD simulations of 2–4 nm rutile to full coalescence, concluding that while surface diffusion is the dominant mechanism, sintering by grain boundary diffusion takes place to a lesser extent. They note that this may explain the conflicting literature on grain boundary versus surface diffusion. In any case, the characteristic sintering times for both mechanisms have the same quartic dependence on particle size. The study showed that the late stage sintering behaviour is in good agreement with the commonly used phenomenological model [89], but observed significantly faster sintering of very small particles.

2.1.4 Population balance modelling

The time evolution of a system of particles can be described by a population balance equation (PBE) of the form:

$$\frac{\partial n(P_q,t)}{\partial t} = \frac{1}{2} \sum_{\substack{P_r,P_s \in E \\ P_r + P_s = P_q}} K(P_r,P_s)n(P_r,t)n(P_s,t) - \sum_{P_r \in E} K(P_q,P_r)n(P_q,t)n(P_r,t) + R_{inc}(P_q) + \sum_{m \in M} \left(\sum_{\substack{P_r \in E \\ g_m(P_r) = P_q}} R_m(P_r)n(P_r,t) - R_m(P_q)n(P_q,t) \right)$$
(2.2)

where $n(P_q, t)$ is the number density of particles of type P_q at time t. P_q is an element of the type space E, which describes the internal coordinates (e.g. mass, composition, surface area etc.) of all possible particles. The first two terms of Eq. (2.2) are the Smoluchowski coagulation equation [176] with coagulation kernel K. $R_{inc}(P_q)$ is the rate of inception of particles of type P_q due to all single particle (i.e. linear) processes, for example, surface growth, condensation and sintering. R_m is the rate of process $m \in M$, M is the index set of linear processes, and $g_m(P_r)$ is the resulting particle from process m acting on a particle of type P_r . The first term in the parentheses represents the production of particles of type P_q by a linear process acting on particles of type P_r , and the second term describes the consumption of P_q by the linear process.
The PBE can rarely be solved analytically and a variety of numerical methods have been developed in the literature, some of which are discussed below. The particular approach chosen for a modelling study will depend on a number of factors. A key consideration is the degree of detail in the model used to describe the particles and particle processes. More detailed models will restrict the range of available methods due to computational cost. An equally important consideration is the complexity of the overall system being modelled; for example, coupling the PBM to gas-phase chemistry, modelling spatial inhomogeneity and particle transport. More complex systems typically require the use of computational fluid dynamics and are generally restricted to particle models with fewer internal coordinates due to computational expense.

Particle models

Univariate models. The simplest, one-dimensional, particle model describes only the mass, volume or monomer composition of a particle [51]. An assumption of spherical geometry is usually made so that the particle surface area and radius can be calculated.

Bivariate models. Two-dimensional models, typically describing a particle by its surface area and volume, can represent a simple aggregate structure and allow internal structural processes to be modelled, such as sintering [95, 188]. Such models do not resolve the internal primary particle distribution, but do allow the average primary diameter and number of primaries to be determined. Equally, an assumption of monodisperse primary particles can be made. Bivariate models can, however, also incorporate primary particle polydispersity. For example, Heine and Pratsinis [67] developed a model that resolves the aggregate particle size distribution in one dimension and use a second dimension to resolve the primary particle size distributions within the aggregates.

High-dimensional multivariate models. Multivariate particle models are able to incorporate an arbitrary degree of detail in the particle description and are not restricted to any number of internal dimensions. Primary particle models are the most detailed in the literature. They are capable of resolving the mass of individual primary particles [184], their connectivity and level of sintering with each individual neighbour [150, 156], and even their detailed internal composition [33].

The most detailed models usually represent an aggregate particle as a union of intersecting spheres [40, 124, 125, 126], providing a full geometrical description of fractal-like particles. Morgan et al. [126] extended the single collector particle model of Mitchell and Frenklach [124, 125] to an ensemble of aggregate particles to simulate the morphological evolution of soot particles in laminar premixed flames and study the interplay between nucleation,

coagulation and surface growth rates. Schmid et al. [151] employed a 'quasi-monodisperse' model to simulate aggregate morphology under coagulation and sintering. The model tracked the connections between primaries of equal mass and resolved the aggregate geometry using an overlapping spheres model.

A different approach was taken by West et al. [184], who extended a surface-volume description with the addition of a list of one-dimensional primary particles for each aggregate. This was later extended by Sander et al. [150] to include a description of the connectivity and level of sintering between neighbouring primaries (this model will be described in more detail Section 2.2.1). The model was subsequently developed further with the incorporation of a kinetic Monte Carlo model for polycyclic aromatic hydrocarbon (PAH) growth [31], providing a detailed description of the PAH composition of individual soot primaries. The high level of detailed permitted the simulation of properties comparable with experimental observations. For example, size distributions of particles [33, 102], transmission electron microscopy (TEM) images, optical band gap [193] and PAH fringe length measurements [194].

Numerical methods

Moment methods. The method of moments describes the evolution of a population of particles by the moments of the distribution, but does not resolve the particle size distribution (PSD). One is typically interested in only the first few moments of the population (number density, mass density etc.); thus, the method is computationally very efficient due to the limited number of equations to be solved. The equations, however, are unclosed. Various methods of closure have been developed, including the method of moments with interpolative closure (MoMIC) [50, 51], quadrature methods [112, 115], and hybrid methods [130].

Due its computational efficiency, the method of moments is often used when simulating problems involving particle transport and when coupling to computational fluid dynamics is necessary [4, 112, 167]. However, the method of moments is typically restricted to one-dimensional [51, 80, 108, 115, 167] and two-dimensional [112, 129, 130, 167, 186] particle models.

Sectional methods. The sectional method [54, 55] divides the distribution of particle properties into discrete bins and an equation for the number of particles in each section is solved. The method was adapted by Hounslow et al. [74] to conserve particle number and mass. Moving sections were introduced to address issues of numerical diffusion associated with surface growth [97]. Two dimensional sectional methods have seen widespread use in modelling studies investigating particle shape and sintering of inorganic nanoparticles [67, 79, 131, 172, 188]. Sectional methods have an advantage over moment methods in that they give some resolution

of the particle size distribution, but at much greater computational expense. Like moment methods, sectional methods can be easily coupled to gas-phase chemistry and flow dynamics, but are also difficult to extend beyond two dimensions in the particle description.

Stochastic methods. The basic principle of a direct simulation Monte-Carlo algorithm (DSMC), introduced by Bird [18], is to represent the real system of particles by some number of computational particles in a homogeneous sample volume. The system is treated as a statistical ensemble and the solution to the population balance equation is then approximated by the random generation of events, where the probability of an event is given by a known rate function, which is dependent on the properties of the system. One early example of the application of the Monte-Carlo method to the Smoluchowski coagulation equation was presented by Gillespie [59]. Assuming a stochastic model of the physical coagulation process, Gillespie [59] derives an exponentially distributed waiting time between successive events, which forms the basis of the waiting time algorithm. This is sometimes called the event driven method. An alternative approach, the time driven method, is to explicitly discretise time into fixed intervals and sample the Poisson distribution to generate the number of events that occurred during each time step [104].

Numerous enhancements have since been made to the direct simulation algorithm, including the introduction of majorant kernels and fictitious jumps to reduce the computational expense associated with coagulation [44, 60]; linear process deferment for the efficient treatment of single particle processes [137]; and ensemble doubling [104, 106] to reduce statistical error due to particle depletion. These will be discussed in more detail in Section 2.2.2. Extending the concept behind ensemble doubling, Smith and Matsoukas [162] proposed a constant number algorithm that maintains a constant number of computational particles under the net gain and net loss of particles. Weighted particle methods [45, 90, 139, 147, 199], were introduced to reduce statistical noise associated with physically rare particles. These differ from the direct simulation methods in that the number of particles remains constant under coagulation. Instead, the statistical weights of particles are adjusted.

The main advantage of stochastic methods is that they allow for models with a large number of internal dimensions and can include a very detailed description of each particle. Stochastic methods combined with very detailed particle models have been used to simulate soot [33, 126, 149], silicon [122], silica [150, 156] and titania [184]. However, stochastic methods can be computationally expensive and spatial inhomogeneity and particle transport are not easily incorporated. Thus, detailed population balance models have been made to apply stochastic methods to systems in which transport effects and spatial inhomogeneity are

important. Xu and Zhao [189] coupled computational fluid dynamics (CFD) to a two and to a three dimensional [190] population balance model solved by a Monte-Carlo method to simulate a co-flow diffusion flame. Higher-dimensional models have been applied to flame simulations using a post-processing methodology [127] – discussed in more detail in Section 2.2.3. This approach has been used successfully to simulate the internal structure of soot formed in laminar flames [33, 126, 161, 193]. Another approach, used to model industrial reactors [19, 120], is to compartmentalise a spatially inhomogeneous system into a network of cells or reactors [77, 96, 201].

2.2 Model framework and simulation methodology

The purpose of this section is to present a background of the model framework and numerical methods that are used, but not developed, in this thesis. The particle model of Sander et al. [150] is applied in Chapter 3 and forms the basic framework from which a new detailed particle model is developed in Chapter 4, so it is worth describing in some detail. The stochastic numerical method used to solve the detailed population balance model is also presented along with the gas-phase coupling methodology. These are referred to throughout the thesis.

2.2.1 Binary tree particle model

The detailed particle model outlined here, termed the binary tree model, was developed by Sander et al. [150] (a detailed description is also given by Shekar et al. [156]) as an improvement of the primary particle list model of West et al. [184]. The primary particle list model extended an earlier two-dimensional surface-volume model [136] by also tracking a list of polydisperse spherical primary particles for each aggregate. The model, however, did not track the connectivity of primaries and sintering was only considered at the aggregate level. The binary tree model improves on this by incorporating primary particle connectivity information using a binary tree data structure (see Section 2.2.2) and modelling the sintering of every pair of connected primaries.

Type space

The description of each aggregate in the population balance model (formally known as the type space) is illustrated in Figure 2.1. An aggregate particle P_q containing $n_p(P_q)$ primary particles p_i with $i \in \{1, ..., n_p(P_q)\}$ is represented as

$$P_q = P_q\left(p_1, \dots, p_{n_p(P_q)}, \mathbf{C}\right).$$
(2.3)



Fig. 2.1 An illustration of the type space of the binary tree model showing an aggregate particle composed of polydisperse primary particles (left panel). The level of sintering between primary particles is resolved by a common surface area (dashed line in right panel) for each pair of neighbouring primaries.

Each primary particle is described by an internal composition variable η_i ,

$$p_i = p_i(\eta_i). \tag{2.4}$$

The composition variable can simply store the number of monomer units in the primary, for example the number of TiO_2 units as is done in this work, or it can contain a more detailed description of the internal structure, such as the crystal phase composition. Shekar et al. [156] tracked the number of Si, O and OH units in a model for silica nanoparticles and Sander et al. [149] incorporated a description of individual PAHs into a model for soot. Primary particle properties, e.g. the mass and volume, are derived from the primary composition.

Neighbouring particles may be in point contact, fully coalesced or anywhere between. The model resolves the common surface area C_{ij} between each pair of neighbouring primary particles (illustrated in the right panel of Figure 2.1). This information is stored in a lower diagonal connectivity matrix **C** of dimensions $n_p(P_q) \times n_p(P_q)$. A matrix element C_{ij} with j < i has the following properties:

$$C_{ij} = \begin{cases} 0, & \text{if } p_i \text{ and } p_j \text{ are not neighbouring;} \\ S_{\text{sph}}(p_i, p_j) \le C_{ij} \le S(p_i) + S(p_j), & \text{if } p_i \text{ and } p_j \text{ are neighbouring.} \end{cases}$$
(2.5)

For neighbouring primaries, C_{ij} takes a value in the range between the surface area of two primaries in point contact and the surface area of a single sphere with the combined volume of the primaries, $S_{\text{sph}}(p_i, p_j)$.

Particle processes

Inception. Inception is modelled as a bimolecular collision of two gas-phase precursor species A and B, creating a particle consisting of a single primary:

$$A + B \rightarrow P_N(p_1) + \text{gas-phase products.}$$
 (2.6)

The rate of inception is given by

$$R_{\rm inc} = \frac{1}{2} K^{\rm fm} N_{\rm A}^2 C_{\rm A} C_{\rm B}, \qquad (2.7)$$

where K^{fm} is the free-molecular kernel (Eq. (2.11)), N_{A} is Avogadro's number, and C_{A} and C_{B} are the concentrations of species A and B, respectively.

Coagulation. An aggregate is formed when two particles, P_q and P_r , stick together following a collision:

$$P_q(p_1,...,p_{n_p(P_q)},\mathbf{C}(P_q)) + P_r(p_1,...,p_{n_p(P_r)},\mathbf{C}(P_r)) \to P_s(p_1,...,p_{n_p(P_q)+n_p(P_r)},\mathbf{C}(P_s)).$$
(2.8)

The rate of collision is calculated using the transition regime coagulation kernel [84, 138], defined as one-half the harmonic mean of the free-molecular and slip-flow kernels

$$\frac{1}{K^{\rm tr}} = \frac{1}{K^{\rm sf}} + \frac{1}{K^{\rm fm}}.$$
(2.9)

The slip-flow and free-molecular kernels [84] are

$$K^{\rm sf}(P_q, P_r) = \frac{2k_{\rm B}T}{3\mu} \left(\frac{1 + 1.257 \text{Kn}(P_q)}{d_{\rm c}(P_q)} + \frac{1 + 1.257 \text{Kn}(P_r)}{d_{\rm c}(P_r)} \right) (d_{\rm c}(P_q) + d_{\rm c}(P_r)), \quad (2.10)$$

and

$$K^{\rm fm}(P_q, P_r) = \varepsilon \sqrt{\frac{\pi k_{\rm B} T}{2} \left(\frac{1}{m(P_q)} + \frac{1}{m(P_r)}\right)} (d_{\rm c}(P_q) + d_{\rm c}(P_r))^2,$$
(2.11)

respectively. Kn is the Knudsen number

$$\operatorname{Kn}(P_q) = \frac{2\lambda}{d_{\rm c}(P_q)},\tag{2.12}$$

where the mean free path and viscosity are approximated as those of air at pressure p and temperature T:

$$\lambda = 2.371 \times 10^{-5} \frac{T}{p} \,\mathrm{m},\tag{2.13}$$

$$\mu = 1.458 \times 10^{-6} \frac{T\sqrt{T}}{T+110.4} \text{ kg m}^{-1} \text{ s}^{-1}.$$
(2.14)

 ε is the collision enhancement factor, *m* is the aggregate particle mass and *d_c* is the particle collision diameter.

The collision diameter is based on the fractal relationship [95, 114, 174]

$$d_{\rm c} = d_{\rm p} \left(n_{\rm p} \right)^{1/D_{\rm f}}, \qquad (2.15)$$

$$= \left(\frac{6V}{S}\right) \left(\frac{S^3}{36\pi V^2}\right)^{1/D_{\rm f}},\tag{2.16}$$

where V is the aggregate volume, S is the surface area of the aggregate and $D_{\rm f}$ is the fractal dimension. Sander et al. [149] estimate the surface area as

$$S = \frac{S_{\rm sph}}{s_{\rm avg}(1 - n_{\rm p}^{1/3}) + n_{\rm p}^{-1/3}},$$
(2.17)

where S_{sph} is the spherical equivalent surface area of the particle, n_p is the number of primary particles, and s_{avg} is the average sintering level of the aggregate (discussed below).

After a coagulation event, two primary particles, uniformly selected from each coagulating particle, are assumed to be in point contact and the connectivity matrix is updated as follows:

$$\mathbf{C}(P_s) = \begin{pmatrix} & \vdots & \\ \mathbf{C}(P_q) & \cdots & 0 & \cdots \\ \vdots & & \vdots & \\ \cdots & C_{ij} & \cdots & \mathbf{C}(P_r) \\ \vdots & & \end{pmatrix}, \qquad (2.18)$$

Surface reaction. Particles can evolve through reactions between gas-phase species and the particle surface. The rate of surface reaction for a particle P_q has the general form

$$R_{\rm sg}(P_q) = k \ f(P_q) \ \prod_{i=1}^{I} C_i^{\nu_i}, \tag{2.19}$$

where $f(P_q)$ is some particle property (e.g. surface area or reactive surface site density), C_i is the concentration of species *i* and v_i is the order of reaction with respect to the species. *k* has a modified Arrhenius form

$$k = A T^{n} \exp\left(-\frac{E_{a}}{RT}\right), \qquad (2.20)$$

with prefactor A, temperature exponent n, and activation energy E_a .

During a surface growth event a primary particle within the aggregate is selected for adjustment. Selection may be uniform or weighted by some primary property such as the surface area. The primary particle evolves as

$$p_i(\eta_i) \to p_i(\eta_i + \Delta \eta).$$
 (2.21)

and the common surface areas stored in the connectivity matrix C will be updated for matrix elements where p_i and p_j are neighbouring:

$$C_{ij} \to C_{ij} + \Delta S(p_i). \tag{2.22}$$

 $\Delta S(p_i)$ is the change in surface area of p_i :

$$\Delta S(p_i) = v_{\text{TiO}_2} \Delta \eta \frac{2\sigma}{d_p(p_i)}, \qquad (2.23)$$

where v_{TiO_2} is the volume of one unit of TiO₂ and σ is the surface smoothing factor which can take a value in the range: $0 \le \sigma \le 2$ [149].

Condensation. Particles can also grow by condensation of gas-phase species, modelled as a free-molecular collision between a single gas-phase molecule and a particle. The rate of collision (per particle) is based on the free-molecular kernel and assumes that the mass and diameter of the condensing species are much smaller than those of the particle:

$$R_{\rm cond}(P_q) = A_{\rm cond}C_{\rm A}N_{\rm A}\varepsilon \sqrt{\frac{\pi k_{\rm B}T}{2m_{\rm A}}} \left(d_c(P_q)\right)^2, \qquad (2.24)$$

where A_{cond} is the collision efficiency, and C_A and m_A are the concentration and mass of the condensing species A.

The state space is adjusted in the same way as for surface reactions.

Sintering. The sintering model considers the reduction in the excess common surface area C_{ij} of a pair of neighbouring primaries p_i and p_j over that of a volume-equivalent spherical

particle $S_{\text{sph}}(p_i, p_j)$. The sintering of each pair of neighbouring primaries is treated individually. It is assumed that the excess surface area decays exponentially according to the equation [89]:

$$\frac{\mathrm{d}C_{ij}}{\mathrm{d}t} = -\frac{1}{\tau_{\mathrm{s}}(p_i, p_j)} \left(C_{ij} - S_{\mathrm{sph}}(p_i, p_j) \right), \qquad (2.25)$$

where $\tau_{s}(p_{i}, p_{j})$ is a characteristic sintering time.

Shekar et al. [156] define a sintering level for two primaries p_i and p_j :

$$s_{ij} = \frac{\frac{S_{\text{sph}}(p_i, p_j)}{C_{ij}} - 2^{-1/3}}{1 - 2^{-1/3}}.$$
(2.26)

Note that $0 \le s_{ij} \le 1^1$. The model assumes that the primaries have coalesced if the sintering level exceeds 0.95. In this case, the two primary particles $p_i(\eta_i)$ and $p_j(\eta_j)$ merge into a single primary $p_k(\eta_i + \eta_j)$. The connectivity matrix is updated so that the neighbours of p_i and p_j become the neighbours of p_k and the common surface areas for each pair are re-estimated using the sintering level.

2.2.2 Stochastic numerical method

Monte Carlo methods lend themselves well to solving high-dimensional population balance models. In this thesis, a Direct Simulation Algorithm (DSA) is used with various enhancements to improve efficiency. The direct simulation approximates a real system by an ensemble of N equally weighted computational particles in a sample volume V_{smpl} . The evolution of the particle ensemble is treated as a Poisson process with exponentially distributed waiting time τ between events [60]

$$\operatorname{Prob}\left(\tau \ge t\right) = \exp\left(-R_{\operatorname{tot}} \cdot t\right), \qquad (2.27)$$

where R_{tot} is the total rate. The probability of a particle process being selected for an event is dependent on its relative rate. The direct simulation Monte Carlo algorithm is presented in Appendix B.1 and the enhancements are described in the sections below.

Particle ensemble

The population balance solver uses a variable size particle ensemble with a predefined maximum number of computational particles N_{max} . The particle ensemble represents a real population of

¹The sintering level of Shekar et al. [156] is a simplification of an earlier form introduced by Sander et al. [150]. The two are equivalent for primary particles of equal size and cover the full range $s \in [0, 1]$; otherwise, the lower bound of Eq. (2.26) is greater than 0.

particles contained in a sample volume

$$V_{\rm smpl} = \frac{N}{M_0}.$$
 (2.28)

The sample volume is adjusted due to gas-phase expansion and contraction, and ensemble contraction and doubling. Ensemble contractions occur when a new particle is incepted into an already saturated ensemble. Since the maximum ensemble size N_{max} cannot be adjusted during simulation, a random particle is discarded instead and the sample volume is contracted proportionately to represent a smaller volume in the real system. Contractions result in a loss of information and can significantly alter the particle size distribution. Therefore, it is important to select an appropriate initial sample volume to minimise the number of contractions. This is done by estimating the maximum value of the particle number density over the course of the simulation, $M_{0,\text{max}}$, such that initially

$$V_{\rm smpl} = \frac{N_{\rm max}}{M_{0,\rm max}}.$$
(2.29)

To maintain a statistically significant number of computational particles, the ensemble is doubled if $N(t) < N_{\text{max}}/2$. In this case, each computational particle is duplicated and the sample volume is doubled. Therefore, during the simulation (except at early times) the actual number of computational particles lies in the range $[N_{\text{max}}/2, N_{\text{max}}]$.

Binary tree data structure

Binary tree data structures are used to improve computational efficiency. A binary tree structure is employed in two instances: (1) to store information about the stochastic particle ensemble and (2) to store the primary particle and connectivity information for each individual aggregate particle. Implementation of the binary tree in the latter instance is illustrated in Figure 2.2 and discussed in more detail below. In the former, a binary tree is connected to a list which stores the ensemble of stochastic particles. Each node in the tree stores the sum of the properties of the particles below it. With this structure, the computational expense of particle selection and system update steps is $\mathcal{O}(\log(N))$, allowing for rapid particle selection and efficient calculation of ensemble statistics and the total process rate [61].

Sander et al. [150] used a binary tree in their implementation of the detailed particle model (described in Section 2.2.1) to store the primary particle and connectivity information for each aggregate. An example of the binary tree representation of a particle is shown in Figure 2.2. Each non-leaf node connects to two child nodes below it and a parent node above it (except for the root node). These are illustrated as squares labelled A...E and the connections are shown



Fig. 2.2 A binary tree data structure used to store an aggregate particle. Non-leaf nodes are shown as squares and connections are shown by the solid lines. The leaf nodes (circles) represent the primary particles. The dashed lines are additional pointers showing the primary particle connectivity.

by the solid lines. The leaf nodes, drawn as circles, store the primary particles $p_1...p_6$. Each non-leaf node stores the sum of the properties of the (primary) particles below it, enabling efficient particle selection and updates to particle properties. Consequently, the root node stores the aggregate particle properties e.g. surface area, volume, number of primaries, etc. Furthermore, each non-leaf node stores information pertaining to a single connection between two primaries p_i and p_j . In this case, the common surface area C_{ij} is stored and the node identifies (or points to) the two primaries p_i and p_j . These pointers are represented by the dashed lines. The connectivity matrix representation of the binary tree structure in Figure 2.2 is

An important consequence of the binary tree data structure is that only branched particles such as that shown in Fig. 2.3a can be represented. The primaries are labelled $p_1...p_6$ and the necks between primaries are indicated by blue dots labelled A...E, corresponding to the labelling of the non-leaf nodes in Fig. 2.2. It is worth noting that the particle model of Sander et al. [150] only tracks which primaries are connected to each other and not their exact spatial



(a) Branched particle structure.

(b) Particle with a connectivity cycle between primaries p_3 , p_5 and p_6 .

Fig. 2.3 (a): branched particle structure represented by the binary tree data structure in Fig. 2.2. (b): an additional connection between p_3 and p_5 , creating a connectivity cycle, cannot be represented.

arrangement. The binary tree fixes the number of connections between primaries at $n_p - 1$. Thus, it is not possible to represent particles with connectivity cycles, for example, a particle with an additional neck between primaries p_3 and p_5 shown in Fig. 2.3b. A cycle is a path that can be taken from a primary that returns to the primary passing through successive neighbours only once.

Linear process deferment

Linear processes involve a single particle interaction, for example, surface growth and condensation of gas-phase species. For systems in which the rates of linear processes dominate those of non-linear processes a typical direct Monte-Carlo simulation will spend a significant amount of computational effort performing single particle events. Patterson et al. [137] introduced the Linear Process Deferment Algorithm (LPDA) to accelerate simulations by reducing the number of single particle operations. In the LPDA, linear processes are removed from the main loop of the stochastic algorithm and instead individual particles are only updated when they take part in a jump process. The algorithm tracks the elapsed time since the last update. Furthermore, all particles are updated at regular intervals to ensure no particle is too out of date. Patterson et al. [137] report up to three orders of magnitude improvement in run times with minimal loss of accuracy in simulations of soot formation in laminar premixed flames.

Majorant kernels and fictitious jumps

Calculation of the total coagulation rate requires summation over every pair of particles

$$R_{\rm cg} = \frac{1}{2} \sum_{q \neq r}^{N} K(P_q, P_r) \tag{2.31}$$

A simple approach to this incurs computational expense of order N^2 . Eibeck and Wagner [44] introduced the majorant kernel and fictitious jumps to avoid this cost. A majorant kernel is a function $\hat{K} \ge K$, for which it is computationally efficient to calculate

$$\hat{R}_{cg} = \frac{1}{2} \sum_{q \neq r}^{N} \hat{K}(P_q, P_r).$$
 (2.32)

Goodson and Kraft [60] presented a majorant kernel for the free-molecular regime (*cf.* Eq. (2.11)) of the form

$$\hat{K}^{\rm fm}(P_q, P_r) = 2\varepsilon \sqrt{\frac{\pi k_{\rm B} T}{2}} \left(\frac{1}{m(P_q)^{1/2}} + \frac{1}{m(P_r)^{1/2}}\right) (d_{\rm c}(P_q)^2 + d_{\rm c}(P_r)^2), \tag{2.33}$$

and Patterson et al. [138] extended the approach to the transition regime, defining the majorant rate

$$\hat{R}_{\rm cg}^{\rm tr} = \min\left(\hat{R}_{\rm cg}^{\rm fm}, R_{\rm cg}^{\rm sf}\right). \tag{2.34}$$

Due to its simpler form, the slip-flow kernel does not require a majorant. The correct rate is returned by rejecting events while still advancing time, i.e., performing a fictitious jump, with probability

$$1 - \frac{K(P_q, P_r)}{\hat{K}(P_q, P_r)}.$$
 (2.35)

This approach takes advantage of the binary tree data structure, which can store and efficiently update pre-calculated sums of particle properties.

2.2.3 Coupling the particle population and gas-phase chemistry

It is clear that some particle processes (see Section 2.2.1) involve the consumption and production of gas-phase species; namely, inception, surface growth and condensation. Thus, the gas-phase and particle population are inherently coupled. Two approaches are taken in this thesis in the treatment of the interaction between the gas and particle phases. The first approach, used in simple batch or plug flow reactor simulations, is coupling the gas-phase and particle population balance by operator splitting. The second, used for laminar flame simulations, is a two-step methodology where the detailed population balance model is applied as a post-process to a gas-phase flame profile obtained from a fully coupled simulation with a simple particle model. The reason for using the two-step approach is the difficulty in coupling a multidimensional population balance model to flow dynamics.

Operator splitting

Coupling of the particle population balance, solved by a stochastic method, to the gas-phase chemistry, solved using an ODE solver, is achieved by the Strang operator splitting technique described in detail by Celnik et al. [29]. The technique employs a refinement introduced by Strang [166], which staggers the two operators by half a splitting time step. Alternative methods of coupling are also available, although not considered in this work, for example, predictor-corrector coupling [30].

Post-processing

The post-processing methodology was developed in order to apply a detailed soot model to simulations of premixed laminar flames [10, 33, 126, 138, 161], and has also been applied to simulations of inorganic nanoparticles [127]. The methodology consists of two simulation steps. In the first step, the flame is simulated as a fully coupled system with one-dimensional flow, gas-phase chemistry and a simple particle population balance model, which approximately captures the effect of the particles on the gas-phase. Solving the coupled system to steady state is computationally expensive. The method of moments with interpolative closure (MoMIC) [50, 51] is used because it is numerically simple and easy to couple.

In the second step, the resulting gas-phase profile is post-processed with the detailed particle model, solved using the stochastic numerical method. The flame conditions and gas-phase species are supplied as input to the stochastic population balance simulation. The simulation considers the Lagrangian view of particles in a spatially homogeneous control volume and requires the computed profiles to be expressed in terms of the residence time of a Lagrangian particle. The spatial coordinates of the computed profiles are transformed into temporal coordinates using the velocity of the flow field [127]. This two-step methodology is discussed further in Chapter 5.

Chapter 3

Relating milling behaviour to particle morphology

This chapter explores whether the morphological data captured by the binary tree model can be applied in a particle breakage model to relate the structure of aggregate particles to their size-reduction behaviour in a post-synthesis milling process. This work aims to relate the reactor conditions under which titanium dioxide particles form to their subsequent milling performance. Five breakage models that utilise the morphological information in the particle model type space are developed and their behaviour is examined in a simple milling test case. Moreover, this work identifies limitations in the type space of the binary tree particle model and makes recommendations for the development of a new detailed particle model.

3.1 Background

The functionality of titanium dioxide as an industrial product is strongly influenced by the size, shape and morphology of the particles. Although the chloride process for manufacturing TiO_2 is widely used, optimisation remains largely empirical. In many cases, the product is milled in order to control the final particle size distribution (PSD). This imposes an additional time and energy cost.

Milling has been widely studied due to the high industrial demand for fine powders with tightly controlled properties. A lot of research has focused on identifying optimal milling parameters such as agitation speed, milling media size, filling ratio and suspension concentration. The effect of operational parameters on the milling performance of titanium dioxide has been investigated for fine grinding and dispersion of particles in wet stirred mills [14, 76, 134]. Other

work has studied the substructure and mechanical properties of titania agglomerates [57], and the changes in fractal morphology of dense aggregates under wet milling [78].

Population balance models have also been used to characterise the milling process, and identify breakage mechanisms in wet stirred media milling [15, 68, 69, 175] by fitting Kapur's approximate first order solution [83] to experimental data. More complex models consider non-linear effects and time-variant PBMs [16, 17].

Over long milling times and for sub-micron sized particles, more complex phenomena are typically observed. This includes time delays in breakage [16], and grinding limits due to a minimum obtainable particle size and agglomeration effects [49, 68, 76, 163]. Modelling multimodal particle size distributions with statistical laws has been used as an alternative method for obtaining the grinding kinetics [14, 49].

Most modelling efforts use a very simple particle description, commonly just the particle mass, and introduce two functions: a size dependent breakage rate and the fragment distribution function [46]. This work aims to develop a milling model based on the binary tree model type space [150] described in Section 2.2.1, where the breakage rate and fragment distribution are both dependent on the morphological properties captured by the particle model. The idea is to relate the reactor conditions under which particles are synthesised to their subsequent performance in the milling process. Particle synthesis in a laboratory-scale hot wall reactor is simulated using the detailed titanium dioxide model outlined in Section 3.2, which describes the time evolution of the internal structure of the fractal-like TiO₂ aggregates. The simulation results are post-processed using breakage models developed in Section 3.3 to provide proof of concept that the morphological data in the detailed model can be related to the milling behaviour of particles.

3.2 Titanium dioxide model

The synthesis of TiO_2 particles by the oxidation of $TiCl_4$ is modelled using a detailed particle population balance model coupled to detailed gas-phase chemistry.

3.2.1 Gas-phase chemistry

The kinetic model for the formation of TiO_2 particles from $TiCl_4$ is based on the mechanism proposed by West et al. [185]. It comprises 28 gas-phase species and 66 reactions.

3.2.2 Particle model

The binary tree particle model of Sander et al. [150], described in Section 2.2.1, is used. Particles consisting of primary particles composed of units of TiO_2 evolve under inception, coagulation, surface growth and sintering processes.

Inception

Inception is modelled as per Akroyd et al. [4] and is assumed to result from the bimolecular collision of gas-phase titanium oxychloride species

$$\operatorname{Ti}_{x_{\alpha}} \mathcal{O}_{y_{\alpha}} \mathcal{Cl}_{z_{\alpha}} + \operatorname{Ti}_{x_{\beta}} \mathcal{O}_{y_{\beta}} \mathcal{Cl}_{z_{\beta}} \longrightarrow \left(x_{\alpha} + x_{\beta} \right) \operatorname{Ti} \mathcal{O}_{2(s)} + \left(\frac{y_{\alpha} + y_{\beta}}{2} - x_{\alpha} - x_{\beta} \right) \mathcal{O}_{2} + \left(\frac{z_{\alpha} + z_{\beta}}{2} \right) \mathcal{Cl}_{2}, \quad x, y, z \ge 1,$$

$$(3.1)$$

where the molecular collision diameter is taken as 0.65 nm [185]. An inception event creates a particle consisting of a single primary composed of $(x_{\alpha} + x_{\beta})$ TiO₂ units.

Surface growth

Surface growth is treated as a single-step reaction as in Akroyd et al. [4]

$$TiCl_4 + O_2 \longrightarrow TiO_{2(s)} + 2Cl_2, \qquad (3.2)$$

with the rate expression

$$\frac{\mathrm{d}[\mathrm{Ti}\mathrm{O}_2]}{\mathrm{d}t} = k_{\mathrm{sg}} S_{\mathrm{v}} [\mathrm{Ti}\mathrm{Cl}_4] [\mathrm{O}_2], \qquad (3.3)$$

where S_v is the surface area per unit volume of the TiO₂ population and k_{sg} has an Arrhenius form

$$k_{\rm sg} = A \, \exp\left(-\frac{E_{\rm a}}{RT}\right) \frac{\rm m}{\rm s} \cdot \frac{\rm m^3}{\rm mol},$$
(3.4)

with activation energy E_a and pre-exponential factor A. One surface growth event adds one unit of TiO₂ to the particle. Equation (3.3) assumes fixed reaction orders with respect to TiCl₄ and O₂. Alternative models for the rate of surface growth are discussed by Shirley et al. [158].

Coagulation

Coagulation is treated in the transition regime as described in Section 2.2.1. The collision enhancement factor for the free-molecular kernel is taken as $\varepsilon = 2.2$ as in previous studies on

titania [4, 184, 185]. For the purpose of modelling the collision diameter, a fractal dimension of $D_{\rm f} = 1.8$ [172] is assumed in Eq. (2.16).

Sintering

The characteristic sintering time is taken from Kobata et al. [88] as per West et al. [185]

$$\tau_{\rm s} = 7.4 \times 10^{16} T d_{\rm p}^4 \exp\left(\frac{258\,{\rm kJ\,mol^{-1}}}{RT}\right) \,{\rm s},\tag{3.5}$$

where d_p is the diameter of the smaller primary [150, 191].

3.2.3 Numerical method

The population balance equations are solved using the stochastic numerical method described in Section 2.2.2. The particle population is coupled to the gas-phase chemistry, solved using an ODE solver, by Strang operator splitting, described in Section 2.2.3.

3.3 Milling model

In the milling process, particles break due to stresses exerted by the milling media. Kwade and co-workers [98, 99] describe the process in terms of the frequency of stress events and the intensity of each stress event. The energy intensity is introduced as a key factor in determining whether a breakage event occurs. A stress event of sufficient intensity will result in breakage.

Low intensity shear stresses are sufficient for breaking weak agglomerates whereas higher intensity normal stresses are required to break crystalline material [100]. Normal stresses arise when a particle is caught in-between milling beads during a collision. The resulting fragment size distribution is dependent on the properties of the material and the mode of fragmentation.

Three types of breakage mechanism are usually discussed in the literature: abrasion, cleavage and fracture [13, 16, 71, 72, 144, 175]. Abrasion involves a continuous loss of mass from the surface of a particle resulting in a bimodal fragment distribution. Cleavage produces fragments of the same order in size as the original particle, while fracture results in disintegration of the particle into small fragments. The different modes of fragmentation often occur simultaneously during milling.

Epstein [46] first introduced population balance equations to the study of milling, modelling breakage as two successive operations represented by a selection and a breakage function. The selection function is the probability of a particle of given size breaking and is usually observed

to increase with particle size [72]. The breakage function describes the shape of the fragment size distribution and is characterised by the fragmentation mechanism.

The idea of this work is to explore whether the information in the type space of the detailed population balance model can be related to the observed milling performance of TiO_2 particles. The particle breakage rate and fragment distribution are determined by a breakage model that utilises the morphological information captured by the detailed particle model.



Fig. 3.1 A sketched milling curve and a possible concept relating the detailed particle type space to the shape of the curve. The coloured arrows indicate a possible influence of a particle property on the shape of the milling curve.

Figure 3.1 shows a sketch of a milling curve. The average particle size is observed to decrease during the initial part of the milling curve. Eventually the system reaches an asymptotic state where no further significant decrease is observed.

One possible concept relating the detailed particle model to the milling curve is shown overlaying Fig. 3.1. The average particle size is obtained from the aggregate size distribution and the asymptotic particle size is a function of the primary particle size distribution. The slope of the milling curve depends on the breakage mechanism and is some function of the aggregate particle structure. Breakage, assumed to occur at the necks between neighbouring primaries, is related to the neck size distribution and the fractal geometry of the particle. The particle geometry is responsible for transmitting milling stresses to necks and the neck strength is related to the neck size.

In this work, we apply a milling model based on Algorithm 1 as a post-process to the detailed population balance model. The particle breakage rate is given by the breakage models discussed in Section 3.3.2. Two of the breakage models utilise a neck radius to characterise

how strongly neighbouring primaries are connected. The neck model is discussed in the next section.

Algorithm 1: Milling algorithm applied as a post-process to the detailed particle model.

Input: Initial state of the particle ensemble at time t_0 ; Final time t_f . **Output:** State of the particle ensemble at final time $t_{\rm f}$. $t \leftarrow t_0$. while $t < t_f$ do Calculate the rate, $R_{part}(P_q)$, for each aggregate particle P_q , $R_{\text{part}}(P_q) = \sum_{i < j} R_{ij},$ where R_{ij} is the breakage rate for the neck between two primaries p_i and p_j . Calculate the total rate, R_{tot} , for all N particles, $R_{\rm tot} = \sum_{q=1}^{N} R_{\rm part}(P_q).$ Calculate an exponentially distributed waiting time Δt with parameter R_{tot} , $\Delta t = \frac{-\ln(U)}{R_{\rm tot}},$ where U is a uniform random variate in the interval [0, 1]. With probability $R_{part}(P_q)/R_{tot}$ select a particle P_q . With probability $R_{ij}/R_{part}(P_q)$ select a neck. Break the neck between primaries p_i and p_j , and update the particle ensemble: $P_q \rightarrow P_r + P_s$, $N \leftarrow N + 1$. Increment $t \leftarrow t + \Delta t$. end

3.3.1 Neck size calculation

A neck between two primary particles is modelled as two overlapping spheres as shown in Fig. 3.2. An assumption in the particle model for the common surface area is that it is calculated separately for each pair of neighbouring primaries without considering other neighbours. The neck size can be calculated from the common surface area C_{ij} and spherical-equivalent radii r_i and r_j of each primary particle. The volume V and surface area S of two overlapping spheres



Fig. 3.2 Geometry of the neck between two primary particles.

are given

$$V(R_1, R_2, d) = \frac{4\pi}{3} \left(R_1^3 + R_2^3 \right) - \frac{\pi}{12d} \left(R_1 + R_2 - d \right)^2 \left(d^2 + 2R_1 d + 2R_2 d - 3R_1^2 - 3R_2^2 + 6R_1 R_2 \right),$$
(3.6)

and

$$S(R_1, R_2, d) = 4\pi \left(R_1^2 + R_2^2\right) - \pi \left(a^2 + H_1^2\right) - \pi \left(a^2 + H_2^2\right),$$
(3.7)

where a is the radius of the neck [180]

$$a(R_1, R_2, d) = \frac{1}{2d} \Big[(R_1 + R_2 + d) (R_1 + R_2 - d) (-R_1 + R_2 - d) (R_1 - R_2 - d) \Big]^{\frac{1}{2}},$$
(3.8)

and where H_1 and H_2 are the heights of the spherical caps

$$H_i = R_i - R_i \cos\left(\arcsin\left(\frac{a}{R_i}\right)\right),\,$$

and R_1 and R_2 are the radii of two spheres whose centres are separated by a distance $d \in [0, R_1 + R_2]$. The final term in Eq. (3.6) is the volume of the three-dimensional lens [180] and the final terms in Eq. (3.7) are the areas of each spherical cap [181] created by the intersection of the spheres.

Under the assumption that the volume of the three-dimensional lens is evenly redistributed over the surface of the particles in an even layer of thickness Δr , the radius of each sphere in Fig. 3.2 can be written in terms of the spherical-equivalent radii of the corresponding primary particles

$$R_i = r_i + \Delta r. \tag{3.9}$$

Equations (3.6) and (3.7) may be reduced to two equations in two unknowns using the substitutions in Eqs. (3.8) and (3.9),

$$V(\Delta r, d) = v_i + v_j,$$

$$S(\Delta r, d) = C_{ij},$$

and can be solved for the values of Δr and d, and hence the radius of the neck $a_{ij}(\Delta r, d)$ for each pair of neighbouring primary particles with corresponding total volume $v_i + v_j$ and common surface area C_{ij} .

3.3.2 Breakage models



Fig. 3.3 A breakage event. An aggregate particle P_q fragments into two daughter particles P_r and P_s at a neck of radius a_{ij} connecting two primaries p_i and p_j . The aggregate is represented as two arms, corresponding to the respective daughter particles, extending from the neck.

Figure 3.3 illustrates a single breakage event where an aggregate particle P_q fragments into two smaller daughter particles P_r and P_s . Breakage is treated as binary and always occurs at a neck connecting two neighbouring primary particles. Individual primaries are assumed not to break.

An aggregate particle is modelled as two arms extending from a neck as depicted by the dashed arrows in Fig. 3.3. Note that this representation can be applied to any chosen neck within the aggregate. The composition of the arms is equivalent to that of the two daughter

fragments formed in the event of breakage. When a particle is caught in a three-body collision with two milling beads the stresses are transmitted by these arms to the neck. The neck that breaks during such a collision will depend on a number of factors including the neck size or strength, and the size, shape and orientation of the respective arms.

The rate of breakage of a neck between two primaries p_i and p_j is expressed as a function of the neck and daughter particle (fragment) properties

$$R_{ij} = R_{ij}(P_r(..., p_i, ..., \mathbf{C}_r), P_s(..., p_j, ..., \mathbf{C}_s), a_{ij}),$$
(3.10)

where $P_r(..., p_i, ..., C_r)$ and $P_s(..., p_j, ..., C_s)$ are the daughter particles formed in the breakage event, a_{ij} is the neck radius, and C is the respective connectivity matrix storing the common surface areas as defined in Shekar et al. [156]. Five different breakage models are discussed below. It is assumed that a rate constant *k* captures the operational parameters of the mill and that the mill is capable of producing collisions of sufficient intensity to break all particle necks. The total particle breakage rate for a particle P_q is

$$R_{\text{part}}(P_q) = \sum_{i < j} R_{ij}, \qquad (3.11)$$

where we sum over i < j to avoid double counting.

Simple neck model

The breakage rate is assumed to be only a function of the neck radius, calculated as per Section 3.3.1

$$R_{ij} = k a_{ij}^{\alpha}, \tag{3.12}$$

for constants k and α .

Total mass model

The probability of breakage is typically observed to increase with particle size. In this model we assume that the rate of breakage for a neck is proportional to the sum of daughter fragment masses $m(P_r)$ and $m(P_s)$ or equivalently, the total particle mass $m(P_q)$

$$R_{ij} = k(m(P_r(..., p_i, ..., \mathbf{C}_r)) + m(P_s(..., p_j, ..., \mathbf{C}_s)))$$
(3.13)

$$= km(P_q(..., p_i, p_j, ..., \mathbf{C}_q)),$$
(3.14)

for constant *k*. Breakage is equally likely for every neck in an aggregate. The rate of breakage for a single aggregate particle is therefore a function of its total mass and the number of necks.

$$R_{\text{part}}(P_q) = k(n_{\text{p}}(P_q) - 1)m(P_q), \qquad (3.15)$$

where $n_p(P_q)$ is the number of primaries and $(n_p(P_q) - 1)$ corresponds to the number of necks, which is always one less than the number of primaries.

Fragment mass model

A simple way to characterise the size of a fragment arm is by its mass. More massive arms are expected to apply greater stresses on a neck due to greater leverage and arms of similar mass will maximise the applied stress. This is modelled by setting the rate of breakage proportional to the product of the daughter particle masses

$$R_{ij} = k \cdot m(P_r(..., p_i, ..., \mathbf{C}_r)) \cdot m(P_s(..., p_j, ..., \mathbf{C}_s)),$$
(3.16)

for a constant k and where $m(P_r)$ and $m(P_s)$ are the masses of the two particle fragments joined at the neck between primaries p_i and p_j .

Fragment radius model

A better measure of the size of a fragment arm is its radius of gyration, which accounts for the fractal structure of the aggregate,

$$r_{\rm g} = d_{\rm p,avg} \left(\frac{n_{\rm p}}{k_{\rm f}}\right)^{1/D_{\rm f}}.$$
(3.17)

 $n_{\rm p}$ is the number of primaries, $d_{\rm p,avg}$ is the average primary diameter, $D_{\rm f}$ is the fractal dimension, and $k_{\rm f}$ is the fractal prefactor. A typical value of 1.8 is assumed for the fractal dimension [172]. Using the same form for the rate as in Eq. (3.16) the breakage rate for a single neck is

$$R_{ij} = k \cdot r_{g}(P_{r}(..., p_{i}, ..., \mathbf{C}_{r})) \cdot r_{g}(P_{s}(..., p_{j}, ..., \mathbf{C}_{s})),$$
(3.18)

for a constant k and where $r_g(P_r)$ and $r_g(P_s)$ correspond to the radii of gyration of the two arms extending from the neck between primaries p_i and p_j .



Fig. 3.4 Two possible breakage events. The selected neck between primaries p_i and p_j is indicated by a dashed line and the fragment arms extending from the neck have radii of gyration $r_g(P_r)$ and $r_g(P_s)$. (a) Symmetrical breakage produces daughter fragments with similar radii of gyration while (b) shows an asymmetrical breakage event.

Fragment and neck radius model

The fragment radius of gyration model in Section 3.3.2 assumes that all necks are equally strong. However, the degree of sintering between primary particles will effect the breakage rate. By combining the fragment radius model (Section 3.3.2) and the simple neck model (Section 3.3.2) we can relate the breakage rate to both the geometry of the aggregate particle and the size of the neck. The rate of breakage is

$$R_{ij} = k \cdot r_{g}(P_{r}(..., p_{i}, ..., \mathbf{C}_{r})) \cdot r_{g}(P_{s}(..., p_{j}, ..., \mathbf{C}_{s})) \cdot a_{ij}^{\alpha},$$
(3.19)

for constants *k* and α .

Figure 3.4 illustrates two possible breakage events. We expect that breakage is most likely if both radii of gyration are large and of similar magnitude as shown in Fig. 3.4a. However, in the case of a very weak neck, an asymmetrical abrasion-like event is also possible as depicted in Fig. 3.4b.

3.4 Results and discussion

3.4.1 Hot wall reactor simulations

The hot wall reactor experiment of Pratsinis et al. [141] was simulated to produce particles for post-processing with the milling models. The reactor was simulated using 8192 stochastic particles, repeated 4 times. The surface growth rate was fitted for the detailed particle model. The original investigation measured the reaction of $5:1 \pmod{0}$ O₂:TiCl₄ in argon (99% by volume) in a 1/8-in-I.D. tube heated to 973-1273 K.

Pratsinis et al. [141] estimate an effective rate constant for the overall oxidation kinetics of TiCl₄ vapour

$$k_{\rm eff} = -\frac{\ln(C_{\rm o}/C_{\rm i})}{t_{\rm res}},\tag{3.20}$$

assuming the reaction is first-order in TiCl₄ with Arrhenius kinetics, and C_i and C_o are the measured inlet and outlet TiCl₄ concentrations. t_{res} is the residence time in the isothermal zone of the reactor held at temperature *T*. The experiment was simulated using the imposed temperature profile of Pratsinis et al. [141, Fig. 3] modelled by Akroyd et al. [4]. The temperature starts at 300 K and rises to the isothermal zone temperature *T* remaining there for the residence time t_{res} . At the end of the isothermal zone the temperature falls back to 300 K and remains at this temperature until the end of the simulation.



Fig. 3.5 Arrhenius plot of the oxidation rate of $TiCl_4$ at three different residence times. Black lines terminating in open symbols: fitted simulation results; Shaded symbols: experimental data [141, Fig. 4].

Figure 3.5 shows good agreement between detailed particle model simulations and the experimental results of Pratsinis et al. [141, Fig. 4]. The data are presented in the original form

for ease of comparison. A reaction that is overall first order in $TiCl_4$ would produce a single straight line through all residence times. The differences observed between the simulation results for the different isothermal residence times suggests a reaction that is close to but not exactly first order overall.

The surface growth rate was fitted with activation energy $E_a = 60 \text{ kJ/mol}$ and pre-exponential factor $A = 1340 \text{ m}^4/(\text{s} \cdot \text{mol})$ (see Eq. (3.4)). The fitted activation energy is in agreement with the theoretically calculated value (55±25 kJ/mol) of Shirley et al. [158].



(a) 0.49 s at 1000 K

(b) 1.1 s at 1100 K

Fig. 3.6 TEM-style images of titania aggregates produced in the simulated hot wall reactor under different conditions. The visualisation does not depict the level of sintering between particles, but this information is captured by the model.

Simulation data is visualised in Fig. 3.6 in the form of TEM-style images showing titania particles produced in the hot wall reactor under two different isothermal zone residence times and temperatures. The examples presented in the figure are for two extremes within the simulated range of reactor conditions showing the greatest difference in particle morphology.

Aggregate particles produced over a longer isothermal residence time at higher temperature (1.1 s at 1100 K shown in Fig. 3.6b) are composed of a smaller number of larger primaries than aggregates produced at a lower temperature and shorter isothermal residence time (0.49 s at 1000 K shown in Fig. 3.6a). This is clear from the primary diameter distribution (Fig. 3.7) and the distribution of the number of primaries per aggregate (Fig. 3.8).

The difference in aggregate particle size is less pronounced. Figure 3.9 shows the distribution of particle collision diameters calculated as per Sander et al. [149]. The aggregate particle size is a function of the number of primary particles, their respective diameters, and the level of sintering between neighbours. This allows for aggregates of comparable size despite the different primary particle properties. The largest particles are of similar size under both sets of reactor conditions, but the distribution in Fig. 3.9a extends to smaller collision diameters. The smallest particles are composed of a single primary particle and the lower minimum value arises due to the smaller mean primary diameter.



Fig. 3.7 Primary particle diameter distributions produced under two different simulated isothermal zone residence times and temperatures. The red line shows the Gaussian kernel density estimate.



Fig. 3.8 Distribution of the number of primaries per titania aggregate produced under two different simulated isothermal zone residence times and temperatures. The red line shows the Gaussian kernel density estimate.

Figure 3.10 shows the distribution of neck radii for the two cases. The distributions are truncated at 0.3 nm: of the order of the rutile unit cell size. Below this size, a second peak was observed in both simulations at a radius of 0.01–0.1 nm: smaller than an atomic diameter. The neck model (Section 3.3.1) permits the neck radius to take any positive value and does not account for quantization at very small length scales. Furthermore, molecular dynamics studies of sintering of nanometre sized titania particles show that the formation of an initial neck is



Fig. 3.9 Collision diameter distributions of titania aggregates produced under two different simulated isothermal zone residence times and temperatures. The red line shows the Gaussian kernel density estimate.

very rapid, of the order of 10 picoseconds [25, 37, 91], whereas in this work sintering is treated as a continuous process with the same characteristic time at all stages.

The bimodal distribution arises due to the simulated temperature profile in which the temperature falls to 300 K at the end of the isothermal zone. The stronger temperature dependence of sintering causes the sintering process to slow faster than coagulation resulting in the formation of small necks. The 0.49 s isothermal zone residence time simulations spent a longer time at 300 K than the 1.1 s simulations which created a larger number of small necks.

Up to 5% of necks were calculated to be in point contact ($a_{ij} = 0$). These necks are considered to represent primaries bound by weak dispersion forces that have yet to begin sintering. Larger necks with well defined radii correspond to sintered primaries joined by strong chemical bonds.

3.4.2 Comparison of breakage models

The breakage models presented in Section 3.3.2 were used to post-process the hot wall reactor simulation results of Section 3.4.1 using Algorithm 1. The results of post-processing the 0.49 s at 1000 K simulation are discussed here as a representative case because they display the general features of the different breakage models also observed in the other reactor simulations. Under the assumption that necks in point contact ($a_{ij} = 0$) break apart easily we processed the data to break these necks prior to milling.



Fig. 3.10 Neck radius distribution for titania aggregates produced in the simulated hot wall reactor under two different conditions. Necks smaller than 0.3 nm are not shown.

Milling curves

Typically observed industrial milling curves (from Huntsman Pigments and Additives) are shown in Fig. 3.11. The volume weighted mean particle size is observed to decrease logarithmically over the period covered by the data. The width of the PSD as measured by the volume weighted geometric standard deviation (GSD) of particle size also exhibits logarithmic decay. The data set does not contain the initial particle size distribution nor the long time behaviour of particles under milling.



Fig. 3.11 Experimental milling curves (Huntsman Pigments and Additives) show logarithmic decay in both the volume weighted mean particle size and geometric standard deviation. Dashed line added to guide the eye.

Figure 3.12 shows the corresponding simulated milling curves for the different breakage models. The time coordinate is non-dimensionalised by defining a characteristic time equal to

the time taken for the mass weighted geometric mean collision diameter to fall to 90% of its initial value. The mass weighted geometric mean (GM) and mass weighted GSD are given by

$$\ln(GM) = \frac{\sum_{q=1}^{N} m(P_q) \ln(d_c(P_q))}{\sum_{q=1}^{N} m(P_q)},$$
(3.21)

$$\ln(\text{GSD}) = \sqrt{\frac{\sum_{q=1}^{N} m(P_q) \left[\ln(d_c(P_q)) - \ln(\text{GM}) \right]^2}{\sum_{q=1}^{N} m(P_q)}},$$
(3.22)

for N particles P_q with mass $m(P_q)$ and collision diameter $d_c(P_q)$.



Fig. 3.12 Milling curves for different breakage models obtained by post-processing hot wall reactor simulation results for the 0.49 s at 1000 K case. (a) shows the mass weighted geometric mean collision diameter and (b) shows the mass weighted geometric standard deviation in the collision diameter. The horizontal dashed line indicates the asymptotic value calculated from the primary particle distribution.

A value of -1 was selected for the exponent α in the simple neck and the fragment radius and neck models yielding rates inversely proportional to the neck radius. A negative exponent implies that larger necks require greater stresses to break. More negative choices of α introduce a long intermediate period during which the GM and GSD change very little. This is observed to a small degree in the simple neck model ($\alpha = -1$ case) in Fig. 3.12b where the gradient changes at around $\tau = 100$.

Figure 3.12a plots the mass weighted geometric mean collision diameter against nondimensionalised time. All models exhibit an intermediate period of approximately logarithmic decay as seen in the experimental milling curves (Fig. 3.11). The total mass and fragment radius models have almost identical mean collision diameter curves. The simple neck and fragment and neck radius models show two distinct phases of size reduction characterised by different gradients. The change in gradient arises due to the bimodal nature of the neck size distribution. The first mode of small necks breaks first followed by the second mode of larger and stronger necks.

The GSD curves (Fig. 3.12b) offer a clearer way to differentiate between models. Most display an intermediate period of approximately logarithmic decay. An interesting feature is the initial increase in GSD seen in the total mass and simple neck models. Such an increase in the variance has been observed experimentally in the grinding of titanium dioxide [14]. This arises due to the formation of small fragments that cause a widening in the particle size distribution and can be seen in the mass weighted collision diameter distributions in Fig. 3.13. The distribution near the maximum GSD for the simple neck model ($\tau = 4.4$ in Fig. 3.13a) is skewed with more mass density at smaller diameters contributing to a wider, lower peak. In comparison, the fragment and neck radius model in Fig. 3.13b maintains a more symmetric distribution due to a preference for symmetrical breakage events.



Fig. 3.13 Mass weighted collision diameter distributions generated using a Gaussian kernel density estimate at different non-dimensionalised times for the 0.49 s at 1000 K reactor simulation post-processed with the (a) simple neck and (b) fragment and neck radius models.

Choice of breakage model

Whilst it is difficult to exclude models based only on the qualitative comparison of milling curves, the current work illustrates the different features produced by each model, particularly with regard to the GSD and evolution of the PSD. Of the five breakage models discussed here only the fragment and neck radius model considers the aggregate particle geometry as well as the neck strength. The dependence on aggregate geometry favours symmetrical breakage in a cleavage type mechanism. On the other hand, the neck size dependence favours small necks allowing for cases of asymmetrical breakage near the particle extremities, similar to an

abrasion mechanism. Since the model accounts for the detailed particle morphology it serves as good candidate for further study.

3.4.3 Effect of reactor conditions on milling curves

The fragment and neck radius model was applied to simulations of the hot wall reactor experiment under different conditions. Results are shown in Fig. 3.14. The time coordinate was non-dimensionalised for all cases using the characteristic time calculated for the 0.49 s at 1000 K case allowing for better comparison along the time axis.



Fig. 3.14 Milling curves for the fragment and neck radius model obtained by post-processing hot wall reactor simulation results under different conditions. The horizontal dashed lines show the asymptotic values calculated from the primary particle distributions.

All simulations take approximately the same time to reach an asymptotic state. Two phases of approximately logarithmic decay, characterised by different gradients, are observed due to the bimodal neck size distribution. In the 1.1 s isothermal zone residence time simulations the first phase is not as well defined. The longer isothermal residence time results show a slower decrease in the mean particle size and a smaller total change. Both 0.49 s simulations display a rapid first phase of size reduction followed by a slower second phase.

This model shows that particles synthesised over a short residence time in the high temperature isothermal zone of the reactor are milled faster and reduced to a smaller asymptotic size. The GSD has a higher initial value but catches up with the longer isothermal zone residence time simulations over the first phase of size reduction. The effect of temperature, within the range used in this study, is less pronounced.

3.5 Conclusions

A detailed population balance was used to model the formation of titanium dioxide particles in the hot wall reactor experiment of Pratsinis et al. [141]. The particle model was shown to resolve morphological differences between particles produced under different reactor conditions.

Breakage models were developed that utilise the morphological information captured by the detailed particle model and were applied in a post-process to simulate the milling of TiO_2 particles produced in the hot wall reactor simulations. The milling curves exhibited features consistent with experimental observations. The chosen breakage model accounts for the fractal structure of the aggregate particles as well as the size of necks between neighbouring primaries. Application of this milling model to particles produced under different residence times and temperatures showed that the model is sensitive to the reactor conditions under which the TiO_2 particles were synthesised.

Further work is needed to compare the model against experimental results and fit the breakage rate constant. Given the nature of applying the milling model as a post-process, an obstacle to performing a quantitative comparison with experimental data is the need for details of the experimental conditions under which the particles were first synthesised as well as experimental data from the subsequent milling of the particles. Moreover, this work highlights a number of limitations in the current binary tree model particle description that should be addressed before making further progress. These are discussed in the following section.

3.5.1 Suggestions for model development

During the course of developing a morphological breakage model, a few observations were made on the limitations of the binary tree particle model. These are outlined here along with suggestions for further model development.

An important consideration in developing the breakage model was a measure of the neck size between two primaries. The neck size is not directly captured by the particle model; instead, the model treats sintering by considering a common surface area for every pair of neighbouring primaries. The neck radius was then calculated in a post-processing step with the assumption of overlapping spherical geometry. Consequently, a number of necks were predicted to have small, unphysical radii. This suggests that either a different neck model needs to be considered in the post-process for particles with low levels of sintering or the neck geometry should be incorporated into the particle type space and sintering model. Molecular dynamics studies [25, 37, 91] show that the phenomenological sintering model [89] used in this work does not capture the early stage behaviour of rapid neck growth well – a caveat to the

model noted by Koch and Friedlander [89] – supporting the latter approach to incorporate a geometric description of the neck into the particle model.

A second observation is that the model does not account for the effect of a primary having multiple neighbours. The common surface area is captured and consequently the neck size is calculated for each pair of neighbours individually, without considering the effect other neighbours on the primary size. For example, in an overlapping spheres model, increasing the number of sintered neighbours will necessarily increase the primary size in order to conserve mass.

Lastly, the model only tracks the connectivity and not the spatial arrangement of primary particles. Therefore, the collision diameter and radius of gyration of the aggregate are dependent on an assumed fractal dimension, fractal prefactor and the average sintering level for the aggregate. This is also a factor in visualising the particle. A breakage model based on the geometry of the aggregate is limited by the accuracy of these assumptions. Furthermore, the sintering level is unreliable in the case of neighbouring primaries with very different sizes as noted in Section 2.2.1.

The above points suggest that there is significant scope to improve the model type space to give a better representation of aggregate particle morphology. Addressing these limitations and developing a new detailed particle model that better captures the particle geometry will be the subject of the next chapter.
Chapter 4

A new detailed particle model

This chapter presents the mathematical description of a new detailed particle model for polydisperse aggregate particles. The new particle description is used to model the aerosol synthesis of TiO_2 aggregates from titanium tetraisopropoxide (TTIP) precursor. The new process models are tested and a numerical study is performed by simulating a simple batch reactor test case to investigate the convergence behaviour of key functionals. Finally, a lab-scale hot wall reactor is simulated to examine some features of the model.

4.1 Background

Population balance models incorporating a detailed particle description provide a powerful tool to investigate the mechanisms that control particle morphology and facilitate the simulation of quantities that are directly comparable to experimental observations. For example, size distributions and mass spectra of particles [33, 102], transmission electron microscopy (TEM) images and optical band gap measurements [193]. Such models also enable the option to include key physical details in the model. For instance, models where the particle growth is a function of the aggregate composition [31, 32], or where sintering and neck growth are resolved for pairs of neighbouring primary particles [128, 149, 150, 182]. Moreover, physical properties are strongly influenced by particle morphology such as the collision diameter [202], mobility diameter [43, 165], or optical properties [48]. The degree of model detail can have a significant impact on the interpretation of simulation results and comparison with experimental measurements. Models that capture sufficient physical detail also make it possible to further post-process simulation data to study the post-synthesis treatment of particles – as in the previous chapter.

In this chapter, we develop a new detailed population balance model for polydisperse aggregate particles. The new particle description, or type-space, represents an aggregate particle

as a collection of overlapping spheres. This is based on the approach used by Mitchell and Frenklach [124, 125] to model aggregation with surface growth for a single collector particle, and later extended by Morgan et al. [126] to an ensemble of particles. An overlapping spheres model was also employed by Eggersdorfer et al. [40, 41] to simulate multiparticle sintering. We utilise the overlapping spheres approach to model surface growth, sintering, primary particle coalescence and coagulation, incorporating a ballistic cluster-cluster collision model [81] to determine the particle configuration following a coagulation event. The radius, composition and position of each individual primary particle are resolved, allowing the morphological evolution of each aggregate to be simulated.

The new model overcomes some of the limitations identified in the earlier binary tree model [150, 156], while preserving its efficient data structure. These limitations were discussed in the previous chapter and are briefly summarised here. The binary tree model resolves sintering by a common surface area for each pair of neighbouring primaries. While this allows individual necks to sinter at different rates, the model does not account for the effect of sintering on the primary diameter, resolving only a spherical equivalent diameter. Furthermore, the geometry of the neck and presence of other neighbours is not considered. Lastly, the binary tree model does not track the coordinates of individual primary particles but only their connectivity, which requires an assumption about the fractal dimension and prefactor when calculating the radius of gyration and collision diameter, or when visualising a particle in TEM-style image.

The next section introduces the gas-phase chemical mechanism for titanium tetraisopropoxide precursor used in this chapter. The mathematical description of a new particle model is presented in Section 4.3; specifically, the model equations and a description of how the particle geometry is manipulated under individual processes. The algorithms used to effect these changes are provided in Appendix B.2. The model is presented in the context of TiO₂ synthesised from TTIP with collision limited inception and growth processes. The model, however, is general and can be easily adapted to different precursors and processes. Section 4.4 presents test cases for each process sub-model, comparing the behaviour of the new detailed particle model with simpler models in the literature. In Section 4.5, we briefly study the numerical behaviour of the model, investigating the convergence of a number of average properties for a simple batch reactor test case. Finally, in Section 4.6 we simulate the hot wall reactor experiment of Nakaso et al. [131].

4.2 Chemical reaction model¹

The chemical reaction model consists of a TTIP decomposition mechanism combined with hydrocarbon combustion chemistry described by the USC-Mech II model [177]. The TTIP mechanism contains 25 Ti species and 61 reactions, and describes the decomposition of TTIP to titanium (IV) hydroxide (Ti(OH)₄) through the C_3H_6 and CH_3 abstraction pathways identified by Buerger et al. [23] as well as dissociation reactions of Ti(OH)₄, assumed to be barrierless. In this work, Ti(OH)₄ is treated as the collision species for the particle inception and growth reactions in the particle model.

4.3 Particle model

In this section, the new detailed particle model is presented. First, the particle type space – the mathematical representation of a particle – is described, followed by the particle processes. Particles evolve through: inception, coagulation, growth, sintering and coalescence. Details of the algorithms implementing the process model are provided in Appendix B.2. In this work, the inception and growth processes are assumed to be collision limited reactions consuming $Ti(OH)_4$ from the gas-phase. Relatively simple reactions are chosen to avoid making unnecessary assumptions about the interaction between the gas-phase and particles – an area that is not well understood in the literature. However, the model framework is easy to extend to new inception and growth processes in future studies.

4.3.1 Type space

The type space is the mathematical description of a particle. The detailed particle type space is illustrated in Fig. 4.1. An aggregate P_q containing $n_p(P_q)$ primary particles, modelled as overlapping spheres [40], is represented by

$$P_q = P_q(p_1, ..., p_{n_p(P_q)}, \mathbf{C}), \tag{4.1}$$

where a primary particle p_i , with $i \in \{1, ..., n_p(P_q)\}$, is represented by

$$p_i = p_i(\boldsymbol{\eta}_i, r_i, \mathbf{x}_i). \tag{4.2}$$

¹The combined chemical mechanism used here was put together by Manoel Manuputty and can be found in the supplementary material of [105].



Fig. 4.1 An illustration of the detailed particle model type space. An aggregate particle composed of primary particles (solid lines) modelled as overlapping spheres (indicated by dashed lines).

 η_i is the primary composition and can represent the number of units of TiO₂, as in this work, or could contain a more detailed description of the internal primary structure; for example, the crystal phase composition. r_i is the radius of the primary, and \mathbf{x}_i is the position of the primary centre. It is convenient to express the primary coordinates relative to the centre of mass of the aggregate particle because this simplifies some computations, such as calculating the radius of gyration or performing rotations of the particle during coagulation. For the purpose of calculating the aggregate centre of mass we assume that the primaries are point masses. The degree of overlap between two neighbouring primaries, p_i and p_j , is resolved by their centre to centre separation

$$d_{ij} = |\mathbf{x}_i - \mathbf{x}_j|. \tag{4.3}$$

The primary particles are stored in a binary tree data structure as in the binary tree model of Sander et al. [150], described in Section 2.2.1. The data structure is retained because it enhances computational performance by allowing very efficient selection of primaries and interrogation of their properties, but it does impose some constraints on the primary connectivity within a particle. It would be possible to determine primary connectivity using only the coordinates; however, for the purpose of performing computations the binary tree connectivity is used.

The binary tree is represented in Eq. (4.1) by the connectivity matrix **C**. The connectivity matrix is a binary lower triangular matrix of dimension $n_p(P_q) \times n_p(P_q)$ with matrix elements

$$C_{ij} = \begin{cases} 0, & \text{if } p_i \text{ and } p_j \text{ are not neighbouring;} \\ 1, & \text{if } p_i \text{ and } p_j \text{ are neighbouring.} \end{cases}$$
(4.4)

Model assumptions

The following assumptions are made in the model equations:



Fig. 4.2 Multiple overlapping primary particles.

- 1. Neck cross-sections are circular;
- 2. Neighbours are determined by the binary tree connectivity.

The first assumption implies that the effect of multiple overlaps between primaries (as shown in Fig. 4.2) are not considered. This is also a consequence of the second assumption since the binary tree does not allow for structures with connectivity cycles. These assumptions introduce inaccuracies into the the model equations e.g. calculation of the primary volume, free surface and neck area. Multiple overlaps tend to occur when primaries, that were not initially in contact, sinter and grow producing a more compact structure such as that shown in Fig. 4.2. To reduce the likelihood of this occurring, primaries can be merged sufficiently early to avoid large deviations from circular necks, but at a point at which it is reasonable to approximate the sintered primaries as a single primary. This is handled by the coalescence process (Section 4.3.2). Another scenario in which these structures arise is if two branches overlap. This cannot be avoided through primary coalescence, but the likelihood is reduced for less compact aggregates.

Derived particle properties

Under the above assumptions, a number of primary particle properties can be derived for the model of overlapping spheres [40]. The volume of a primary p_i is given by the volume of a sphere of radius r_i minus the volume of the caps created by overlaps with its neighbours

$$v_{i} = V_{\rm sph}(r_{i}) - \sum_{j} V_{\rm cap}(r_{i}, x_{ij}),$$

$$= \frac{4}{3}\pi r_{i}^{3} - \frac{1}{3}\pi \sum_{j} (2r_{i}^{3} + x_{ij}^{3} - 3r_{i}^{2}x_{ij}), \qquad (4.5)$$

where we sum over *j* neighbours of p_i , and x_{ij} is the distance from the centre of primary p_i to the neck formed with a neighbour p_j

$$x_{ij} = \frac{d_{ij}^2 - r_j^2 + r_i^2}{2d_{ij}}.$$
(4.6)

Primary particles are assumed to be composed of units of TiO₂, so $\eta_i = \eta_{\text{TiO}_{2},i}$, and the volume is also given by

$$v_i = \frac{\eta_{\text{TiO}_2,i} M_{\text{TiO}_2}}{\rho_{\text{TiO}_2} N_{\text{A}}},\tag{4.7}$$

where M_{TiO_2} is the molar mass of TiO₂, ρ_{TiO_2} is the density of TiO₂ (taken here to be that of anatase, $\rho_{\text{TiO}_2} = 3.9 \,\text{g}\,\text{cm}^{-3}$), and N_A is the Avogadro constant.

The partial derivatives of v_i give the area of the neck created by the overlap with a neighbour p_j

$$A_{n,ij} = \frac{\partial v_i}{\partial x_{ij}} = \pi (r_i^2 - x_{ij}^2), \qquad (4.8)$$

and the free surface area of the primary p_i

$$A_{i} = \frac{\partial v_{i}}{\partial r_{i}} = 4\pi r_{i}^{2} - 2\pi \sum_{j} (r_{i}^{2} - r_{i}x_{ij}).$$
(4.9)

Binary tree data structure

The binary data structure is described in Section 2.2.2 and particular features of its implementation for the new detailed particle model are described here. An important detail of the model equations is that they require summation over neighbours of a primary to calculate properties such as the primary volume, free surface and neck area etc. The binary tree offers an efficient way to do this. A feature of the binary tree is that two primaries lie below their connecting node in the tree. For example, in Fig. 4.3, node C represents the neck connecting primaries p_3 and p_6 . Node C could not, for instance, connect primaries p_2 and p_3 ; this can only be achieved by a node above both primaries i.e. node A. Since each neck must be a non-leaf node located above the primary, it is only necessary to take a path from the primary of interest to the root node to find the neighbours; the rest of tree does not need to be explored. Figure 4.3 shows an example of interrogating the binary tree for neighbours of p_3 . The path taken is shown by the solid red lines along the route: p_3 -D-C-A.



Fig. 4.3 Left panel: Interrogating the binary tree for neighbours of p_3 by moving up the tree from the leaf node to the root node along the path in bold red. The neighbours of p_3 and connections to non-leaf nodes are highlighted. Right panel: Illustration of the primary particle connectivity with p_3 and its neighbours highlighted.

4.3.2 Particle processes

Inception

Inception is modelled as a bimolecular collision of two Ti(OH)₄ molecules forming a particle consisting of a single spherical primary containing two units of TiO₂:

$$Ti(OH)_4 + Ti(OH)_4 \longrightarrow P_N(p_1) + 4H_2O.$$
(4.10)

The rate of inception is calculated using the free molecular kernel:

$$K_{\rm inc}^{\rm fm} = \varepsilon \sqrt{\frac{\pi k_{\rm B} T}{m_{\rm Ti(OH)_4}}} \left(2d_{\rm Ti(OH)_4}\right)^2,\tag{4.11}$$

where $m_{\text{Ti}(\text{OH})_4}$ and $d_{\text{Ti}(\text{OH})_4}$ are the mass and diameter of a single Ti(OH)_4 molecule, respectively. The collision diameter $d_{\text{Ti}\text{OH}_4} = 0.5128 \text{ nm}$, is estimated from the geometrical parameters calculated by Buerger et al. [24]. ε is the size-dependent collision enhancement factor. Here it is assumed to be size-independent and taken as $\varepsilon = 2.2$ as in previous studies on titania [4, 184, 185]. This value is the average size-independent enhancement factor due to van der Waals forces calculated by Harris and Kennedy [66] for spherical soot particles.

Coagulation



(a) Particles P_r and P_q before collision.

Primary p_i from P_r and p_i from P_a are in point contact.



An aggregate is formed when two particles stick together following a collision and the rate is given by the transition kernel presented in Section 2.2.1 (see Eq. (2.9)).

Ballistic cluster-cluster aggregation² Once two particles are selected for coagulation, the orientations and point of contact between the colliding particles are determined by ballistic cluster-cluster aggregation (BCCA) with a random impact parameter [81]. This process is illustrated in Fig. 4.4. To model a collision three random parameters are generated: the particles are randomly rotated around their centres of mass using the method described by Arvo [8]; a random direction is generated by uniformly picking a point on a sphere centred on one of the particles [179]; and, a random impact parameter is applied by placing the second particle at a random point in the plane perpendicular to the collision trajectory. The random impact parameter offsets the collision trajectory from the particle centres of mass. The collision is initialised such that the particle bounding spheres, estimated using the method described by Ritter [146], do not overlap. A detailed algorithm for performing BCCA is given in Appendix **B.2.1**.

Diffusion limited cluster aggregation Ballistic cluster-cluster aggregation is valid in freemolecular regime. In the slip-flow and continuum regimes, collisions become diffusion limited

²Implementation of BCCA was initiated by Edward Yapp into the old binary tree particle model. The algorithm was subsequently adopted into the new detailed particle model with minor modifications.

and a diffusion limited cluster aggregation (DLCA) algorithm should be used. The DLCA algorithm is computationally more expensive than BCCA due to the simulation of a Brownian random walk. This increases the number of computational steps and increases the likelihood of a collision failing when a particle 'escapes'. With these considerations in mind and the fact that collisions under typical aerosol synthesis conditions are in the free-molecular regime, BCCA is chosen to model collisions between particles in this work unless otherwise stated. A straightforward implementation of both BCCA and DLCA, though not done in this work, would be to select the appropriate aggregation model for each collision based on the Knudsen number. An algorithm for performing DLCA is provided in Appendix B.2.2 and a test case is presented in Appendix C.2.

Connectivity matrix Following the collision, two primaries p_i and p_j (one from each colliding particle determined by the BCCA algorithm) are assumed to be in point contact and the connectivity matrix is updated as follows:

$$\mathbf{C}(P_s) = \begin{pmatrix} & \vdots & \\ \mathbf{C}(P_q) & \cdots & 0 & \cdots \\ \vdots & & \vdots & \\ \cdots & C_{ij} & \cdots & \mathbf{C}(P_r) \\ \vdots & & \end{pmatrix}, \qquad (4.12)$$

where $C_{ij} = 1$.

Collision diameter The diameter of gyration d_g is commonly used as the collision diameter d_c in both the free-molecular and continuum regimes. The diameter of gyration is given by the standard fractal relationship

$$n_{\rm p} = k_{\rm f} \left(\frac{d_{\rm g}}{d_{\rm p,avg}}\right)^{D_{\rm f}},\tag{4.13}$$

where $d_{p,avg}$ is the average primary diameter, D_f is the fractal dimension and k_f is the fractal pre-factor.

A number of studies using bivariate models with monodisperse primaries [95, 114, 174] and multivariate models [149] (see Section 2.2.1) use the fractal relationship to define the collision diameter as

$$d_{\rm c} = d_{\rm p,avg} n_{\rm p}^{1/D_{\rm f}}.\tag{4.14}$$

Kruis et al. [95] note that the characteristics of this collision diameter are:

1. For $n_p = 1$: the collision diameter is equal to the primary particle diameter.

2. For $n_p \gg 1$: the collision diameter approaches the diameter of gyration of the aggregate.

The drawback of this definition is that the fractal dimension D_f is a model parameter, typically assumed to be $D_f \approx 1.8$ [152, 172], and does not evolve as particles grow and sinter. Moreover, the pre-factor is often assumed to be $k_f \approx 1$ or absorbed into the constant of proportionality between the collision and gyration diameters. In our new model, the ability to track individual primary coordinates permits the diameter of gyration of an individual aggregate to be calculated without assuming a value for k_f and D_f . This can then be used as the collision diameter.

The diameter of gyration is defined [101] as

$$d_{\rm g}^2 = \frac{4}{\sum_i m(p_i)} \sum_i m(p_i) \left(|\mathbf{x}_i|^2 + r_{\rm g}(p_i)^2 \right), \tag{4.15}$$

where $r_g(p_i)$ is the radius of gyration of primary p_i and $|\mathbf{x}_i|$ is the distance from the centre of mass of the aggregate to the centre of the primary. For a sphere $r_g(p_i) = \sqrt{3/5}r_i$; however, following Filippov et al. [48] we choose $r_g(p_i) = r_i$, the radius of the primary, so that in the limit of $n_p = 1$ the collision diameter yields the primary diameter. The collision diameter can then be defined as

$$d_{\rm c}^2 = \frac{4}{\sum_i m(p_i)} \sum_i m(p_i) \left(|\mathbf{x}_i|^2 + r_i^2 \right).$$
(4.16)

In the limit of large n_p this tends to the diameter of gyration. This definition shares the same characteristics as Eq. (4.14) as discussed by Kruis et al. [95]. Furthermore, in the case of two primaries of the same size in point contact the collision diameter ($d_c = 2\sqrt{2}r_p$) is close to that obtained by Zurita-Gotor and Rosner [202] ($d_c = 2.892r_p$).

Growth

Particles can grow by condensation of gas-phase species and surface reactions. In both cases, geometrical adjustments to the particle are performed the same way. In the present application, we consider only a collision limited condensation-like growth process, consuming $Ti(OH)_4$ from the gas-phase and adding TiO_2 to surface of a particle. The rate of collision is based on the free molecular kernel and assumes that the mass and diameter of the condensing species is much smaller than that of the particle

$$K_{\text{cond}}^{\text{fm}} = \varepsilon \sqrt{\frac{\pi k_{\text{B}} T}{2m_{\text{TiO}_2}}} \left(d_{\text{c}}(P_q) \right)^2.$$
(4.17)

The mass of the condensing species is assumed to be similar to TiO_2 .



Fig. 4.5 A surface growth event. Mass is added to the free surface of primary p_i (dark shaded region). The new particle geometry is shown by the red dashed line. Immediate neighbours of p_i are labelled p_j , and neighbours of neighbours are labelled p_k .

Fig. 4.5 shows a particle undergoing a growth event. A primary, p_i , is selected with probability proportional to its relative free surface area. The condensing mass is added to the free surface of p_i (shaded region in Fig. 4.5) increasing the primary radius r_i . We assume that the primary positions \mathbf{x}_i , and all other primary radii r_j remain unchanged during the event. The change in radius given a change in the aggregate particle volume $V(P_q)$ is

$$\frac{\mathrm{d}r_i}{\mathrm{d}t} = \frac{1}{A_i} \frac{\mathrm{d}V(P_q)}{\mathrm{d}t}.$$
(4.18)

Following a growth event, the positions of the necks between p_i and its neighbours p_j will have changed as illustrated by the red dashed lines in Fig. 4.5. This amounts to a redistribution of mass between primaries and requires an adjustment to the compositions of p_i and its neighbours p_j . The adjustment is performed in discrete units of TiO₂, with unit volume

$$v_{\text{TiO}_2} = \frac{M_{\text{TiO}_2}}{\rho_{\text{TiO}_2} N_A}.$$
(4.19)

The change in volume of a neighbour p_j is

$$\frac{\mathrm{d}v_j}{\mathrm{d}t} = \frac{\partial v_j}{\partial r_j} \frac{\mathrm{d}r_j}{\mathrm{d}t} + \sum_k \frac{\partial v_k}{\partial x_{jk}} \frac{\mathrm{d}x_{jk}}{\mathrm{d}t},\tag{4.20}$$

where we sum over the neighbours p_k of primary p_j . Under the assumption that the radius of p_j remains constant and noting that the position of the neck between p_j and some other neighbour p_k ($k \neq i$) does not change, this is reduced to

$$\frac{\mathrm{d}v_j}{\mathrm{d}t} = A_{\mathrm{n},ji} \frac{\mathrm{d}x_{ji}}{\mathrm{d}t},\tag{4.21}$$

where we have used Eq. (4.8). Under the same assumptions, differentiating Eq. (4.6), allows the change in volume of p_i to be expressed in terms of the change in the radius of p_i :

$$\frac{\mathrm{d}v_j}{\mathrm{d}t} = -A_{\mathrm{n},ij} \frac{r_i}{d_{ij}} \frac{\mathrm{d}r_i}{\mathrm{d}t},\tag{4.22}$$

from which the integer change in composition of p_i can be determined:

$$\Delta \eta_{\text{TiO}_2,j} = \frac{\Delta v_j}{v_{\text{TiO}_2}}.$$
(4.23)

The surface adjustment algorithm and a discussion of the consequence of limiting the mass redistribution to discrete unit changes can be found in Appendix B.2.3.

Sintering



Fig. 4.6 Sintering of a single neck between primaries p_i and p_j . Neighbours not sintering are labelled p_k . The centre to centre separation decreases by Δd_{ij} . To conserve mass, the radii of the sintering primaries increase by Δr_i and Δr_j respectively and the separation with neighbouring primary p_k increases by Δd_{ik} .

Sintering is performed on each neck individually. A single sintering event on primaries p_i and p_j is shown in Fig. 4.6. The centres of primaries p_i and p_j approach each other, increasing their overlap and neck radius. For titania particles the sintering rate is evaluated using a grain boundary diffusion model [41]. The geometrical model can also accommodate other sintering mechanisms, such as viscous flow for silica [150, 171]. Mass conservation requires that the primary radii r_i and r_j increase. It is assumed that all other neighbours p_k and their respective necks remain unchanged during the event. This requires that the separation d_{ik} increases in response to the change in r_i .

Grain Boundary Diffusion. Following Eggersdorfer et al. [41], the change in distance from the centre of p_i to the neck formed with p_j is

$$\frac{\mathrm{d}x_{ij}}{\mathrm{d}t} = -\frac{2\pi D_{\mathrm{v}}C_{\mathrm{v}0}\delta_{\mathrm{gb}}\gamma\Omega}{k_{\mathrm{B}}TA_{\mathrm{n},ij}} \left(\frac{1}{r_{i}-x_{ij}}-\frac{1}{a_{ij}}\right),\tag{4.24}$$

where a_{ij} is the neck radius, $A_{n,ij}$ is the neck area, and r_i is the primary radius. The product of the vacancy diffusion coefficient, D_v , the equilibrium vacancy concentration, C_{v0} , and grain boundary thickness, δ_{gb} , is taken from Astier and Vergnon [9],

$$D_{\rm v}C_{\rm v0}\delta_{\rm gb} = 1.6 \times 10^{-14} \exp\left(\frac{-258\,\rm kJ\,mol^{-1}}{RT}\right)\,\rm m^{3}\,\rm s^{-1}. \tag{4.25}$$

The surface free energy, $\gamma = 0.6 \text{ J m}^{-2}$, and vacancy volume, $\Omega = 1.57 \times 10^{-29} \text{ m}^3$, are from Anderson [5].

The rate of change in centre to centre separation is

$$\frac{dd_{ij}}{dt} = \frac{dx_{ij}}{dt} + \frac{dx_{ji}}{dt},
= \frac{-6.859 \times 10^{-20}}{TA_{n,ij}} \left(\frac{1}{r_i - x_{ij}} + \frac{1}{r_j - x_{ji}} - \frac{2}{a_{ij}} \right)
\cdot \exp\left(\frac{-258 \,\text{kJ} \,\text{mol}^{-1}}{RT} \left(1 - \frac{d_{\text{p,crit}}}{\min(d_{\text{p}}(p_i), d_{\text{p}}(p_j))} \right) \right).$$
(4.26)

Here we have introduced a critical sintering diameter $d_{p,crit}$ into the exponential term of a form similar to that first introduced by Tsantilis et al. [171] for silica to allow effectively instantaneous coalescence of primaries with $d_p < d_{p,crit}$. Rapid coalescence of very small particles is consistent with findings from molecular dynamics studies [25], and has also been suggested in other works [153]. Buesser et al. [25] found that primaries with $d_p < 4$ nm sinter significantly faster than what would be predicted by the models of Kobata et al. [88] and Seto et al. [153]. In this chapter we use $d_{p,crit} = 4$ nm.

Conservation of mass. Assuming that the density does not change, mass conservation implies that primary particle volume is conserved. The volume conservation of primary p_i is [40]

$$\frac{\mathrm{d}v_i}{\mathrm{d}t} = \frac{\partial v_i}{\partial r_i} \frac{\mathrm{d}r_i}{\mathrm{d}t} + \sum_k \frac{\partial v_i}{\partial x_{ik}} \frac{\mathrm{d}x_{ik}}{\mathrm{d}t} = 0, \qquad (4.27)$$

where p_k is some neighbour of p_i . Rearranging and substituting Eqs (4.8) and (4.9):

$$\frac{\mathrm{d}r_i}{\mathrm{d}t} = \frac{-\sum_k A_{\mathrm{n},ik} \frac{\mathrm{d}x_{ik}}{\mathrm{d}t}}{A_i}.$$
(4.28)

The time derivative of x_{ik} , the distance from the centre of p_i to the neck with a neighbour p_k , is

$$\frac{\mathrm{d}x_{ik}}{\mathrm{d}t} = \frac{r_i}{d_{ik}}\frac{\mathrm{d}r_i}{\mathrm{d}t} - \frac{r_k}{d_{ik}}\frac{\mathrm{d}r_k}{\mathrm{d}t} + \left(1 - \frac{x_{ik}}{d_{ik}}\right)\frac{\mathrm{d}d_{ik}}{\mathrm{d}t}.$$
(4.29)

For $k \neq j$ (i.e. a neighbour that is not sintering)

$$\frac{\mathrm{d}r_k}{\mathrm{d}t} = 0 \quad \text{and} \quad \frac{\mathrm{d}x_{ki}}{\mathrm{d}t} = 0.$$
 (4.30)

Equation (4.29) can then be reduced to

$$\frac{\mathrm{d}x_{ik}}{\mathrm{d}t} = \frac{r_i}{d_{ik}}\frac{\mathrm{d}r_i}{\mathrm{d}t} + \left(1 - \frac{x_{ik}}{d_{ik}}\right)\frac{\mathrm{d}x_{ik}}{\mathrm{d}t},$$

$$= \frac{r_i}{x_{ik}}\frac{\mathrm{d}r_i}{\mathrm{d}t} \quad \text{for } k \neq j,$$
(4.31)

and Eq. (4.28) becomes

$$\frac{\mathrm{d}r_{i}}{\mathrm{d}t} = \frac{-A_{\mathrm{n},ij}\frac{\mathrm{d}x_{ij}}{\mathrm{d}t} - \sum_{k \neq j} A_{\mathrm{n},ik} \frac{r_{i}}{x_{ik}} \frac{\mathrm{d}r_{i}}{\mathrm{d}t}}{A_{i}},$$

$$= \frac{-A_{\mathrm{n},ij}}{B_{ij}}\frac{\mathrm{d}x_{ij}}{\mathrm{d}t},$$

$$= \frac{-A_{\mathrm{n},ij}}{d_{ij}B_{ij} + r_{i}A_{\mathrm{n},ij}} \left(-r_{j}\frac{\mathrm{d}r_{j}}{\mathrm{d}t} + x_{ji}\frac{\mathrm{d}d_{ij}}{\mathrm{d}t}\right),$$
(4.32)

where

$$B_{ij} = A_i + \sum_{k \neq j} A_{n,ik} \frac{r_i}{x_{ik}}.$$
 (4.33)

A similar expression can be derived for r_j

$$\frac{\mathrm{d}r_j}{\mathrm{d}t} = \frac{-A_{\mathrm{n},ij}}{d_{ij}B_{ji} + r_jA_{\mathrm{n},ij}} \left(-r_i \frac{\mathrm{d}r_i}{\mathrm{d}t} + x_{ij} \frac{\mathrm{d}d_{ij}}{\mathrm{d}t} \right). \tag{4.34}$$

Combining Eqs (4.32) and (4.34) gives the change in radius as a function of the change in centre to centre separation:

$$\frac{\mathrm{d}r_i}{\mathrm{d}t} = \frac{-r_j A_{n,ij}^2 - x_{ji} B_{ji} A_{n,ij}}{d_{ij} B_{ij} B_{ij} + r_j A_{n,ij} B_{ij} + r_i A_{n,ij} B_{ji}} \frac{\mathrm{d}d_{ij}}{\mathrm{d}t}.$$
(4.35)

The centre to centre separations of neighbours that are not sintering are adjusted according to Eq. (4.31). The sintering algorithm is presented in Appendix B.2.4.

Coalescence



Fig. 4.7 Primary particle coalescence. Primary p_j is merged into p_i . The neighbour of p_j , labelled p_l , is added to p_i preserving the neck radius.

The sintering level for a neck is defined as the ratio of the neck radius to the radius of the smaller primary

$$s_{ij} = \frac{a_{ij}}{r_j}$$
 where $r_j \le r_i$. (4.36)

Note that $0 \le s_{ij} \le 1$. Both sintering and growth processes increase the sintering level. Once the sintering level exceeds 0.95, the two primaries are assumed to have coalesced into a single primary. Two primaries, p_i and p_j , are shown coalescing in Fig. 4.7. During a coalescence event the smaller primary, in this case p_j , is merged into the larger primary p_i . The other neighbour of p_j , labelled p_l , is added to the new merged primary preserving the neck radius such that $a_{il,new} = a_{jl}$. The primary is translated along the vector $\mathbf{x}_l - \mathbf{x}_i$ to its new position. The other neighbour of p_i , labelled p_k , also preserves its neck radius.

Following the merger, the radius of p_i has changed to $r_{i,\text{new}}$, which requires the neighbour separations to be recalculated since we assume that the neighbours are unchanged by the merger.

The volume of the newly merged primary is

$$v_{i,\text{new}} = v_i + v_j, \tag{4.37}$$

and expressed in terms of the new radius, the volume (Eq. (4.5)) is

$$v_{i,\text{new}} = \frac{4}{3}\pi r_{i,\text{new}}^3 - \frac{\pi}{3}\sum_{m\in\{k,l\}} \left(2r_{i,\text{new}}^3 + \left(r_{i,\text{new}}^2 - \frac{A_{n,im}}{\pi}\right)^{3/2} - 3r_{i,\text{new}}^2\left(r_{i,\text{new}}^2 - \frac{A_{n,im}}{\pi}\right)^{1/2}\right),\tag{4.38}$$

where we sum over all the neighbours, p_k and p_l , of new merged primary $p_{i,\text{new}}$. Equation (4.38) is solved for $r_{i,\text{new}}$ using the Newton-Raphson method and the new primary separation can be determined using Eq. (4.6). For more detail on the merger algorithm refer to Appendix B.2.5

4.4 Particle process model evaluation

4.4.1 Ballistic cluster-cluster aggregation

A simple test case was created to determine the average fractal dimension generated by the BCCA algorithm. A zero-dimensional batch reactor was simulated with an initial population of 4096 monodisperse spherical particles with diameter $d_p = 1.81$ nm (corresponding to 100 units of rutile). Particles were allowed to coagulate in the free-molecular regime with no other processes turned on. The simulation was repeated 8 times producing a total of 25794 particles with a median of 118 primaries per particle.

The fractal dimension D_f and prefactor k_f were estimated by fitting the standard fractal relationship to the data, expressed in the following form:

$$\ln\left(\frac{d_{\rm g}}{d_{\rm p,avg}}\right) = \frac{1}{D_{\rm f}}\ln(n_{\rm p}) - \frac{1}{D_{\rm f}}\ln(k_{\rm f}). \tag{4.39}$$

The diameter of gyration d_g is calculated as per Jullien [81]:

$$d_{\rm g}^2 = \frac{2}{n_{\rm p}^2} \sum_{i,j} \left(\mathbf{x}_i - \mathbf{x}_j \right)^2,$$
(4.40)

which assumes point-like primaries. The data and a least squares fit to a subset of the data (particles with $n_p \ge 16$) are shown in Fig. 4.8a. Figure 4.8b shows how the fitted values of D_f and k_f vary as function of the minimum number of primaries per aggregate included in the fit, $n_{p,min}$. Both D_f and k_f show slight sensitivity to small values of $n_{p,min}$ and approach their asymptotic values for $n_{p,min} > 10$, consistent with the findings of Goudeli et al. [64].



Fig. 4.8 BCCA with particle selection based on the free-molecular kernel. (a): estimate of fractal dimension and prefactor by least squares fit to aggregates with $n_p \ge 16$; the result reported by Eggersdorfer and Pratsinis [42] is included for reference; error bars indicate the confidence interval with P = 0.999. (b): fractal dimension and prefactor as a function of $n_{p,min}$ with P = 0.999 confidence intervals. The error bars increase with increasing $n_{p,min}$ due to the smaller sample size.

This behaviour is expected since particles are not fractal-like in the small n_p limit. The values obtained in Fig. 4.8a ($D_f = 1.91 \pm 0.01$ and $k_f = 1.33 \pm 0.04$) are in good agreement with the results reported by Eggersdorfer and Pratsinis [42] ($D_f = 1.89 \pm 0.03$ and $k_f = 1.36 \pm 0.10$) and Jullien [81] ($D_f = 1.91 \pm 0.03$, k_f not reported).

BCCA with uniform selection of particles was also examined. Results are presented in Appendix C.1. The fractal dimension D_f obtained by uniform selection ($D_f = 1.91 \pm 0.01$) is in good agreement with that obtained with particle selection based on the free-molecular kernel. The fractal prefactor, on the other hand, appears to be sensitive to the method of particle selection with uniform selection yielding a lower fractal prefactor ($k_f = 1.19 \pm 0.03$) than the free-molecular kernel – which favours collisions between small and large particles.

4.4.2 Surface growth

Three test cases are presented for the growth process model. The first, constant growth model, evaluates the particle transformation model against two limiting cases. For simplicity, a constant rate of growth in particle volume is assumed. The next two cases compare the behaviour of the detailed particle model under collision limited and surface area dependent growth against

one and two dimensional particle models with different model assumptions. The one and two dimensional particle model equations are given in Appendix C.3

Constant growth

The detailed particle model is evaluated against the analytical solutions for two limiting cases: growth of a single sphere with the same initial volume, and growth of the same initial number of spherical primary particles that remain in point contact.

The test case was initialised with 64 primary particles of radius $r_{p,0} = 0.91$ nm in point contact. In the case of the single sphere model, the initial mass is the same. For the new detailed particle model, 10 initial configurations were generated using the BCCA algorithm. Simulations were repeated twice.

Figure 4.9 shows the evolution of the surface area and average primary diameter against dimensionless time. The dimensionless time is defined as

$$t^* = \frac{\beta t}{V_0}.\tag{4.41}$$

The point contact model is a limiting case showing the fastest surface area growth and slowest growth in average primary diameter. The single sphere model with the same initial mass is the limiting case of complete rounding, in the long time limit. The detailed model starts in point contact and tends towards the single sphere due to rounding, as expected.

Collision limited growth

The detailed particle model is compared to three particle models: a spherical particle model, and a surface-volume model with and without particle rounding. The latter case corresponds to $n_{p,0}$ primary particles in constant point contact. The model test case was initialised with 64 primary particles of radius $r_{p,0} = 0.91$ nm in point contact. The point contact and surface-volume models assume a constant fractal dimension of $D_f = 1.9$, consistent with initial fractal dimension of the BCCA generated particles. In the case of the single sphere model, two different initial conditions were considered: equivalent initial mass

$$r_0 = r_{\rm p,0} n_{\rm p,0}^{1/3},\tag{4.42}$$

and equivalent initial surface area

$$r_0 = r_{\rm p,0} n_{\rm p,0}^{1/2}. \tag{4.43}$$



Fig. 4.9 Particle evolution with a constant growth rate. The detailed particle model is compared two limiting cases: growth of a single sphere, and growth of primaries that remain in point contact.

For the detailed particle model, 20 initial configurations were generated using the BCCA algorithm. Simulations were repeated twice. The surface-volume model equations (Eqs. C.16 and C.18) were numerically integrated.

Figure 4.10 shows the evolution of the (aggregate) particle volume, surface area, collision diameter and average primary diameter as a function of dimensionless time for the test case. The dimensionless time is defined as

$$t^* = \frac{\beta t}{4\pi r_{\rm p,0}}.$$
 (4.44)

The point contact model grows much faster than the other models due to the rapid increase in collision diameter – a consequence of no rounding. For large t^* the surface-volume and detailed particle models converge to the spherical model solution due to particle rounding, as is expected. The detailed particle model converges from below as a result of slower increase in the modelled collision diameter (proportional to the gyration diameter). This is a consequence of maintaining a rigid structure while adding mass uniformly to the surface of the particle.

Surface area dependent growth

The detailed particle model is compared to the same particle models as in the previous case of collision limited growth. Figure 4.11 shows the evolution of the (aggregate) particle volume,



Fig. 4.10 Evolution of particle properties as a function of dimensionless time for different particle models undergoing collision limited growth. The single sphere cases with equivalent initial volume and surface area are distinguished by V_0 and S_0 , respectively.

surface area, collision diameter and average primary diameter as a function of dimensionless time for the test case. The dimensionless time is defined as

$$t^* = \frac{\beta t}{r_{\rm p,0}}.$$
 (4.45)

Similar to the previous, collision limited growth test case the point contact model displays significantly faster growth, while the detailed particle and surface-volume models converge

to the spherical particle model solution at large t^* . The detailed particle model shows faster growth in particle volume and surface area than the surface-volume model and converges on the spherical model from above. This is a consequence of adding mass uniformly to the surface of the particle while maintaining a rigid structure. Meanwhile, the surface-volume model shows identical behaviour in surface area as a spherical particle with the same initial surface area, due to the rounding assumption [136] (Eq. (C.15)). The collision diameters show very similar behaviour. The average primary diameter predicted by the detailed model diverges from the point contact model at $t^* = 2$. The sudden nature of the divergence is due to the discrete treatment of coalescence events where two primaries are merged if they have sufficient overlap.

4.4.3 Sintering

The detailed particle model is compared to the commonly used model of Koch and Friedlander [89] that describes the decay in excess surface area of a particle over that of a sphere of the same mass (referred to as the "K-F model"). The K-F model is implemented using a surface-volume particle description. Sintering is assumed to progress by grain boundary diffusion. Two variations of this model are considered: sintering with constant characteristic sintering time $\tau_s = \kappa r_{p,0}^4$, where the radius is taken as the initial primary radius, $r_{p,0}$; and sintering with time dependent $\tau_s = \kappa r_p^4(t)$, where the primary radius evolves with time. The model equations for the two cases are given in Appendix C.4.

The test case is initialised with 64 primary particles of radius $r_{p,0} = 0.91$ nm in point contact. For the detailed particle model, 15 initial configurations were generated using the BCCA algorithm.

Figure 4.12 shows the evolution of the normalised surface area and average primary diameter against dimensionless time. To facilitate comparison of the models, a dimensionless time t^* is defined such that the excess surface has decreased by 63% at $t^* = 1$, i.e.

$$\frac{S(t^*=1) - S_{\rm sph}}{S_0 - S_{\rm sph}} = e^{-1}.$$
(4.46)

This is consistent with the characteristic time of an exponential decay commonly used to model sintering.

The detailed particle model and K-F model with time dependent τ_s show similar sintering behaviour, particularly the evolution of the primary diameter. Over long times both cases are significantly slower than the constant τ_s model because their sintering rates vary as r_p^{-4} , which grows as the particles sinter.



Fig. 4.11 Evolution of particle properties as a function of dimensionless time for different particle models undergoing surface area dependent growth. The single sphere cases with equivalent initial volume and surface area are distinguished by V_0 and S_0 , respectively.

The average primary diameter tends to the same value in all cases – that of a single sphere with the same initial volume. The average primary diameter predicted by the detailed model does not vary smoothly as the particle approaches a single sphere due to the imposed coalescence threshold, which merges two primaries once their level of sintering reaches 95% – introducing a step change in the diameter. This also causes the detailed model to approach the final primary diameter faster than the surface-volume model with time dependent τ_s . Otherwise, the two models are in very good agreement.



Fig. 4.12 Sintering by grain boundary diffusion. The detailed particle model is compared to the model of Koch and Friedlander [89] with constant and time dependent characteristic time.

4.5 Convergence studies

The numerical behaviour of the model is investigated using a simple test case. A zerodimensional batch reactor was simulated with 500 ppm of titanium tetraisopropoxide (TTIP) precursor in nitrogen gas. The temperature was kept constant at 1200 K and the pressure at 1 atm. The reactor residence time was 0.5 s. These conditions were chosen to yield a reasonable degree of aggregation and sintering. The gas-phase chemistry (Section 4.2) was coupled to the particle population balance, solved by DSA (Section 2.2.2), using Strang operator splitting (Section 2.2.3). Simulations were performed on 2.80 GHz Intel Xeon CPUs.

The numerical parameters that affect the numerical error are:

- Maximum number of computational particles (*N*_{max});
- Number of runs (*L*);
- Splitting time step (Δt_s) .

First, we look at the convergence behaviour with respect to the splitting time step in order to select an appropriate splitting time for the rest of the study. Then we investigate the convergence of six macroscopic properties with respect to the maximum number of computational particles N_{max} , while keeping $N_{\text{max}} \times L$ constant. The functionals studied are given in Table 4.1.

Functional	Formula		
Zeroth moment	$M_0(t) = \frac{N(t)}{V_{\rm smpl}(t)}$		
Volume fraction	$F_{v}(t) = \frac{1}{V_{\text{smpl}}(t)} \sum_{q=1}^{N(t)} V(P_{q}(t))$		
	V: aggregate volume		
Average collision diameter	$ar{d_c}(t) = rac{1}{N(t)} \sum_{q=1}^{N(t)} d_{ ext{c}}(P_q(t))$		
	$d_{\rm c}$ defined in Eq. (4.16).		
Average number of primaries per particle	$\bar{n}_{\rm p}(t) = rac{1}{N(t)} \sum_{q=1}^{N(t)} n_{\rm p}(P_q(t))$		
	$n_{\rm p}(P_q)$: number of primaries in P_q		
Average primary diameter	$\bar{d}_{\mathrm{p}}(t) = \frac{1}{N(t)} \sum_{q=1}^{N(t)} d_{\mathrm{p,avg}}(P_q(t))$		
	$d_{p,avg}(P_q)$: average primary diameter of P_q		
Average sintering level	$\overline{\overline{s}(t)} = \frac{1}{N(t)} \sum_{q=1}^{N(t)} \overline{s_{\text{avg}}(P_q(t))}$		
	$s_{\text{avg}}(P_q)$: mean sintering level of P_q		

Table 4.1 Functionals studied.

4.5.1 Error calculations

The systematic and statistical errors can be assessed by generating *L* independent estimates of the particle system and comparing the macroscopic quantities of the system $\xi_l(t)$ for a given set of parameters. The empirical mean at time *t* is

$$\mu_1(t) = \frac{1}{L} \sum_{l=1}^{L} \xi_l(t), \qquad (4.47)$$

and the variance is

$$\mu_2(t) = \frac{1}{L} \sum_{l=1}^{L} \left[\xi_l(t) \right]^2 - \left[\mu_1(t) \right]^2.$$
(4.48)

The half-width of the confidence interval for $\mu_1(t)$ is calculated using the central limit theorem:

$$c_P(t) = a_P \sqrt{\frac{\mu_2(t)}{L}}.$$
 (4.49)

For a confidence level of P = 0.999, a critical value of $a_P = 3.29$ is obtained from the standard normal distribution. The confidence interval I_P is then given by

$$I_P(t) = [\mu_1(t) - c_P(t), \mu_1(t) + c_P(t)].$$
(4.50)

The relative error at time t is

$$e_{\rm r}(t) = \frac{|\mu_1(t) - \zeta(t)|}{\zeta(t)}$$
(4.51)

where $\zeta(t)$ is an approximation for the true solution which is obtained from a high-precision calculation with a very large number of particles. In this case, $N_{\text{max}} = 2^{17}$ and L = 10 is used. The total relative error, averaged over J time steps is

$$e_{\text{tot}} = \frac{1}{t_{\text{res}}} \sum_{j=1}^{J} e_{\text{r}}(t_j) \Delta t_j, \qquad (4.52)$$

where

$$t_{\rm res} = \sum_{j=1}^{J} \Delta t_j. \tag{4.53}$$

4.5.2 Numerical results

Convergence with respect to splitting time step

The length of the operator splitting time step size Δt_s affects the accuracy and stability of the coupling between the gas-phase and particle population balance. If the time step is too long, the operator splitting can cause unphysical oscillations to arise in the concentrations of species that have source terms in the gas-phase and sink terms in the particle-phase (or vice versa). For example, Ti(OH)₄ is first formed in the gas-phase as a product of the decomposition of TTIP and then consumed by the particle phase as the inception and growth species. On the other hand, taking unnecessarily small time steps when species concentrations are varying slowly increases the computational time due to the cost of initialising the ODE solver. Thus, an appropriate time step needs to be chosen to maintain adequate coupling while keeping computational cost at a minimum.

The convergence behaviour with respect to the splitting time step of three key particle ensemble properties (M_0 , F_v and \bar{d}_c) and the concentration of Ti(OH)₄, the collision species, is investigated. Simulations were performed with a sufficiently large number of particles and number of runs for convergence: $N_{\text{max}} = 8192$ and L = 4. The relative error is measured against a high precision solution: $N_{\text{max}} = 131072$, L = 10 and Δt_s given by the variable splitting time scheme discussed below.



Fig. 4.13 Mean $Ti(OH)_4$ concentration as a function of time and the total relative error for different splitting step sizes. The horizontal dashed line indicates the value for the variable splitting scheme (Eq. (4.54)).

Figure 4.13 shows the time evolution and the total relative error of the concentration of Ti(OH)₄ for different splitting time step sizes. The solution converges rapidly with decreasing step size and appears converged with $\Delta t_s = 10 \ \mu$ s. Figure 4.13a shows that the collision species is consumed rapidly and its concentration becomes negligible by t = 0.1 s. This suggests that a small splitting time step is only necessary during this initial phase of the simulation where there is a strong coupling between the gas-phase and particle-phase. Once the precursor and collision species have been consumed a longer time step can be taken. The dashed horizontal line in Fig. 4.13b shows the total relative error for a variable splitting time scheme in which the step size is increased after t = 0.1 s:

$$\Delta t_{\rm s} = \begin{cases} 10\,\mu\,{\rm s}, & t \le 0.1\,{\rm s}; \\ 100\,\mu\,{\rm s}, & t > 0.1\,{\rm s}. \end{cases}$$
(4.54)

The variable splitting scheme achieves the same total relative error as $\Delta t_s = 10 \ \mu s$.

The computational time for one run using each of the different step sizes is shown in Fig. 4.14. There is a clear increase in computational cost with decreasing step size: almost an order of magnitude increase in CPU time with an order magnitude decrease in step size. The CPU time for the variable step size (Eq. (4.54)) is also shown, and demonstrates a significant



Fig. 4.14 Computational time as a function of simulation time for different splitting time steps. Variable refers to the splitting scheme given in Eq. (4.54).

reduction in computational cost compared to the $\Delta t_s = 10 \ \mu s$ case for approximately the same total error.

Figure 4.15 shows the convergence behaviour of M_0 , F_v and $\bar{d_c}$ with respect to splitting step size. Similar convergence behaviour is observed for these functionals as for the concentration of Ti(OH)₄, with all converging by $\Delta t_s = 10 \ \mu s$. The variable splitting scheme (Eq. (4.54)) shows similar convergence properties to $\Delta t_s = 10 \ \mu s$. Due to the computational time advantage, this splitting scheme was selected for the remaining numerical studies.

Convergence with respect to number of particles

The maximum number of computational particles should be chosen such that systematic error is sufficiently small. In practice this means choosing the maximum number of computational particles so that increasing N_{max} is not statistically significant. The number of runs is selected such that the statistical error is acceptable. The convergence behaviour of the functionals given in Table 4.1 was investigated with respect to the maximum number of computational particles N_{max} , while keeping the product of the number of computational particles and number of runs constant: $N_{\text{max}} \times L = 2^{17}$.

The time evolution of each of the functionals within their confidence intervals $I_P(t)$ is shown in Fig. 4.16 for three different values of N_{max} and the high precision solution. The evolution of M_0 and F_v indicate the rapid conversion of gas-phase precursor to TiO₂ in the particle phase. There is an initial spike in M_0 as many small single primary particles are incepted, followed by a rapid decrease in M_0 and corresponding increase in \bar{d}_p and \bar{d}_c as particles grow



Fig. 4.15 Mean functional value as a function of time and the total relative error for different splitting step sizes. The horizontal dashed line is the variable splitting scheme (Eq. (4.54)).



Fig. 4.16 Time evolution of functionals given in Table 4.1 within their confidence intervals $I_{\rm P}(t)$ for different values of $N_{\rm max}$, and the high precision solution.

via condensation and coalescence. Aggregate formation, shown by the increase in \bar{n}_p , begins after F_v has plateaued i.e. the gas-phase precursor has been consumed, and once the primary size exceeds the critical sintering diameter. At this point primary diameter growth slows and further growth is due to sintering. The initial sintering level is $\bar{s} = 1$: the value assigned to single primaries. Once aggregates begin to form the average sintering level falls rapidly before plateauing at around $\bar{s} = 0.886$.

The functionals plotted in Fig. 4.16 display different rates of convergence with respect to the maximum number of computational particles. For example, M_0 and F_v show very rapid convergence to the high precision solution. On the other hand, the average sintering level \bar{s} and average number of primaries \bar{n}_p both demonstrate a slower rate of convergence.

The rates of convergence with respect to the maximum number of computational particles of the functionals are investigated further in Fig. 4.17: a plot of the total relative error e_{tot} as a function of N_{max} . A first order slope is also plotted as a guide. All the functionals are observed to converge as N_{max} is increased. The volume fraction displays the smallest total error, likely due to the fact that the gas-phase precursor is consumed rapidly and F_v reaches a steady value within the first 0.1 s as seen in Fig. 4.16b. The ensemble properties M_0 and F_v , and average collision diameter $\bar{d_c}$ are the fastest to converge at $N_{max} = 2048$. The average number of primaries $\bar{n_p}$ shows the slowest convergence at $N_{max} = 8192$.

The computational times for a single run with different values of N_{max} are plotted in Fig. 4.18 together with the total relative error for M_0 , \bar{n}_p and \bar{s} . The total computational time and computational time of the Monte-Carlo algorithm are shown. The CPU time of the Monte-Carlo algorithm increases steadily as a function N_{max} . The total CPU time, however, is constant for small N_{max} . At low N_{max} , changing the number of particles does not affect the total computational time very much because most of the CPU time is spent on the ODE solver, which is independent of the number of computational particles. For large N_{max} the majority of the computational time is spent on the Monte-Carlo algorithm. M_0 converges the fastest with $N_{\text{max}} = 2048$ in approximately 9 min, while \bar{n}_p is the slowest, converging with approximately $N_{\text{max}} = 8192$ in 27 min.

4.6 Hot wall reactor simulations

In this section we simulate the hot wall reactor experiment of Nakaso et al. [131]. The original investigation produced TiO₂ particles from TTIP precursor evaporated into nitrogen carrier gas in a tubular hot wall flow reactor. In our simulation we impose the temperature profile modelled by Nakaso et al. [131, Fig. 4] for maximum furnace temperature $T_{\text{max}} = 1200^{\circ}$ C. The temperature profile is expressed in terms of reactor residence time by assuming constant mass



Fig. 4.17 Total relative error as a function of N_{max} for the functionals given in Table 4.1. $N_{\text{max}} \times L = 2^{17}$ is kept constant. A first order slope (dotted line) is plotted as a guide.



Fig. 4.18 Total and Monte-Carlo algorithm CPU time per run (RHS), and total relative error for number density M_0 , average number of primaries \bar{n}_p and average sintering level \bar{s} (LHS) for different values of N_{max} .

flow and accounting for the thermal expansion of the gas-phase. The initial TTIP mole fraction was calculated as 18.7 ppm for an initial concentration of 7.679×10^{-7} mol/l in nitrogen gas at 24°C and 1 atm. The total reactor residence time was calculated to be $t_{\rm res} = 3.60$ s. The numerical parameters used in the simulation are given in Table 4.2.

Table 4.2 Numerical parameters.

Numerical parameter	Value	
Maximum number of stochastic particles, N_{max}	8192	
Number of runs, L	4	
	100 µ s	for $t \leq 1$ s
Splitting time step size, Δt_s	10 µ s	for $1 s < t \le 1.5 s$
	100 µ s	for $t > 1.5$ s

4.6.1 Time evolution

Figure 4.19 shows the simulated time evolution of key gas-phase species, the imposed temperature profile and average particle properties. The simulation was performed using the model parameters given Section 4.3. In Fig. 4.19a we see the rapid decomposition of TTIP as the



Fig. 4.19 Time evolution of (a) key gas-phase species and imposed temperature profile, and (b) particle properties.

temperature increases, accompanied by a spike in the concentration of Ti(OH)₄, the collision species. The Ti(OH)₄ concentration has two peaks, a consequence of the different speeds of the two reaction pathways in the chemical reaction model. The time evolution of average particle size, plotted in Fig. 4.19b, follows a similar trajectory. An initial peak in particle size is observed corresponding to the first Ti(OH)₄ peak, which causes particle inception followed by growth through condensation and coalescence. A subsequent decrease in average primary size is a consequence of the second peak in Ti(OH)₄ resulting in the inception of new small particles. In the high temperature region, the particles remain spherical due to their small size and the high sintering rate resulting in rapid coalescence of coagulating particles. Only once the temperature begins to decrease at $t \approx 1.5$ s do we observe the beginning of aggregate formation. After this point, primary particle growth stops and aggregate growth proceeds via coagulation in the low temperature region of the reactor.

Conversion of TTIP to TiO₂ particles in the simulation was found to be only 66% with most of the remainder (31%) as Ti(OH)₃OCHCH₂ in the gas-phase. This is a consequence of the chemical mechanism and choice of collision species for particle inception and growth processes for this particular set of conditions. However, full conversion is expected (*cf.* different hot wall reactor study by Nakaso et al. [132]). As noted in Section 2.1.1, recent work by Ershov et al. [47] suggests that the decomposition mechanism used here [23] is incomplete. Moreover, the choice of collision species is restricted to Ti(OH)₄, the final decomposition product of the chemical mechanism, and could be extended. While it is not possible to draw meaningful



Fig. 4.20 Sensitivity of simulated aggregate and primary particle size distributions to coagulation collision efficiency A_{cg} and inception collision efficiency A_{inc} . Experimental and simulation data from Nakaso et al. [131, Fig. 9-2] are included for comparison.

conclusions about the parameters from comparison with the experimental results here, we can nonetheless study the model behaviour and sensitivity with respect to key parameters.

4.6.2 Sensitivity

In Fig. 4.20, we compare our detailed particle model simulations against the experimental and simulated aggregate and primary particle size distributions of Nakaso et al. [131, Fig. 9-2]. Our base case simulation results, using the parameters given in Section 4.3, are shown by the solid blue lines. Simulated primary particle diameters, $d_{p,i} = 2r_i$, are compared directly with the experimental primary diameters obtained from TEM measurements. The experimental aggregate mobility size measurements are compared to a modelled aggregate mobility diameter d_m for the free-molecular regime, estimated from the projected area A_{pr} [148]:

$$d_{\rm m} = \sqrt{\frac{A_{\rm pr}}{\pi}}.\tag{4.55}$$

Aggregate projected areas of 2048 randomly selected particles were obtained from image analysis (using the method described in [111]) of projections produced using the algorithm given in Appendix B.3.

Figure 4.20 shows the sensitivity of the aggregate and primary PSDs to the collision efficiency of coagulation and inception. The inception and coagulation rates are varied by



Fig. 4.21 Simulated TEM-style images.

introducing a multiplicative prefactor A_{inc} and A_{cg} to the respective kernels. Both the aggregate and primary PSDs are insensitive to an increase in the inception efficiency. Meanwhile, increasing the coagulation collision efficiency shifts both the aggregate and primary PSDs to the right and reduces the number density of aggregates and primary particles. The behaviour of the primary PSD is due to increased coalescence of coagulating primaries in the high temperature region of the reactor. A substantial increase in the coagulation efficiency improves the agreement in the aggregate PSD, but this is accompanied by a shift in the primary PSD away from the experimental data.

The present coagulation model assumes ballistic aggregation of particles. However, near the end of the reactor the largest aggregates are in the transition regime (Kn \approx 1), so collisions may in fact be diffusion limited. The effect of using a different aggregation model was investigated and simulations of the hot wall reactor with diffusion limited cluster aggregation (DLCA) showed no appreciable difference to the BCCA results. These results are included in Appendix C.5.

Simulated TEM-style images produced using the method described in B.3 are presented in Fig. 4.21 for two cases: $A_{cg} = 1$ and $A_{cg} = 10$. Qualitatively, the images show aggregates with similar numbers of primaries but significantly larger primary particles in the latter case and correspondingly larger aggregates. This is consistent with the PSDs in Fig. 4.20.

Lastly, we look at the effect of the critical sintering diameter. Figure 4.22 shows the effect of varying $d_{p,crit}$ on the aggregate and primary PSDs. The aggregate PSD is largely insensitive, while the primary particle size distribution shows much greater sensitivity. For $d_{p,crit} = 0$ nm we observe good agreement with the left hand tail of the experimental data while larger values shift the distribution towards the right hand tail of the experimental data. The best agreement in the position of the peak in the distribution is obtained for $d_{p,crit} = 4$ nm. In all cases the number density of primaries and width of the primary PSD is underpredicted.



Fig. 4.22 Sensitivity of simulated aggregate and primary particle size distributions to the critical sintering diameter $d_{p,crit}$. Experimental and simulation data from Nakaso et al. [131, Fig. 9-2] are included for comparison.

In summary, the base case model parameters produced reasonably good agreement in the position of the primary PSD. However, the predicted width was narrower and primary number density was smaller. This is likely due in part to incomplete conversion to TiO_2 and conclusions with regard to the goodness of fit cannot be made here. The position of the aggregate PSD was underpredicted, and the number density of aggregates was overpredicted. The sensitivity of the aggregate and primary PSDs with respect to three parameters was investigated. The PSDs were relatively insensitive to the collision efficiency of inception. Both the aggregate and primary size distribution were shown to be sensitive to the coagulation efficiency, while the critical sintering diameter was observed to only affect the primary PSD. The findings suggest that primary particle growth is driven by coagulation and sintering/coalescence in the high temperature region of the reactor with aggregate growth occurring in the subsequent low temperature region.

Given the observed sensitivity of the system to the coagulation and sintering processes, a more extensive study should start by exploring the multi-dimensional parameter space for these processes in order to improve the model. Note that in the present work only one parameter was varied at a time, while the other parameters took their base case values. Moreover, the process rates could have additional dependencies that were not considered in the current work. For example, a recent study by Sharma et al. [155] showed that the coagulation efficiency of TiO₂ nanoparticles is strongly temperature dependent with significantly larger values at
low temperature. This suggests that the coagulation rate may be underpredicted in the low temperature region of our simulations. If the rate was higher in this region, agreement in the aggregate PSD would be expected to improve while leaving the primary PSD unchanged.

4.7 Conclusions

This chapter introduced a new detailed particle model for polydisperse titanium dioxide aggregates with inception, coagulation, condensation, sintering and coalescence processes. The new particle description resolves the radius, composition and position of each individual primary particle, representing an aggregate as a collection of overlapping spheres. The detailed geometrical description permits the morphological evolution of each aggregate to be simulated. The particle model developed in this work was presented in the context of titanium dioxide synthesised from TTIP precursor. However, the model can be easily adapted to wider applications such as different precursor chemistry (e.g. TiCl₄), materials (e.g. soot or silica) or particle process models (e.g. viscous flow sintering). Crucially, the model type space incorporates sufficient physical detail to relate particle processes to specific morphological transformations and provides a framework suitable for testing and discriminating between different process models.

The new particle model overcomes some of the limitations identified in previous models [150, 156] by adding more geometrical detail to the particle description; thereby permitting more physical detail to be incorporated into the process models. For example, a detailed description of the aggregate structure obtained by tracking individual primary coordinates allowed a more physical ballistic collision model to be implemented and avoided the need to assume fractal dimension in calculations. Most importantly, the detailed geometrical description allows for better comparison with experimental data. For instance, through visualisation of particles using TEM images that can be analysed in a similar manner to experimental TEMs (e.g. projected areas) or by considering the effect of particle morphology on mobility measurements.

A numerical study was conducted using a simple batch reactor test case to investigate the convergence behaviour of a number of average properties. The study demonstrated that under conditions similar to the test case, convergence can be achieved in key properties for a feasible number of computational particles. Furthermore, the computational time for a converged solution was shown to be reasonable given an informed choice of operator splitting time step size.

Lastly, the hot wall reactor experiment of Nakaso et al. [131] was simulated. This was not intended to be a comprehensive evaluation of the model nor parameter fitting, but to briefly examine the model performance and make suggestions for future work. The base case model parameters produced reasonable agreement with the PSDs of Nakaso et al. [131], but the current mechanism and choice of collision species resulted in incomplete conversion of TTIP to TiO_2 particles under the simulated conditions. The simulated PSDs were shown to be sensitive to the coagulation efficiency and critical sintering diameter, suggesting that future work should investigate these process rates in more detail, paying particular attention to their size and temperature dependence. Next, it is important to further evaluate the model against experimental data under different conditions and perform a thorough parametric sensitivity study.

Chapter 5

Extending the post-processing methodology to stagnation flames

In this chapter, a two-step simulation methodology is presented that allows a detailed particle model to be used to resolve the complex morphology of aggregate nanoparticles synthesised in a stagnation flame. A thermophoretic correction is introduced to the second step post-process through a simulation volume scaling term to account for thermophoretic transport effects arising due to the steep temperature gradient near the stagnation surface. The methodology is evaluated by applying it to a test case: the synthesis of titanium dioxide from titanium tetraisopropoxide (TTIP) precursor. The thermophoretic correction is shown to improve the ability of the post-process to recreate the conditions of the first fully-coupled simulation. The methodology is demonstrated to be feasible for simulating the morphology of aggregate nanoparticles formed in a stagnation flame, permitting the simulation of quantities that are directly comparable to experimental observations.

5.1 Background

Premixed stagnation flame experiments have been used to synthesise and study nanoparticles, including ultra-fine titanium dioxide [119, 169, 197] and soot [1, 27]. The stagnation flame was introduced to avoid flame perturbations during sampling by embedding the sampling probe into the stagnation surface. Modelling is facilitated by this configuration since the probe may be treated as a boundary condition and a pseudo one-dimensional numerical solution to the flame becomes possible.

Nanoparticles formed in flames are often aggregates composed of polydisperse primary particles such as those shown in the transmission electron microscopy (TEM) image in Fig. 5.1.



Fig. 5.1 A typical experimental TEM image of stagnation flame synthesised TiO_2 (image by Manoel Manuputty).

A detailed description of the aggregate particle morphology is therefore necessary to simulate quantities that are directly comparable with experimental observations. Menz and Kraft [121] emphasise the importance of selecting an appropriate model for the system being simulated, and warn of using an over-simplified model to interpret experimental data. Moment methods [112, 129, 130, 167, 186] and sectional methods [67, 131, 172, 173, 188] allow for some description of aggregate morphology, but are generally limited to tracking only two internal particle dimensions. Stochastic methods allow for the extension of the particle model to include a detailed description of each particle and allow key physical details to be included, providing a powerful tool to investigate the mechanisms that control particle growth and morphology.

Flow dynamics, however, are not easily incorporated into models with a high-dimensional particle description. Instead of direct coupling, one approach has been to post-process existing flame data [127]. This technique, introduced in Section 2.2.3, has been used successfully to simulate soot formation in premixed laminar flames with no stagnation surface [10, 33, 126, 138, 161]. Yapp et al. [192] applied the technique to model soot formation in a stagnation flame, but found that the simulations did not reproduce the experimental particle size distribution data well. While some of the differences can be attributed to uncertainties in the models used, the results also suggest that the post-processing methodology employed is unsuitable in cases with strong temperature gradients and significant thermophoretic transport effects.

The purpose of this chapter is to formalise and extend the two-step simulation methodology to allow a detailed particle model to be applied to the modelling of nanoparticle aggregates synthesised in a stagnation flame. The first step in the method couples detailed gas-phase chemistry, flow and a spherical particle model solved with the method of moments with interpolative closure (MoMIC) to simulate the flame profile and particle model solved using a stochastic numerical method to resolve the aggregate particle morphology. We discuss how the steep temperature gradient at the stagnation surface requires the effect of thermophoresis to be accounted for in the post-processing step. To address this, we introduce a correction to the post-process through a modified simulation sample volume scaling term.

The simulation methodology is applied to the combustion synthesis of TiO_2 nanoparticles from titanium tetraisopropoxide (TTIP) precursor. A detailed particle description facilitates comparison with experimental observation such as TEM images and allows morphology dependent processes such as sintering and phase transformation to be studied. The methodology is evaluated by comparing results from both simulation steps for consistency. Finally, we simulate the stagnation flame experiment of Tolmachoff et al. [169] to demonstrate the ability of a detailed description of particles to provide additional insight into experimental results. The methodology presented in this chapter is not dependent on the specific details of a particular particle model and can be applied to the study of various nanoparticles formed in stagnation flames.

Burner nozzle Sampling flow Water cooled plate

5.2 Burner configuration

Fig. 5.2 Schematic of experimental set-up being modelled (figure by Manoel Manuputty).

A premixed laminar stagnation flame is modelled in this chapter. The set-up, shown in Fig. 5.2, is similar to that used in previous studies of titania and soot formation [28, 119, 169]. An aerodynamic nozzle issues a laminar jet of TTIP-doped premixed $C_2H_4/O_2/Ar$ that impinges on a water-cooled stagnation plate. A thin flame is formed and stabilised by stretch above the surface. Particles are sampled through an orifice at the centre of the plate.

5.3 Model detail

5.3.1 Flow model

The flow is assumed to be an axisymmetric stagnation flow and is modelled using a pseudo one-dimensional approximation. This is described in detail in [108].

5.3.2 Chemical reaction model

The chemical model consists of the TTIP decomposition mechanism combined with hydrocarbon combustion chemistry described in Section 4.2.

5.3.3 Particle model

In this chapter we use a spherical and a detailed type space. The dynamics of the particle population are described by the Smoluchowski coagulation equation with additional terms for inception, condensation and sintering (detailed model only) [94].

Spherical particle model

The spherical particle model characterises a particle using its number of constituent TiO₂ monomers, *i*. The particle mass is $i \cdot m_{\text{TiO}_2}$, where m_{TiO_2} is the mass of a single monomer of TiO₂; and, assuming spherical geometry the particle diameter can be calculated. The collision limited inception and condensation processes are the same in both spherical and detailed particle models. The particle models differ primarily in their treatment of a coagulation event: the spherical model effectively assumes instantaneous coalescence following the collision.

Detailed particle model

The detailed particle model was introduced in Chapter 4. In this work, the critical sintering diameter is set to $d_{p,crit} = 0$ nm; otherwise, the model is as described in Section 4.3.

5.4 Methodology

5.4.1 Two-step simulation methodology

Figure 5.3 illustrates the two-step simulation methodology. In the first step¹, the flame is simulated with a one-dimensional stagnation flow approximation, coupled with gas-phase

¹The first simulation step was performed by Manoel Manuputty.



Fig. 5.3 Two-step simulation methodology.

chemistry and a spherical particle model solved with method of moments with interpolative closure (MoMIC). MoMIC is chosen because it is easy to couple, less computationally demanding than other moment methods and sufficient to capture the effect of the particles on the gas-phase. This first step is solved as a boundary-value problem using the *k*inetics[®] software package [35] with the boundary conditions specified according to experimental conditions. A solution-adapted grid refinement is used in order to achieve convergence with 240–260 grid points. This first simulation is discussed in detail in [108].

The boundary conditions are consistent with the experimental work of Manuputty et al. [110]. The burner-surface separation is 1.06 cm, and the burner and plate temperatures are 423.15 K and 503 K respectively. The exit velocity is 436 cm/s, and species mole fractions of the gas mixture in the nozzle are 3.5% C₂H₄/30% O₂/66.5% Ar (equivalence ratio $\phi = 0.35$) and 580 ppm TTIP, corresponding to a TTIP loading rate of 12 ml/h (this loading rate is used in results hereafter unless otherwise specified).

In the second step, the resulting gas-phase profile is post-processed with the detailed particle model to resolve the aggregate particle morphology, solved using a stochastic numerical method (DSA introduced in Section 2.2.2). The flame conditions and gas species are supplied as input to the population balance simulation. The simulation requires the computed profiles to be expressed in terms of the residence time of a Lagrangian particle travelling from the burner to the stagnation plate [127]. The combined convective and thermophoretic velocities are used to

calculate the particle time history as per Abid et al. [1]. Simulation results in this study are an average of 4 runs with 8192 stochastic particles.

5.4.2 Governing equations

First simulation

In the first simulation, the particle population balance is coupled to the flow and gas-phase chemistry through the moment transport equations. This step is discussed in detail by Manuputty et al. [108]. The transport equation for the r^{th} -moment, M_r , is composed of the moment source, advective, thermophoretic and diffusive transport terms [192]

$$\dot{M_r} - \rho u \frac{\mathrm{d}}{\mathrm{d}z} \left(\frac{M_r}{\rho} \right) - \frac{\mathrm{d}}{\mathrm{d}z} \left(v_{\mathrm{T}} M_r \right) + \frac{\mathrm{d}}{\mathrm{d}z} \left(\rho D_{p,1} \frac{\mathrm{d}}{\mathrm{d}z} \left(\frac{M_{r-2/3}}{\rho} \right) \right) = 0, \tag{5.1}$$

where ρ is the gas-phase density, v_T is the thermophoretic velocity, and u is the convective velocity. \dot{M}_r is the r^{th} moment source term, z is the spatial displacement along the flame and $D_{p,1}$ is the Brownian diffusion coefficient of a TiO₂ monomer. As per Manuputty et al. [108], the thermophoretic velocity and Brownian diffusion coefficient are

$$v_{\rm T} = -\frac{3}{4} \left(1 + \frac{\pi \alpha_{\rm T}}{8} \right)^{-1} \frac{\mu}{\rho} \frac{\mathrm{dln}\,T}{\mathrm{d}z},\tag{5.2}$$

$$D_{p,1} = \frac{3}{2\rho} \left(1 + \frac{\pi \alpha_{\rm T}}{8} \right)^{-1} \sqrt{\frac{\bar{W} k_{\rm B} T}{2\pi N_{\rm A}}} \left(\frac{1}{d_{\rm TiO_2}^2} \right), \tag{5.3}$$

where the thermal accommodation factor $\alpha_{\rm T}$ is 0.9. \bar{W} is the average molar mass of the gas mixture, $k_{\rm B}$ is the Boltzmann constant, $N_{\rm A}$ is the Avogadro number and μ is the gas-phase viscosity. $d_{\rm TiO_2}$ is the diameter of a single TiO₂ monomer and is calculated from the bulk density of anatase (3.84 g/cm³).

Second simulation

In the stochastic simulation, the population balance equations are spatially homogeneous. We consider a Lagrangian description of an ensemble of particles in a sample volume travelling from burner to stagnation plate. The particle ensemble evolves in time with the governing equation:

$$\frac{\mathrm{d}n(x)}{\mathrm{d}t} = R(x) - \Gamma n(x), \tag{5.4}$$

where n(x) is the number density of particles of type x. R(x) is the rate of production of particles of type x: a function of the inception, condensation, coagulation and sintering rates given in

Section 4.3. Γ is the rate of gas-phase expansion: a function of temperature and the rate of production of gas-phase species. The gas-phase conditions in the sample volume (temperature, pressure, and species concentrations) are supplied as input from the first simulation and expressed as a function of the residence time of the Lagrangian sample volume using the combined convective and thermophoretic velocities [1].

The stochastic method approximates real particles with a collection of computational particles in a sample volume V_{smpl} . The sample volume corresponds to the actual volume in the real system in which the number of real particles matches the number of computational particles. Γ adjusts the sample volume in response to gas-phase expansion and contraction:

$$\frac{1}{V_{\text{smpl}}}\frac{\mathrm{d}V_{\text{smpl}}}{\mathrm{d}t} = \Gamma.$$
(5.5)

Thermophoretic correction

In order to perform the post-process we need to impose the same conditions on the particle population in the second simulation as modelled in the first. Therefore, the governing equations for both steps of the methodology need to be similar. To compare the governing equations it is convenient to rewrite Eq. (5.4), the governing equation for the second simulation, in terms of the number density moments, defined as

$$M_r = \sum_{i=1}^{\infty} i^r n_i, \tag{5.6}$$

where n_i is the number density of aggregate particles containing a total *i* units of TiO₂. Expressed in terms of the moments, the governing equation has the form

$$\frac{\mathrm{d}M_r}{\mathrm{d}t} = \dot{M_r} - \Gamma M_r,\tag{5.7}$$

where \dot{M}_r is the moment source term: a function of the process rates in the second simulation. It is important to note that the moment source in this case is not identical to the moment source term for the first simulation step. This is due to (1) the different particle models used in the two simulations steps, and thus the effect of different particle geometry on process rates, for example, the calculation of the particle collision diameter; and (2) the different treatment of the source terms by the numerical method employed, for example, interpolated closure of fractional order moments by MoMIC. The methodology and analysis here assumes that the source terms are not significantly different. The equation for the stochastic simulation (Eq. (5.7)) does not currently account for thermophoretic and diffusive transport. If, however, the thermophoretic and diffusive transport effects in the modelled system are small and can be neglected in the post-process it is straightforward to show that the governing equation in second simulation (Eq. (5.7)) approximates the moment transport equation solved in the first simulation (Eq. (5.1)). This is the case for premixed laminar flames with no stagnation plate such as those simulated in [10, 33, 126, 138, 161]. Neglecting the thermophoretic and diffusive transport terms, the moment transport equation for the first simulation (Eq. (5.1)) becomes

$$\dot{M}_r - \rho u \frac{\mathrm{d}}{\mathrm{d}z} \left(\frac{M_r}{\rho}\right) = 0.$$
(5.8)

Expressing Eq. (5.8) in terms of the residence time of a Lagrangian particle by making the coordinate transformation dz = u dt yields the equation for the second simulation (Eq. (5.7)) with a gas-phase expansion rate

$$\Gamma = -\frac{1}{\rho} \frac{\mathrm{d}\rho}{\mathrm{d}t}.$$
(5.9)

Here, the sample volume adjustment corresponds to the change in gas-phase density i.e. the gas-phase mass contained within the sample volume is conserved (mass transfer to the particle phase is assumed to be negligible).

In the case of a stagnation flame, as modelled in this work, thermophoresis is significant near the cooled stagnation plate due to a steep temperature gradient, so the thermophoretic transport term cannot be neglected. Assuming instead that only the diffusive term is negligible Eq. (5.1) becomes

$$\dot{M}_r - (u + v_{\rm T})\frac{\mathrm{d}M_r}{\mathrm{d}z} + \left(\frac{u}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}z} - \frac{\mathrm{d}v_{\rm T}}{\mathrm{d}z}\right)M_r = 0, \tag{5.10}$$

Using the convective and thermophoretic velocities, we make the coordinate transformation $dz = (u + v_T) dt$ to express Eq. (5.10) in terms of the residence time of a Lagrangian particle

$$\dot{M}_r - \frac{\mathrm{d}M_r}{\mathrm{d}t} + \frac{1}{u + v_\mathrm{T}} \left(\frac{u}{\rho} \frac{\mathrm{d}\rho}{\mathrm{d}t} - \frac{\mathrm{d}v_\mathrm{T}}{\mathrm{d}t}\right) M_r = 0, \tag{5.11}$$

which has the form of the governing equation for the second simulation (Eq. (5.7)) with

$$\Gamma = -\frac{1}{(u+v_{\rm T})} \left(\frac{u}{\rho} \frac{d\rho}{dt} - \frac{dv_{\rm T}}{dt} \right).$$
(5.12)

Thus, the effect of thermophoresis is now accounted for in the volume adjustment term in the stochastic population balance where the convective and thermophoretic velocities, and gas-phase density are supplied as input. Note that setting $v_T = 0$ returns the earlier relation (Eq. (5.9)).

The diffusive term cannot be dealt with in the same way because it is a second order derivative of the moments. A possible method could be to apply a diffusion correction to the reactor volume for a specific moment order. For example, applying the correction for r = 1 to ensure the system mass remains in agreement between the two simulations. However, the correction would only be approximate for other moments and is outside the scope of this work.

5.5 Results and Discussion

5.5.1 Transport terms



Fig. 5.4 Temperature and velocity profiles obtained from the first simulation.

Figure 5.4 shows the simulated temperature and velocity profiles obtained from the first step. We observe two regions with significant thermophoresis: at the flame front where the temperature increases steeply; and near the cooled stagnation plate where the temperature rapidly decreases. The region near the stagnation surface is of particular significance because the convective velocity is low, so in the Lagrangian view a particle will spend a large fraction of its residence time here. It is therefore important to correctly account for the effect of transport processes on the particle population dynamics in this region.

In Fig. 5.5 we compare the relative sizes of the individual terms in the moment transport equation (Eq.(5.1)) solved in the first simulation step. The advective, thermophoretic, diffusive,



Fig. 5.5 Moment transport equation terms from the first simulation.

and moment source terms are shown for the first three moments r = 0, 1, 2. The plots show that for a stagnation flame the transport terms are significant and need to be considered in the second step post-process. In particular, the thermophoretic term dominates in the region near the stagnation surface for the higher order moments, and will influence the PSD near the point of experimental measurement.

Diffusion is much less significant at the stagnation surface and can be assumed to be negligible here. However, at the flame front the diffusive term is non-negligible, particularly in the zeroth moment. Here, the convective velocity is very high so in the Lagrangian view diffusive effects will occur over a short period of time early in the evolution of the particle population; thus, the impact of diffusion on the final PSD is likely to be much less significant than thermophoresis.

5.5.2 Evaluation of the post-processing method

Evaluation of the post-processing methodology is necessary to ensure that meaningful results are obtained from the post-processing step; specifically, that the particle population evolves under similar conditions in the post-process as modelled in the first, fully coupled simulation. We can evaluate the effect of applying the thermophoretic correction (Eq. (5.12)) to the second step simulation by post-processing the flame profile with the spherical particle model and comparing the results of the post-process with the moments calculated in the first simulation. Using the same particle model in both simulation steps eliminates particle model dependent effects on the solutions. Therefore, any differences in the moments obtained from the first and second simulations are either due to (1) the treatment of transport in the governing equations or (2) assumptions and approximations made in the numerical methods used to solve the governing equations. For the purpose of comparison, the moments solved by MoMIC in the first simulation are treated as the reference solution because this is the fully coupled simulation solved with transport.



Fig. 5.6 (a) Moments obtained from the first-step MoMIC simulation and from post-processing with a spherical particle model with and without the thermophoretic correction. The $Ti(OH)_4$ collision species mole fraction is added for reference. (b) The relative difference in the moments at the stagnation surface measured against the MoMIC solution for the spherical (sph.) and detailed (det.) particle models.

Figure 5.6a shows the moments obtained by post-processing using the spherical particle model with and without thermophoretic correction, together with the MoMIC reference solution. The Ti(OH)₄ collision species mole fraction is included for reference. The thermophoretic correction was found to significantly improve the agreement between the post-process and the MoMIC reference solution near the stagnation surface (at z = 0 cm) where thermophoretic transport effects are most significant.

The large difference in the predicted moments at the flame front is a consequence of the resolution of the stochastic method. A statistically significant solution only exists once the concentration of $Ti(OH)_4$, the collision species, is high enough and therefore the particle inception rate is large enough for particles to be incepted into the simulation sample volume with reasonable probability.

The relative difference in the moments predicted by the post-process at the stagnation surface measured against the MoMIC reference solution is plotted as a function of moment order, r, in Fig. 5.6b. Results from post-processing with the spherical and detailed particle model are shown, with and without thermophoretic correction. For $r \ge 1$ a significant reduction in the relative difference is observed with the introduction of the thermophoretic correction for both particle models. Naturally, the spherical particle model shows better agreement (for $r \ge 2$) than the detailed model because a spherical model is also used in the first simulation. The aggregate particle structure described by the detailed model is expected to affect the shape of the predicted PSD, and thus, the higher order moments.

The zeroth moment shows little to no improvement when the thermophoretic correction is introduced. Two possible reasons for this are: the greater relative importance of diffusion on M_0 (Fig. 5.5); and differences in the numerical methods, especially in the treatment of coagulation. A difference between the two solutions is expected because MoMIC introduces a numerical approximation, while the stochastic method treats coagulation exactly. In particular, the MoMIC calculation of the M_0 source term requires an extrapolated negative order fractional moment [50], which is prone to numerical error. Furthermore, the divergence in M_0 in Fig. 5.6a does not coincide with extrema in the M_0 diffusion term in Fig. 5.5 suggesting that diffusion is not the cause. At the point of divergence the M_0 diffusion term is negligible. This would suggest that the error arises from differences between the two numerical methods.

Figure 5.7 shows a comparison of the average particle diameter as a function of TTIP loading for spherical and detailed particle models, with and without the thermophoretic correction. For the detailed particle model the collision diameter is calculated as per Sander et al. [149] (Eq. (2.16)). We see that the thermophoretic correction reduces the error substantially for both spherical and detailed models. However, the difference observed in the zeroth moment in Fig. 5.6 is carried over into the average particle properties, hence the agreement is not as good



Fig. 5.7 Relative difference in particle collision diameter measured against the MoMIC reference solution plotted as a function of TTIP loading. Results from post-processing using a spherical particle model (sph.) and detailed particle model (det.) are shown with and without thermophoretic correction.

as for the individual moments. The plots show a general trend of improving agreement with increased TTIP loading. This is primarily driven by the behaviour of the divergence in M_0 and not an effect of the thermophoretic correction.



Fig. 5.8 Mole fraction of Ti(OH)₄, the collision species, and the average number of primaries per particle as a function of distance from the stagnation surface.

The methodology considers two-way coupling between the gas and particle phases only in the first simulation step. The assumption is that the spherical particle model employed in the first simulation provides a reasonable approximation of particle morphology when coupling to the gas-phase is most important. Non-spherical particles would give different process rates for gas-phase interactions due to different particle morphology affecting properties such as the collision diameter and free surface area. The mole fraction of the gas-phase collision species (Ti(OH)₄) obtained from the first simulation and the average number of primaries per particle predicted by the post-process are plotted in Fig. 5.8 as function of the distance from the stagnation surface. We observe that the collision species is exhausted prior to the formation of aggregates suggesting that a spherical particle model provides a reasonable description of particle morphology when Ti(OH)₄ is being consumed from the gas-phase and two-way coupling is most important. Particles remain spherical in this high temperature region due to rapid coalescence of colliding particles. The detailed model predicts aggregate formation only after the particle processes have effectively decoupled from the gas-phase chemistry.

5.5.3 Evolution of aggregate particle morphology



Fig. 5.9 (a) An experimental TEM image (unpublished data, Manoel Manuputty) and (b) a simulated TEM-style image.

Figure 5.9 shows an experimental TEM image of aggregate TiO_2 particles synthesised in a stagnation flame and a simulated TEM-style image produced under similar modelled conditions. In both images we observe sintered aggregate particles of comparable aggregate and primary size. This illustrates that resolving the aggregate structure and modelling morphology dependent processes such as sintering are important for making proper comparison with experimental results.

In Fig. 5.10 the average number of primaries per aggregate predicted by the post-process as a function of distance from the stagnation plate is plotted together with the simulated temperature profile. The formation of aggregates is observed as the temperature decreases substantially



Fig. 5.10 Simulated temperature profile and average number of primaries per aggregate predicted by the post-process. Four simulated TEM-style snapshots are shown at different points along the flame.

near the stagnation surface. This is due to the rate of sintering having a stronger temperature dependence than coagulation. The TEM-style snapshots generated at different points along the flame illustrate this change in particle morphology.

5.5.4 Comparison with experimental PSD

In this section we use the methodology presented in this paper to simulate the premixed stagnation flame experiment of Tolmachoff et al. [169] using a detailed particle model. The experiment has been previously simulated by Manuputty et al. [108] using a single step TTIP decomposition model with the overall rate given by Okuyama et al. [135]. In this work, we simulate the experiment using the gas-phase chemistry described in Section 5.3.2 and collision limited inception and condensation reactions with $Ti(OH)_4$ as the collision species. Otherwise, the details of the modelled burner configuration and first simulation step are the same as in [108].

In the experimental investigation by Tolmachoff et al. [169] a TTIP-doped premixed laminar flame (3.96% C₂H₄/26.53% O₂/ Ar, $\phi = 0.45$) issued from an aerodynamically shaped nozzle impinges on a rotating stagnation plate. In the present analysis, as in the previous modelling

work performed by Manuputty et al. [108], it is important to consider two aspects of this burner configuration: the stagnation surface temperature and the particle sampling technique.

Cooling jets and convection maintained the stagnation plate temperature at $T_{\rm s} \sim 400$ K for rotational speeds in the range of 100–600 RPM. Without rotation, the absence of convective cooling increased the plate temperature as high as $T_{\rm s} \sim 1000$ K. As in [108], other effects of rotation are not considered here. Tolmachoff et al. [169] suggest that rotation results in little to no change in flame characteristics due to the thin boundary layer, hence it is reasonable to only vary the stagnation plate temperature.

Two different particle sampling techniques were used in the experimental study: a scanning mobility particle sizer (SMPS) with sampling probe mounted in the plate was used for the non-rotating plate; while TEM image analysis was performed on particles collected by rapid insertion of a TEM grid fastened to the plate when the plate was rotating.



Fig. 5.11 Particle size distributions of TiO₂ produced at (a) 306 ppm and (b) 1070 ppm TTIP loadings. Symbols: experimental data from Tolmachoff et al. [169, Fig. 8]; Solid lines: collision diameter distribution; Dashed lines: primary particle size distribution; Dotted lines: log-normal PSD from MoMIC results. Simulation results are presented for stagnation plate temperatures of 400 K and 1000 K.

Simulations were performed using a collision enhancement factor of $\varepsilon = 2.64$ as per Manuputty et al. [108], and a critical sintering diameter of $d_{p,crit} = 2$ nm, which was found to give the best fit of the right tail of the simulated collision diameter distribution to the 0 RPM experimental case. This value is consistent with the molecular dynamics study of Buesser et al. [25], who found that small primaries with $d_p < 4$ nm sinter significantly faster than rates predicted by models developed for larger particles. Figure 5.11 shows the simulated particle size distributions for two different TTIP loadings (306 ppm and 1070 ppm) with the two different plate temperatures (400 K for the rotating plate and 1000 K for the stationary plate). Gaussian kernel density estimates are plotted for the collision diameter and primary particle diameter distributions obtained from the detailed model post-process. Log-normal distributions were generated from the first simulation step MoMIC data with median particle diameter and geometric standard deviation calculated as per Manuputty et al. [108]:

$$\langle d \rangle = \frac{d_{\text{TiO}_2} \mu_{1/3}}{\sqrt{1 + \frac{\mu_{2/3} - \mu_{1/3}^2}{\mu_{1/3}^2}}}$$
(5.13)

GSD = exp
$$\sqrt{\ln\left(1 + \frac{\mu_{2/3} - \mu_{1/3}^2}{\mu_{1/3}^2}\right)},$$
 (5.14)

where μ_r are the fractional reduced moments. The experimental data are from Tolmachoff et al. [169, Fig. 8].

Our simulations predict a small degree of aggregate formation indicated by the differing collision diameter and primary diameter distributions; notably, the position of the respective right hand tails of each distribution. We begin by comparing the aggregate collision diameter distribution for stagnation temperature $T_s = 1000$ K (solid red lines) with the 0 RPM SMPS data (solid symbols) because the instrument measures the aggregate particle size. The 1070 ppm loading case shows excellent agreement with the experimental data of Tolmachoff et al. [169]. For the lower loading 306 ppm case, however, our simulation predicts a broader distribution compared to the experimental results. It is worth noting that we are comparing our modelled collision diameter with SMPS measured mobility diameter and the two are unlikely to be identical measures of particle size, which may contribute to some of the observed differences.

To compare our simulations with the rotating disc experimental data we use the primary diameter distribution. In the experimental study [169] measurements of particle size for the rotating disc were performed using TEM image analysis, in which case the diameters of individual primaries were measured. Thus, we compare the primary diameter distribution for $T_s = 400$ K (dashed blue line) with the experimental results with rotation (open symbols). The agreement with the experimental data is reasonably good in both cases; although the simulated median size is slightly larger and the distribution is shifted to the right. On the other hand, the aggregate collision diameter distributions (solid blue lines) are broader and extend to larger particle sizes. Tolmachoff et al. [169] attribute the difference in the rotating vs. non-rotating disc PSDs to the change in disc temperature rather than measurement technique, supported

by an earlier study showing that diameters measured by SMPS agree with those measured by TEM analysis in the size range of interest [198]. In contrast, our simulation results suggest that while some of the difference can be attributed to the stagnation surface temperatures it is also possible that a small degree of aggregation can result in different measured distributions. In this case the mean number of primaries per aggregate was $\bar{n}_p < 2$ for all simulations.

It is also worth comparing the detailed model simulation results with the log-normal distributions obtained from the first step MoMIC simulations (dotted lines) with spherical particle assumption. The MoMIC results underpredict the median size for the non-rotating (0 RPM, $T_s = 1000$ K) disc (dotted red lines vs. solid symbols) while the rotating case ($T_s = 400$ K) is in better agreement (dotted blue lines vs. open symbols), likely because of the spherical particle assumption. This would suggest that a simple spherical particle model is not sufficient and a detailed particle description is needed to model the system and provide additional insight.

5.6 Conclusions

This chapter introduced a general two-step modelling methodology able to resolve the complex aggregate morphology of nanoparticles synthesised in a stagnation flame. The methodology was applied to the combustion synthesis of TiO_2 particles from TTIP precursor. A detailed particle model is necessary to simulate the evolution of aggregate particles observed in experiments.

The first step of the two-step methodology couples detailed gas-phase chemistry, a onedimensional flow model and spherical particle model solved with MoMIC. The resulting flame profile is then post-processed using a detailed particle model capable of tracking individual primary coordinates to resolve the aggregate structure. The method allows for comparison with experimental observations such as TEM images and enables the study of morphology dependent particle processes.

Examination of the magnitude of the terms in the MoMIC equations showed that thermophoretic transport effects are significant near the stagnation surface and must be accounted for in the second step where the flame profile is post-processed. To do this, a thermophoretic correction to the simulation sample volume was introduced. Comparison of moments predicted by the second-step post-process against the first-step MoMIC solution showed that the thermophoretic correction leads to a significant reduction in the error associated with the post-process. However, a divergence in the zeroth moment was observed, which has an impact on the average particle properties. This is suspected to be caused by differences between the two numerical methods used; in particular, their treatment of coagulation. The stagnation flame experiment of Tolmachoff et al. [169] was simulated using the two-step methodology with detailed particle model to demonstrate the ability of a detailed description of particles to provide additional insight and explain experimental observations. The detailed model was better able to reproduce the measured PSDs compared to a simple spherical particle model. While the model itself was not the subject of this chapter, the methodology presented here allows it to be applied to a widely used class of flame, and thus provides a means to evaluate the model against experimental data such as aggregate size, primary size and primary number distributions. This will be the subject of the next chapter.

Chapter 6

Detailed simulation and parametric sensitivity study of TiO₂ particles synthesised in a stagnation flame¹

This chapter combines the new particle model and the two-step post-processing method introduced in the last two chapters to simulate the formation of titanium dioxide nano-aggregates in a stagnation flame from TTIP precursor. This work aims to perform a comprehensive comparison of model prediction with experimental data to evaluate the model and explore the sensitivity to key model parameters. The stagnation flame allows us to study the choice of sintering parameters for sub-10 nm particles. The detailed particle model permits direct comparison with experimental measurements through simulated TEM-style images.

6.1 Background

Development of an accurate model of TiO_2 formation relies on a comprehensive description of the gas-phase chemistry and a particle model that is able to represent the morphology of aggregate particles. Most attempts at modelling high temperature TiO_2 formation from TTIP assume a one-step thermal decomposition [108, 195, 200]. A first-order reaction rate was proposed by Okuyama et al. [135] and later combined with a surface decomposition reaction by Tsantilis et al. [172] to model TiO_2 formation in a premixed flat flame. Nonetheless, experimental studies have shown that TTIP decomposition at flame temperature is a complex reaction involving

¹The investigation presented in this chapter was performed in collaboration with Manoel Manuputty and published in [105]. The extent of collaboration and division of work is discussed in Appendix A. The work presented here focuses on the detailed particle modelling aspect of the investigation, which was performed by the author.

many intermediate species [160]. Buerger et al. [23] proposed a systematically derived and thermodynamically consistent detailed kinetic mechanism of TTIP decomposition.

Previous simulations of the stagnation flame experiment [108] employed a spherical particle model and used the method of moments with interpolative closure (MoMIC) to solve the population balance equations. The approach permitted full coupling of the particles to the gas-phase and flow dynamics. However, the model was constrained to one internal coordinate in the particle description. Yet, particles are often observed to be aggregate structures composed of a polydisperse population of primary particles with different levels of sintering. A multivariate model is needed to fully capture the particle morphology. The new detailed particle model and two-step simulation methodology developed in this thesis seek to address these limitations. Combined with the detailed chemistry proposed by Buerger et al. [23], we can now begin to develop a better model of TiO₂ formation in flames.

A detailed particle model allows for the simulation of quantities that are directly comparable to experimental data, such as particle size measurements from TEM imaging and mobility size analysis [6, 172, 198]. For example, simulated TEM-style images can be analysed in a similar manner to experimental data to obtain the aggregate size distribution – as is done in this work. In addition, a detailed particle description permits the modelling and study of processes that are fundamental to the evolution of particle morphology, but which cannot be fully captured by simpler models. For instance, sintering is commonly modelled by considering the evolution of the surface area of an aggregate with a defined characteristic time [89]; however, these models often extrapolate late stage behaviour over the entire process. More detailed geometrical models permit a more complete picture of the evolution of particles during sintering [40, 41, 191]. Furthermore, the sintering behaviour is strongly influenced by the morphological properties of the particle, particularly at the nano-scale ($d_p < 10$ nm). For example, in a molecular dynamics study on the sintering of 2-4 nm TiO₂ Buesser et al. [25] found the sintering rate to be much faster than that predicted by extrapolating the characteristic sintering time typically used in studies on larger particles [88, 153]. The stagnation flame setup, used to synthesise ultra-fine TiO₂ particles, provides an excellent system to study the behaviour of sintering models for very small particles.

The purpose of this chapter is to evaluate the new detailed particle model for titanium dioxide nano-aggregates introduced in Chapter 4 against experimental measurements [110], and perform a parametric sensitivity study to understand the influence of key parameters on the particle properties. We simulate the synthesis of titanium dioxide nano-aggregates from TTIP precursor in a stagnation flame using the two-step simulation methodology introduced in Chapter 5. A detailed chemical mechanism is used to describe the thermal decomposition of TTIP [23] and the detailed particle model is used to resolve the particle morphology.

The detailed particle description permits comparison of simulated quantities with equivalent experimental measurements; namely, the aggregate projected spherical equivalent diameter distribution (particle size distribution, PSD) and the primary particle size distribution (PPSD), obtained by TEM image analysis.

6.2 Stagnation flame experiment

In this chapter, we simulate the stagnation flame experiments performed by Manoel Manuputty. Full details of the experimental investigation are presented in [110], and in the supplementary material of [105]. A summary of details relevant to the modelling work is given here.

A laminar stagnation flame, stabilised by flow stretch, was used to prepare TiO₂ nanoparticles from titanium tetraisopropoxide (TTIP) precursor. The premixed gas was heated to 150°C with exit velocity of 436 cm/s. Premixed gas mixtures with two different equivalence ratios (ϕ) were used: $\phi = 0.35$, i.e. a lean flame (3.5% C₂H₄-30% O₂-66.5% Ar) and $\phi = 1.67$, i.e. a rich flame (10.3% C₂H₄-18.5% O₂-71.2% Ar). The TTIP loading rates used were 4, 12 and 30 ml/h, corresponding to 194, 582, and 1454 ppm TTIP respectively.

Particles were sampled through an orifice in the stagnation plate and diluted with nitrogen gas in the sample line to reduce aggregation. Nanoparticle morphology was characterised by analysing TEM images and mobility measurements. The experimental investigation found that the particle morphology was sensitive to the TTIP loading, but was relatively insensitive to the equivalence ratio. Here we choose five descriptors of particle morphology from the TEM image analysis for comparison with the simulation results. These are the mean (\bar{d}_p) and coefficient of variation (CV_p) of the primary particle diameter; mean (\bar{d}_a) and coefficient of variation (CV_a) of the aggregate projected spherical equivalent diameter; and the fraction of aggregates with circular projection (f_{α}) . The mean diameter, standard deviation and coefficient of variation are defined for *N* aggregate or primary particles as:

$$\bar{d} = \frac{1}{N} \sum_{i=1}^{N} d_i,$$
 (6.1)

$$SD = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (d_i - \bar{d})^2},$$
(6.2)

$$CV = \frac{SD}{\bar{d}}.$$
(6.3)

The dimensionless coefficient of variation, or the ratio of the standard deviation to the mean, is used as a measure of the distribution widths in this work to allow for comparison across all TTIP loading rates, i.e. cases with varying mean sizes. The aggregate projected spherical

equivalent diameter is

$$d_{\rm a} = 2\sqrt{\frac{A_{\rm pr}}{\pi}},\tag{6.4}$$

where A_{pr} is the aggregate projected area. Manuputty et al. [110] define a parameter α_i for an aggregate as the ratio of projected diameter of gyration, $d_{g,2D}$, and the projected spherical equivalent diameter:

$$\alpha(P_q) = \frac{d_{g,2D}(P_q)}{d_a(P_q)}.$$
(6.5)

The fraction of aggregates with circular projection, f_{α} , is defined as the fraction of particles with $\alpha(P_q) < 0.73$.

The uncertainties of the primary particle and aggregate sizes are based on the resolution limits of the analysed images, estimated by Manuputty et al. [110] as ± 4 and ± 2 pixels, respectively. These correspond to ± 0.48 nm for the primary sizes (all loadings) and ± 0.5 nm (4 ml/h TTIP), ± 0.64 nm (12 ml/h), and ± 0.94 nm (30 ml/h) for aggregate sizes.

6.3 Computational detail

The same models and simulation methodology are used here as in the previous chapter. The flow model is described in [108], the detailed chemistry in Section 4.2, and the detailed particle model in Section 4.3. In this work, the form of the characteristic sintering time is studied in more detail – the model equations are discussed below. The stagnation flame is simulated using a two-step methodology with thermophoretic correction introduced in Chapter 5. Results from the second simulation step are averaged over 4 runs, each with 8192 stochastic particles. The model parameters are summarised in Table 6.1.

6.3.1 Characteristic sintering time

Sintering is commonly modelled by considering the excess surface area of an aggregate over that of a sphere with the same mass [95, 131, 153, 185, 188]. The model of Koch and Friedlander [89], valid for $t \gg \tau_s$, describes the evolution of the surface area:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{1}{\tau_{\rm s}}(S - S_{\rm sph}),\tag{6.6}$$

where *S* is the surface area of the aggregate, S_{sph} is the surface area of a sphere with the same mass and τ_s is the characteristic sintering time. Multivariate particle models [150, 156] have extended this approach to consider the surface area of each pair of neighbouring primary

Parameter	Value	Range	Sensitivity
Sintering:			
Prefactor, $A_{\rm s}$	0.25	0.01–10	+
Critical diameter, $d_{p,crit}$	2.5 nm	1–4 nm	++
Critical exponent, α_{crit}	7	1–7	++
Collision limited processes:			
Enhancement factor, ε	2.64	2.2-3.0	+
Inception efficiency, γ_{in}	1	0.01-1	-
Surface growth efficiency, γ_{sg}	1	0.01-1	-
Other:			
Density, ρ_{TiO_2}	3.84 g/cm^3	3.84, 4.25 g/cm ³	-

Table 6.1 Summary of model parameters and sensitivity. The base case value, range studied and an indication of the sensitivity (++: sensitive; +: slightly sensitive; -: insensitive) are given. The sintering base case values correspond to sintering model 1.

particles individually. It should be noted that Eq. (6.6) applies to late stage sintering behaviour, but is often extrapolated to all stages of sintering.

If the characteristic sintering time τ_s is constant, Eq. (6.6) yields an exponential decay with τ_s corresponding to a 63% reduction in the excess surface area. However, in general τ_s does not remain constant, but varies as a function of temperature and particle diameter [153]. Buesser et al. [25] remark that the characteristic time is the time needed for the neck diameter to reach 83% of the initial primary particle diameter [88], corresponding to a 67% reduction in the excess surface area and close to the commonly used exponential decay.

Various expressions for the characteristic sintering time of titanium dioxide particles have been proposed. Kobata et al. [88] proposed a characteristic time based on a surface diffusion model:

$$\tau_{\rm s} = 7.44 \times 10^{16} d_{\rm p}^4 T \exp\left(\frac{258\,{\rm kJ\,mol}^{-1}}{RT}\right) \,{\rm s},\tag{6.7}$$

where d_p is the primary diameter (m), *R* the ideal gas constant and *T* is the temperature (K). Seto et al. [153] considered a grain boundary diffusion based model with

$$\tau_{\rm s} = 9.75 \times 10^{15} d_{\rm p}^4 T \exp\left(\frac{258\,{\rm kJ\,mol^{-1}}}{RT}\right) \,{\rm s.} \tag{6.8}$$

Both studies investigated particles larger than 10 nm, with Seto et al. [153] noting that the sintering behaviour of nano-sized particles may be quite different.

Buesser et al. [25] performed molecular dynamics simulations to study the sintering of 2–4 nm rutile particles at 1500–2000 K, and found that smaller nanoparticles ($d_p < 4$ nm) sinter significantly faster than predicted by a d_p^4 dependence. They fitted a characteristic sintering time,

$$\tau_{\rm s} = 3.7 \times 10^{16} d_{\rm p}^4 T \exp\left(\frac{258\,{\rm kJ\,mol^{-1}}}{RT} \left(1 - \left(\frac{3.4\,{\rm nm}}{d_{\rm p}} - \frac{T}{4100\,{\rm K}}\right)^{3.76}\right)\right) \,{\rm s},\tag{6.9}$$

which includes a particle size dependence in the exponential term. This is consistent with an earlier theoretical study by Tsantilis et al. [171] on the viscous flow sintering of silica particles, in which a particle size dependence was introduced to the activation energy based on the size dependence of the melting point:

$$\tau_{\rm s} \propto \exp\left(\frac{E_{\rm a}}{RT}\left(1 - \frac{d_{\rm p,crit}}{d_{\rm p}}\right)\right).$$
 (6.10)

The result is effectively instantaneous sintering below a critical diameter $d_{p,crit}$. This form of the characteristic time has been used in multivariate particle models for silica [150, 156] and has also been applied to soot modelling [33, 192].

The preceding models considered the evolution of the surface area of an aggregate. In contrast, the detailed geometrical description used in this work requires the sintering equations to be formulated in terms of the primary separations and radii. Following Eggersdorfer et al. [41] (see Chapter 4 for more details), the rate of change in primary centre to neck distance is

$$\frac{\mathrm{d}x_{ij}}{\mathrm{d}t} = -\frac{d_{\rm p}^4}{16\theta A_{{\rm n},ij}} \left(\frac{1}{r_i - x_{ij}} - \frac{1}{a_{ij}}\right),\tag{6.11}$$

where x_{ij} is the distance from the centre of primary p_i to the neck formed with neighbour p_j , $A_{n,ij}$ is the neck area, a_{ij} is the neck radius and r_i is the radius of the primary p_i . The characteristic time is

$$\theta = 9.11 \times 10^{17} d_p^4 T A_s \exp\left(\frac{258 \,\mathrm{kJ}\,\mathrm{mol}^{-1}}{RT} \left(1 - \left(\frac{d_{\mathrm{p,crit}}}{d_{\mathrm{p}}}\right)^{\alpha_{\mathrm{crit}}}\right)\right) \,\mathrm{s.} \tag{6.12}$$

where we previously introduced a critical diameter $d_{p,crit}$, with a similar form to that proposed by Tsantilis et al. [171]. In this work, we introduce an additional prefactor A_s and critical exponent α_{crit} . The effect of these parameters is discussed in Section 6.4.2. The primary diameter d_p is taken as the smaller of the two primary diameters, $d_p = \min(d_p(p_i), d_p(p_j))$.

It is important to note that the characteristic time defined in Eq. (6.12) for the centre to neck separation model is not directly comparable to the characteristic times in Eqs. (6.7)–(6.9),

which are defined with respect to the change in excess surface area. A method of comparison is discussed in Appendix D.1.

6.4 **Results and discussion**

This section focuses on the evaluation of the detailed particle model against experimental results and the parametric sensitivity study. A discussion of the simulated flame profiles and associated uncertainties is included in Appendix D.2.

6.4.1 Particle temperature-time history



Fig. 6.1 Time evolution of mean primary diameter (dashed lines) and collision diameter (solid lines) for different TTIP loadings for a the lean and b the rich flames. The simulated temperature profiles (dotted lines) are included for reference.

Figure 6.1 shows the evolution the mean primary diameter and mean aggregate collision diameter as a function of particle residence time for the six flames, using the base case model parameters given in Table 6.1. The collision diameter is defined in Eq. (4.16). It should be noted that this is not equivalent to the aggregate diameter obtained from image analysis that is used for comparison with the experimental data.

All flames show rapid growth in particle size as the temperature peaks, followed by slower growth as the temperature begins to decrease. The particles are initially single primaries – illustrated by the coincident primary and aggregate collision diameters. The subsequent

deviation of the collision and primary diameters indicates the onset of aggregate formation as the sintering rate slows sufficiently relative to the rate of coagulation. This happens once the temperature falls into the 1500–2000 K range, with lower temperatures correlating with smaller mean particle size. At high temperature, the rapid sintering kinetics in the model cause near instantaneous coalescence and liquid-like behaviour of colliding particles. The observed range of transition temperatures is consistent with the melting point depression of nanoparticles [65]. After this point, primary growth effectively ceases and aggregates grow by coagulation.

We observe that the total residence time decreases with increasing maximum flame temperature, and the trend with respect to TTIP loading reverses between the lean and the rich flames. Meanwhile, the trends in particle size with respect to TTIP loading are consistent across both flames. The higher loading cases show faster growth in particle size and larger final particle diameters. Both 30 ml/h cases show very similar particle evolution. However, the evolution of particles in the 4 ml/h cases differ substantially between the lean and the rich flames. The lean flame shows a significantly longer period of aggregate growth and larger final particle size as a consequence of the longer residence time.

6.4.2 Parametric sensitivity

Base case sintering parameters

The sensitivity of the aggregate and primary particle size distributions to three sintering parameters is investigated: the critical diameter $d_{p,crit}$, prefactor A_s , and critical exponent α_{crit} (see Eq. (6.12)). The effect of varying each of the parameters on the sintering time is shown in Fig. 6.2. The characteristic sintering times τ_s of Kobata et al. [88], Seto et al. [153] and Buesser et al. [25] (Eqs. (6.7)–(6.9), respectively) are also plotted. As noted in Section 6.3.1, these three characteristic sintering times cannot be directly compared to Eq. (6.12) (the characteristic time θ defined for the model used in this study) because the model equations are different (compare Eqs. (6.6) and (6.11)). To facilitate comparison, we determine a time τ_s for the present model, which is consistent with the typical use of Eqs. (6.7)–(6.9) in modelling work. In this case, τ_s is defined as the time needed to reduce the excess surface area of two equal sized primaries by 63% and corresponds to $\tau_s = 0.14\theta$ (see Appendix D.1).

The characteristic time τ_s is plotted as a function of primary diameter for two different temperatures. The temperatures are the minimum and maximum temperatures used in the molecular dynamics study of Buesser et al. [25]. The base case sintering parameters for this work (referred to as "sintering model 1") are chosen to give the best fit to the characteristic time of Buesser et al. [25] (Eq. (6.9)). These values are: $A_s = 0.25$, $d_{p,crit} = 2.5$ nm and $\alpha_{crit} = 7$.



Fig. 6.2 Effect of varying each sintering parameter on the characteristic sintering time. The base case parameters chosen for this study (dotted lines; $A_s = 0.25$, $d_{p,crit} = 2.5$ nm, $\alpha_{crit} = 7$) are a fit to the characteristic time of Buesser et al. [25]. The shaded regions indicate the range over which the parameter is varied. The characteristic times of Kobata et al. [88] and Seto et al. [153] are included for reference. T = 1500 K and T = 2000 K are the minimum and maximum of the range covered by the MD study in [25].

The shaded regions indicate the range over which the parameter is varied in this sensitivity study.

Varying the prefactor results in a vertical shift in the characteristic time as shown by the shaded regions in Fig. 6.2a. The effect of changing the critical diameter, shown in Fig. 6.2b, changes the location of the asymptote and only affects the sintering time of small particles. The critical exponent α_{crit} affects the sharpness of the transition from large particle sintering behaviour ($\tau_s \propto d_p^4$) to near instantaneous sintering of small particles. A small exponent such as $\alpha_{crit} = 1$, the lower bound of the shaded regions in Fig. 6.2c, results in a long transition while larger values of α_{crit} create a sharper transition near the critical diameter. The consequence of a long transition is that the sintering time is reduced for particles significantly larger than the prescribed critical diameter; thus, near instantaneous sintering occurs for particles larger than the value of $d_{p,crit}$ suggests. For example, Fig. 6.2c shows that the sintering time begins to deviate from a linear relationship for values of d_p that are an order of magnitude greater than $d_{p,crit}$.

Simulated and experimental primary and aggregate particle size distributions are shown in Fig. 6.3 for the six flame conditions. The experimental particle size data, obtained by TEM image analysis, are from Manuputty et al. [110, Fig. 11]. In the experimental investigation, primary particle diameters were measured by manually specifying the centre of a sphere and a point on the circumference. This measure is directly comparable to $d_p(p_i) = 2r_i$ defined in the particle model. The aggregate size was obtained by measuring the two-dimensional projected area of each aggregate in the image to determine a projected spherical equivalent diameter. In order to directly compare our simulation results to this data, similar analysis was performed on simulated TEM-style images generated from the simulation data using the procedure described in Appendix B.3. 100 images were generated for each simulation with an average of 43 particles per image.

PSDs simulated using sintering model 1 are shown by the blue lines in Fig. 6.3. For comparison, the red lines show PSDs simulated with the sintering parameters used in Chapter 4: $A_s = 1$, $d_{p,crit} = 4$ nm and $\alpha_{crit} = 1$ (henceforth referred to as "sintering model 2"). The other simulation parameters are summarised in Table 6.1. The simulated aggregate size distribution are similar for both sets of sintering parameters and are in good agreement with the experimental data. On the other hand, the primary particle size distributions are considerably different. Sintering model 1 yields very good agreement with the experimental data, while sintering model 2 produces a much wider PPSD at lower TTIP loading.

The effect on the width of the PPSD is also evident in the trend displayed by the coefficient of variation as a function of TTIP loading, plotted in Fig. 6.4. Sintering model 1 produces a trend that is consistent with the relatively flat trend shown by the experimental data. Model 2,



Fig. 6.3 Simulated and measured primary and aggregate size distributions for the base case sintering parameters used in this work (sintering model 1, blue lines) and parameters from Chapter 4 (sintering model 2, red lines). The experimental data points [110, Fig. 11] are normalised particle counts with a bin width of 0.5 nm. The lines are from kernel distribution fits using 1 nm bandwidth. f_{α} denotes the fraction of spherical particles from TEM image analysis.

however, displays a decreasing trend with a significantly larger CV at low TTIP loading. The trends observed in the mean primary and aggregate size, and aggregate CV are consistent across both simulations and in reasonable agreement with the experimental data.

Another useful descriptor of particle morphology is the fraction of particles with circular projection f_{α} , defined in [110], and shown in Fig. 6.3. The experimental results show a fairly constant fraction across both TTIP loading and equivalence ratio. In general, sintering model 1



Fig. 6.4 The primary and aggregate mean diameters and CVs for sintering model 1 (solid blue lines) and sintering model 2 (dashed red lines), for lean ($\phi = 0.35$, left panels) and rich ($\phi = 1.67$, right panels) flames. The shaded areas indicate estimated uncertainty bounds of the experimental measurements and error bars show the simulation uncertainties (see Appendix D.2).

slightly underpredicts the fraction of spherical particles (except for the 4 ml/h rich flame case), while model 2 significantly overpredicts the fraction. Overall, simulations with sintering model 1 are in much better agreement with the experimental data. The largest discrepancy in f_{α} is seen in the 4 ml/h rich flame case. Sintering model 1 overpredicts the fraction of spherical particles by 11 percentage points, while model 2 overpredicts the fraction by 33 percentage points. The difference in predicted particle morphology is apparent in the TEM-style images presented in Fig. 6.5. Qualitatively, the TEM image produced with sintering model 1 (Fig. 6.5b) shows the presence of small aggregated particles, in agreement with the experimental TEM image produced model 2 (Fig. 6.5c) shows mostly fully sintered spherical particles.

This underscores the importance of comparing a range of morphological descriptors when evaluating simulation data against experiment. On the basis of the mean values alone, plotted in Fig. 6.4, sintering model 2 may have been preferred; however, the CV and f_{α} suggest otherwise. The sensitivity to each individual sintering parameter and reasons for the observed trends in the descriptors will be investigated in the next section.



(a) Experimental TEM.

(b) Sintering model 1.

(c) Sintering model 2.

Fig. 6.5 Experimental TEM (image by Manoel Manuputty) and simulated TEM-style images for the rich flame ($\phi = 1.67$) with 4 ml/h TTIP loading.

Sensitivity to sintering parameters



Fig. 6.6 Sensitivity to the sintering prefactor A_s for lean ($\phi = 0.35$, left panels) and rich ($\phi = 1.67$, right panels) flames. The shaded areas indicate estimated uncertainty bounds of the experimental measurements.

The sensitivity of the aggregate and primary mean diameter and CV to the sintering prefactor A_s are shown in Fig. 6.6. The base case values of the other parameters used in the simulation are given in Table 6.1. Overall, the descriptors are not particularly sensitive to the sintering prefactor, considering that it is varied over three orders of magnitude. Notably, the mean aggregate diameter shows almost no sensitivity to the sintering prefactor. This is unsurprising since sintering is an internal structural change and the aggregates are composed of a small

number of primaries; thus, remain fairly compact in all configurations. The general insensitivity can to some extent be explained by the proximity of the average primary diameter to the critical diameter. In this region, the characteristic sintering time rapidly becomes less sensitive to the prefactor, as seen in Fig. 6.2a.

Increasing the prefactor results in a narrower primary distribution with smaller mean size, but broader aggregate distribution. The effect is slightly more pronounced at higher TTIP loading due to the larger average particle size, which is farther from the critical diameter. Smaller A_s seems to give better agreement with the experimental data in the mean primary size, but the width of the distribution is overestimated.



Fig. 6.7 Sensitivity to the critical sintering diameter $d_{p,crit}$ for lean ($\phi = 0.35$, left panels) and rich ($\phi = 1.67$, right panels) flames. The shaded areas indicate estimated uncertainty bounds of the experimental measurements.

Figure 6.7 shows the sensitivity of the morphological descriptors to the critical sintering diameter. The mean primary and aggregate size, and aggregate CV are not particularly sensitive. In contrast, the primary coefficient of variation is sensitive to the choice of critical diameter, with larger values of $d_{p,crit}$ producing a smaller CV, indicating a narrower PPSD. This is because the critical diameter imposes an effective lower bound on the size of a primary in an aggregate (small primaries can of course exist as single particles). Lower TTIP loadings show greater sensitivity due to the average primary diameter being closer to the critical value. The results suggest that a value of $d_{p,crit} = 4$ nm is a better fit to the experimental data.


Fig. 6.8 Sensitivity to the critical sintering exponent α_{crit} for lean ($\phi = 0.35$, left panels) and rich ($\phi = 1.67$, right panels) flames. The shaded areas indicate estimated uncertainty bounds of the experimental measurements.

The effect of the critical exponent on the mean primary and aggregate diameter and coefficient of variation is shown in Fig. 6.8. The greatest sensitivity is observed between $\alpha_{crit} = 1$ and $\alpha_{crit} = 3$ for lower TTIP loading. This is notable in both CVs and the mean primary size. In particular, the decreasing trend in the primary CV as a function of TTIP loading changes to a relatively flat trend, which is more consistent with the experimental data. The reason for this is the fact that the mean primary size is close to the critical diameter; thus, the sharpness of the transition (see Fig. 6.2c) from large particle behaviour to instantaneous sintering has a significant impact on the evolution of the PPSD. For a large value of α_{crit} , instantaneous sintering only occurs at the tail of the distribution, thereby resulting in a narrower size distribution. With $\alpha_{crit} = 1$, the sintering rate of large primaries is also increased significantly; thus, the entire size distribution evolves. The effect is most pronounced for the low TTIP loading cases due to their lower mean primary size, so more of the PPSD is located in this intermediate region around the transition.

The simulation results appear less sensitive to values larger than $\alpha_{crit} = 3$; therefore, $\alpha_{crit} = 3$ appears as reasonable a choice as $\alpha_{crit} = 7$. In any case, a reasonably sharp transition near the critical diameter is needed to obtain the correct sintering behaviour of particles near the transition. This is consistent with the fitted value of 3.76 obtained by Buesser et al. [25]. Their fitted sintering time also included an additional temperature dependence, which is not considered here.

Inception and surface growth efficiency



Fig. 6.9 The bimodality of the primary particle distributions in lean flames ($\phi = 0.35$) with varying γ_{sg} .

Sensitivity to the inception and growth efficiencies, γ_{in} and γ_{sg} respectively, was investigated over the range $\gamma = 0.01-1$. A bimodal primary size distribution, shown in Fig. 6.9, was observed in the lean flame simulations with small γ_{sg} . The minor mode of small primaries is more pronounced in simulations with smaller γ_{sg} and lower TTIP loading. The mode arises due to inception from unreacted Ti(OH)₄ near the stagnation surface, which is still present in the mixture due to very slow consumption by the growth process (see Ti(OH)₄ profiles in Fig. 6.10). No bimodality was seen in the rich flame simulations, possibly due to the higher reaction temperature increasing the consumption rates. This would also explain why the mode is less prominent at higher TTIP loading for $\gamma_{sg} = 0.1$ (see simulated temperature profiles in Appendix D.2). The bimodality is not present in the modelled aggregate size distributions due to the small particles falling below the size threshold for image analysis. Given the mode exists near the resolution limit of the experimental results, the presence of a small particle mode cannot be completely ruled out in this study.

Sensitivity to the inception and growth efficiencies are shown in Fig. 6.11a and Fig. 6.11b, respectively. Note that the small particle mode in the $\gamma_{sg} < 1$ cases is excluded from this analysis. The results show no sensitivity to either parameter. This is unsurprising if we consider how the particle processes compete with each other during the early stages of particle evolution. A particle is first formed by inception and can then grow either through the surface growth process or by coagulation with other particles. Sintering is effectively instantaneous in the high temperature region so the particle remains spherical following coagulation; therefore, the morphology of the particle is not influenced by the particular route taken (see flame profiles in



Fig. 6.10 Simulated Ti(OH)₄ mole fraction for the lean flame ($\phi = 0.35$, left) and rich flame ($\phi = 1.67$, right) at 12 ml/h TTIP loading, with $\gamma_{sg} = 0.01$ and $\gamma_{sg} = 1$.

Fig. 6.1). Inception and growth are competing for the same gas-phase species so adjusting the collision efficiency of one process primarily affects the relative rates. The overall rate remains sufficiently rapid (except for the lean flame with very small γ_{sg}) to consume the precursor before aggregate formation and sintering become significant; thus, the final morphology is unaffected.

These results appear to contradict observations in earlier modelling studies, which reported significant sensitivity to the rate of surface reaction [108, 172]. However, the observations at the stagnation surface do not give the full picture. Figure 6.12 shows the evolution of the mean primary diameter as a function of particle residence time. In the high temperature region, the mean primary diameter displays a high degree of sensitivity to both γ_{in} and γ_{sg} . As the temperature decreases near the stagnation surface, the different cases begin to converge towards the same final diameter, explaining the previously observed insensitivity. This is especially apparent in the rich flame ($\phi = 1.67$) simulations, but not as clear in the lean flame simulations due to the formation of the small particle mode, which causes a decrease in the mean diameter near the stagnation surface.

The behaviour seen here is consistent with the findings of Tsantilis et al. [172], who, for a premixed flat flame, found that the sensitivity to the surface reaction could only be observed from measurements made near the burner. Further along the flame, the mean primary diameter was found to be much less sensitive to the surface reaction due to the dominance of coagulation.



Fig. 6.11 Sensitivity to the (a) inception efficiency γ_{in} and (b) surface growth efficiency γ_{sg} for lean ($\phi = 0.35$, left panels) and rich ($\phi = 1.67$, right panels) flames. A cutoff point of 2.5 nm is applied here for primary particle sizes to remove the first distribution mode observed for lean flames with $\gamma_{sg} < 1$. The shaded areas indicate estimated uncertainty bounds of the experimental measurements.

Summary

A summary of the parameters studied is provided in Table 6.1. The base case value, range over which the parameter was varied, and an indication of the observed sensitivity are given. Sensitivity analysis for the collision enhancement factor ε and density ρ_{TiO_2} is presented in Appendix D.3. The base case value for the enhancement factor was taken as $\varepsilon = 2.64$ [196] and density is that of anatase $\rho_{\text{TiO}_2} = 3.84$ g/cm³.

Overall, the particle morphology was found to be most sensitive to the choice of sintering parameters; in particular, the critical diameter and critical exponent due to the proximity of the average particle size to the critical size. Furthermore, the analysis suggested a larger value for the critical diameter $d_{p,crit} = 4$ nm, and a smaller value for the critical exponent $\alpha_{crit} = 3$ would be more appropriate. These are consistent with results from molecular dynamics studies [25]. The mean aggregate size was not affected by any of the three sintering parameters. This is unsurprising since the sintering process is an internal structural change.



(a) Lean flame ($\phi = 0.35$), 12 ml/h TTIP load-(b) Rich flame ($\phi = 1.67$), 12 ml/h TTIP load-ing.

Fig. 6.12 Evolution of mean primary size for different values of γ_{in} and γ_{sg} as a function of particle residence time. The temperature profile is included for reference.

The sensitivity analysis of the inception and surface growth parameters suggests that the final PSD at the stagnation surface is largely insensitive to the reaction mechanisms governing particle evolution early on in the flame. Experimental measurements from inside the combustion zone would be needed to discriminate between different models and parameters. A bimodal distribution at very small γ_{sg} was observed in the lean flame simulation; but, the small particle mode was too near the resolution limit of the experimental results to draw conclusions from the comparison.

Slight sensitivity was shown to the collision enhancement factor over the range studied, as expected, but not enough to discriminate between different values. It should be noted that the collision efficiency of titania nanoparticles has been shown to be strongly size and temperature dependent [155, 196], and necessitates a more detailed investigation.

6.5 Conclusions

In this chapter, we simulated the synthesis of titanium dioxide nano-aggregates from TTIP precursor in a premixed stagnation flame using a new detailed population balance model and two-step simulation methodology. A detailed chemical mechanism was used to describe the thermal decomposition of TTIP. Six flame cases from the experimental investigation of Manuputty et al. [110] were simulated: a lean and a rich flame, each at three different precursor

loadings. The detailed description of particle morphology in the population balance model was used to make direct comparisons with experimental measurements of primary and aggregate size distributions. Simulated TEM-style images were analysed in an identical manner to the original experimental procedure to obtain an aggregate size distribution based on the projected particle area; and the modelled primary particle size distribution was compared to the corresponding PPSD obtained from TEM image analysis in the experimental work. The simulated primary and aggregate particle size distributions were in excellent agreement with the experimental data.

The ultra-fine particles produced by the stagnation flame provided an excellent test case to investigate the characteristic sintering time of very small particles. New sintering parameters, informed by the molecular dynamics simulations of Buesser et al. [25], were introduced into the model to account for the faster sintering behaviour of nano-sized particles. Three parameters were considered: a multiplicative prefactor; a critical diameter below which sintering becomes effectively instantaneous; and a critical exponent to control the transition from the large particle to small particle sintering behaviour. Simulation results with the new sintering parameters significantly improved the agreement with the experimental data, compared to parameters used in a previous work.

A parametric sensitivity study was performed to investigate the importance of individual model parameters. Particle morphology was found to be most sensitive to the critical sintering diameter and critical exponent, demonstrating the need to give careful consideration to the form of the characteristic time when the average particle size is at the transition from large particle sintering behaviour to the near instantaneous coalescence of nano-sized particles. Other model parameters, notably the inception and growth efficiencies, were found to not affect the final particle properties, despite the simulations showing significant sensitivity to these two parameters in the combustion zone. In a future work, it would be insightful to compare model prediction with experimental measurements from the combustion zone, and to investigate the effect of temperature and particle size on the collision efficiency.

Chapter 7

Conclusions

This final chapter presents a review of the findings of this thesis and makes suggestions for further development of the titanium dioxide model.

7.1 Summary

This thesis began by exploring whether the morphological information captured by an existing detailed particle model could be used to relate the structure of aggregate particles to their behaviour in a post-synthesis milling process. In Chapter 3, five breakage models were developed and used to post-process hot wall reactor simulation data. Breakage was assumed to occur at the necks between primary particles with breakage forces applied through the fractal structure of the aggregate. The work demonstrated that the particle model is able to resolve morphological differences between particles synthesised under different reactor conditions and the breakage models exhibited behaviour qualitatively consistent with experimental observations and showed a degree of sensitivity to particle structure. Further work is needed to compare the model against experimental results. Given the nature of the post-process, an obstacle to performing a quantitative comparison is the need for details of both the particle synthesis conditions as well as the subsequent milling conditions.

More importantly, however, the work identified a number of limitations in the existing particle model. For example, the lack of geometrical detail about the necks between primaries and sintering was considered for each pair of neighbouring primaries separately without accounting for the presence of other neighbours. Furthermore, while the model captured the connectivity of primary particles in an aggregate it did not track their spatial positions. This required the introduction of additional assumptions in order to visualise aggregate particles and calculate their properties e.g. collision diameters.

A new geometrical particle model was introduced in Chapter 4 to address these limitations. The overlapping spheres model allows us to track the coordinates of each individual primary particle and the necks between them, while accounting for the effect of increasing overlap on the primary diameter. The new model incorporates sufficient physical detail to relate particle processes to specific morphological transformations and permits the accurate visualisation of simulated particle morphology, for example in TEM-style images. The implementation of a ballistic collision model to generate fractal-like structures removed the need to make an assumption about the fractal dimension and prefactor when calculating the particle radius of gyration and collision diameter.

A numerical study was conducted using a simple batch reactor test case to investigate the convergence behaviour of the new model. Convergence was achieved in key ensemble properties with a feasible number of stochastic particles and in reasonable CPU time. A hot wall reactor experiment producing TiO_2 particles from TTIP precursor was simulated. Under the simulated conditions, the chosen chemical mechanism and collision species gave incomplete conversion to TiO_2 . Nevertheless, the simulated PSD was observed to be sensitive to the coagulation efficiency and the critical sintering diameter.

In order to develop our understanding of the titania system and evaluate the performance of the model it is necessary to combine simulations with experiments. The high-dimensional nature of the model and use of the stochastic method requires a post-processing method to apply the detailed particle model to flame simulations where particle transport is considered. An existing post-processing method was found to be inadequate for stagnation flames due to the strong temperature gradient near the stagnation surface. Inspecting the model equations showed that the effect of thermophoresis could not be accounted for in the post-processing methodology. A thermophoretic correction was therefore introduced in Chapter 5 to address this problem. The thermophoretic correction was shown to improve the agreement between the particle number moments obtained from the post-processing step with those from a fully coupled simulation by orders of magnitude.

Finally, the new titanium dioxide particle model and post-processing methodology were combined with a detailed chemical mechanism for the thermal decomposition of TTIP and used to simulate a stagnation flame experiment. The experimental investigation included detailed characterisation of particle morphology. A comprehensive evaluation of the model against these experimental results and a parametric sensitivity study was performed in Chapter 6. The particle model permitted comparison of quantities obtained from experimental TEM images with identical quantities obtained from simulated TEM-style images. The model was found to give excellent agreement with experimental data and the work identified the importance of the form of the characteristic sintering time on the formation of nano-aggregates. Most importantly,

the study demonstrated the benefits of a detailed model framework that are not available with simpler models. For example, the ability to simulate quantities that are directly comparable with experimental measurements and the flexibility to study individual process sub-models.

7.2 Review and suggestions for future work

An immediate area for further work is further application of the particle model and stagnation flame methodology to simulate more experiments in order to improve and calibrate the model. Extension of the model and application to different systems should also be considered. Work is already being done in this area. The model was recently extended to investigate the formation of the anatase and rutile crystal phases in flames [111]. The detailed titania model is also being applied in simulations of the synthesis of titanium dioxide in industrial reactors [20]. Moreover, the model framework and post-processing methodology has been used to study formation of soot in stagnation flames [73].

Over the course of this work and in the process of reviewing it, a few areas for development of the particle model were identified. The sections below take a critical look at those areas and make suggestions for further improvement of the model.

7.2.1 Improving the particle model

The new detailed particle model introduced in Chapter 4 is built on two key assumptions:

- 1. Neck cross-sections are circular;
- 2. Neighbours are determined by the binary tree connectivity.

In addition, the implementation of the model inherited the binary tree data structure from the existing framework. This relates to the second assumption. Despite offering computational efficiencies, it is clear that the binary tree cannot represent all particle structures and a different method of storing primary connectivity information should be implemented.

Furthermore, exact methods for calculating the volumes and surface areas of a collection of spheres with multiple overlaps exist [26]. Implementation of such a method would remove the first assumption. This is particularly important for dense aggregates composed of many primaries. However, the computational expense of such a method should be carefully considered.

7.2.2 Extending the particle model

The possibility of extending the type space composition variable was briefly discussed in Section 4.3.1. For instance, to model the crystal phase composition of particles. This could be as simple as tracking the number of anatase and rutile units in a primary and adding a phase transformation process to the model. Alternatively, if the importance of oxidation state is being investigated, as in [111], the primary composition can be further decomposed into the number of Ti and O atoms in each phase. A similar approach was taken by Shekar et al. [156] to model silica, where the number of Si, O and OH groups was important.

A potential consideration is further extension of the model to include another layer of depth, for example, by including a description of the crystal grain structure within each primary particle. An analogous approach has been taken for soot through the development of the PAH-PP model by Sander et al. [149], which incorporates a detailed description of the PAH composition of each primary particle. In the model, the structure and growth of individual PAHs is described by a kinetic Monte-Carlo aromatic site (KMC-ARS) model [31, 143]. Before embarking on such an approach, it is first important to improve and calibrate the current model and build up an understanding of its limitations. The utility of incorporating additional detail should be determined first with investigations using simple extensions of the type space, as discussed in the previous paragraph, to avoid incorporating unnecessary complexity.

7.2.3 The value of a detailed model

As well as improving and extending the particle model it is also important to ask how much detail is enough or even too much. Future work should think carefully about the desired degree of detail and balance this with a consideration of computational expense and the feasibility of coupling the particle model to the rest of the system being studied i.e. the chemical, reactor and flow models. Particularly important is developing an understanding of the actual accuracy gained from a detailed particle description when considered in conjunction with approximations necessary to implement it. For instance, Chapter 5 developed a post-processing method to introduce a detailed particle model to the modelling of nano-aggregates in a stagnation flame. While this increased the degree of detail in the simulations, it also introduced new sources of error and uncertainty. Such as the one-way coupling to the gas-phase in the second step, which assumes that the effect of the particles is already accounted for by the simple particle model used in the first step, and the inability to account for all transport effects in the second step; namely, diffusion.

The first, fully-coupled simulation step is also not without uncertainties, for example, inherent assumptions and approximations in the method of interpolative closure, the pseudo

one-dimensional flow approximation, and the simple particle model etc. These errors are propagated into the results of the second simulation. An earlier discussion warned of using an over-simplified model to interpret experimental data; it also worth warning of the risk of increasing the apparent level of detail without actually improving accuracy. In certain circumstances, simpler models, which are easier to apply, may be adequate for a particular investigation. Future work should focus on further understanding and reducing sources of uncertainty in the methodology (as was done with the introduction of the thermophoretic correction in Chapter 5). Equally important is to improve and calibrate the individual submodels – the gas-phase chemistry and particle processes – ideally using simple test cases that reduce the need to introduce approximations and assumptions into the simulation.

Often the application of a model and comparison with experimental data involves some degree of parameter fitting. This, however, should be done with caution. The uncertainty in a fitted parameter obtained from a complex simulation, involving many coupled models, can be substantial. Moreover, the specific value of a fitted parameter may only be appropriate to the particular system and conditions being simulated. What is more useful, in the author's opinion, are sensitivity studies used to understand the influence of model parameters and the importance of individual processes on particle evolution. Such studies can be used to test hypotheses and direct subsequent modelling efforts with model refinement or even simplification where appropriate.

That is not to say that parameter fitting is unnecessary, just that the value assigned to a parameter be treated with caution. In fact, most important in developing a detailed model for the formation of titanium dioxide is evaluation and calibration of the process models against experimental data. A model is of little use if the relative rates of competing processes are incorrect and do not accurately represent the morphological evolution of a particle. Future work should attempt to focus on individual processes and ensure that they are correctly calibrated. Of course, the difficulty is in obtaining experimental data to calibrate against because it is difficult to study individual processes in isolation.

Gas-phase chemistry

It is worth briefly touching on the gas-phase chemical reaction models used in this thesis. In particular, the TTIP decomposition model and choice of collision species for particle inception and growth processes. In this thesis, $Ti(OH)_4$, the main decomposition product in the mechanism of Buerger et al. [23] was used as the collision species. The stagnation flame simulations showed near complete conversion of TTIP to TiO_2 and the study in Chapter 6 showed that the final PSDs were largely insensitive to the efficiencies of the inception and growth processes, suggesting that the choice of $Ti(OH)_4$ was appropriate and adequate.

Recent work by shows Ershov et al. [47] suggests that other pathways, not considered in [23], are also important. Thus, further investigation and development of the model, in particular, a study of particle evolution in the combustion zone, should consider updated chemistry and explore the involvement of other gas-phase species in particle inception and growth processes. This is particularly important given the incomplete conversion of TTIP to TiO₂ particles observed in the hot-wall reactor simulations of Chapter 4.

One advantage of using detailed chemistry, as opposed to a simple one-step reaction, is the ability to test a variety of particle inception and growth mechanisms. For example, the importance of different gas-phase species, as mentioned above, or more complex growth reactions. The TiCl₄ model in Chapter 3 considered a very simple single step growth reaction. Earlier work by Shirley et al. [158] suggested an Eley-Rideal model is appropriate. The detailed model framework with detailed chemistry would allow these to be explored.

Appendix A

Collaboration in this thesis

Elements of this thesis form part of a collaborative effort with Manoel Manuputty to investigate the formation of titanium dioxide nano-aggregates through a combination of experiments and simulations. Specifically, the aim was to simulate the formation of TiO_2 aggregates in a stagnation flame experiment using a detailed particle model. This is done in Chapter 6 using the model and methods developed by the author in Chapters 4 and 5.

The investigation presented in Chapter 6 was designed in collaboration. The following elements of the investigation were performed by Manoel Manuputty:

- The experimental work (previously published in [110]).
- The work associated with the first simulation step i.e. the fully coupled simulation with gas-phase chemistry, flow model and spherical particle model solved using method of moments with interpolative closure (MoMIC), based on the framework published in [108].
- Development of the image analysis script (for the previous experimental investigation [110]).
- Creation of plotting scripts for figures with experimental data: Fig. 6.3, Fig. 6.4, Fig. 6.6, Fig. 6.7, Fig. 6.8, Fig. 6.9, Fig. 6.11a, Fig. 6.11b, Fig. D.2, Fig. D.3, Fig. D.4 and Fig. D.5.

In addition, Manoel Manuputty also performed the first-step simulations used in Chapter 5. The second simulation (the detailed model post-process), sensitivity study with focus on the sintering parameters, which are solely a component of the detailed particle model, and the write-up presented in Chapter 6 were done by the author.

Appendix B

Algorithms

B.1 Direct simulation Monte-Carlo

The direct simulation algorithm discussed in Section 2.2.2 is presented in Algorithm 2. The Linear Process Deferment Algorithm (LPDA) [137] is employed for all single particle processes, for example, sintering, surface growth and condensation. The majorant kernel and fictitious jumps, and ensemble contractions and doublings are performed as discussed in Section 2.2.2. The method of selecting particles is discussed by Patterson et al. [138].

*/

*/

```
Algorithm 2: Direct simulation Monte-Carlo.
Input: State of system Q_0 at t_0; Final time t_f.
Output: State of system Q_f at t_f.
begin
    Q \leftarrow Q_0;
    t \leftarrow t_0;
    while t < t_f do
         Calculate total rate of non-deferred processes:
                                              R_{\rm tot}(Q) = \sum_m R_m(Q),
         with m \in \{\text{inc}, \text{cg}\} and where R_{\text{cg}} = \hat{R}_{\text{cg}}(Q);
         Calculate an exponentially distributed waiting time:
                                                   \tau = -\frac{\ln U}{R_{\rm tot}},
         where U is a uniformly distributed random variable, U \in [0, 1];
         Select a process with probability:
                                                P(m) = \frac{R_m(Q)}{R_{\rm tot}(Q)};
         if m = \text{inc then}
              /* This is an inception event
              Create a new particle P_N and add it to the ensemble;
              if N > N_{\text{max}} then
                  Uniformly remove a particle;
                  Contract ensemble;
              end
         else
              /* This is a coagulation event
              Select two particles P_q and P_r;
              Calculate majorant for two particles: \hat{K}_{cg}^{tr}(P_q, P_r);
              Perform deferred processes for P_q and P_r;
              Calculate true kernel for the two particles: K_{cg}^{tr}(P_q, P_r);
              With probability
                                                  P = \frac{K_{\rm cg}^{\rm tr}(P_q, P_r)}{\hat{K}_{\rm cg}^{\rm tr}(P_q, P_r)},
               perform BCCA coagulation: P_q + P_r \rightarrow P_s;
              if N < N_{\rm max}/2 then
                  Double the ensemble;
              end
         end
         t \leftarrow t + \tau;
    end
    Perform deferred processes for all particles;
```

return Q

end

B.2 Detailed particle model algorithms

Algorithms for the particle process models developed in Chapter 4 are described here.

B.2.1 Ballistic cluster-cluster aggregation

The implementation of the ballistic cluster-cluster aggregation with a random impact parameter (BCCA) described by Jullien [81] is shown in Algorithm 3. Particle rotations are performed using the method proposed by Arvo [8] and particle bounding spheres are calculated using the method proposed by Ritter [146]. Sphere point picking is performed as per Weisstein [179]. Note: ϕ is the azimuthal angle and θ is the polar angle.

B.2.2 Diffusion limited cluster aggregation

The implementation of diffusion limited cluster aggregation is shown in Algorithm 4. Particle rotations are performed using the method proposed by Arvo [8] and particle bounding spheres are calculated using the method proposed by Ritter [146]. The Brownian step size is taken as the average primary diameter \overline{d}_p , and the collision is deemed to fail if the particle separation exceeds twice the sum of the bounding sphere radii. Sphere point picking is performed as per Weisstein [179]. Note: ϕ is the azimuthal angle and θ is the polar angle.

B.2.3 Surface adjustment

A surface adjustment as a results of a condensation event is performed according to Algorithm 5. Note that we assume a primary is composed solely of discrete units of TiO_2 . Therefore, a redistribution of composition (mass) between primaries only takes place if the volume change of the neighbour is sufficiently large. This can lead to some deviation between the volume derived from the composition

$$v_i = \frac{\eta_{\text{TiO}_2,i} M_{\text{TiO}_2}}{\rho_{\text{TiO}_2} N_{\text{A}}},\tag{B.1}$$

and the volume derived from the primary geometry

$$v_i = \frac{4}{3}\pi r_i^3 - \frac{1}{3}\pi \sum_j (2r_i^3 + x_{ij}^3 - 3r_i^2 x_{ij}).$$
(B.2)

The system, however, is to some extent self-correcting due to two processes. First, the movement of a neck during a surface adjustment will to a certain degree be offset by an opposing change during a possible future surface adjustment to the other primary. Second, the need to redistribute mass is eliminated by the merger of the two primaries during a coalescence event. Furthermore,

the likelihood of the primaries coalescing is increased with more surface growth of one primary at the expense of the other.

B.2.4 Sintering

Sintering is performed on a particle P_q using Algorithm 6. Where two primaries are in point contact (i.e. their neck area is $A_{n,ij} = 0$) the sintering rate is undefined. In this case, we assume a neck radius of 1% of the smaller primary radius, $a_{ij} = \min(r_i, r_j)/100$.

B.2.5 Coalescence

Neighbouring primaries p_i and p_j in a particle P_q are merged according to Algorithm 7, once the sintering level (Eq. (4.36)) exceeds $s_{ij} \ge 0.95$. The sintering level is defined while the neck remains between the primary particle centres and the primaries are merged if the neck leaves this region. Algorithm 3: Ballistic cluster-cluster algorithm with a random impact parameter.

Input: Particles P_q and P_r chosen for coagulation.
Output: Daughter particle P_s .
begin
Randomly rotate P_q and P_r around their centres of mass (using [8])
Calculate the bounding spheres $r_b(P_q)$ and $r_b(P_r)$ (using [146])
Centre the bounding spheres at the origin
repeat
/* Determine random trajectory */
Uniformly select a point $G_1(\theta, \phi)$ on a unit sphere (using [179]):
$\phi = 2\pi U$ and $\theta = \arccos(2U-1)$,
where U is a uniformly distributed random variable:
Construct a rotation matrix B that rotates the vector $(0, 0, -1)$ to the point G_1 :
/* Determine random impact parameter */
Uniformly select a point:
$G_2 = (R\sqrt{r}\cos\theta, R\sqrt{r}\sin\theta, -R),$
on a disk of radius $R = r_b(P_q) + r_b(P_r)$ centred on $(0,0,-R)$ in the $z = -R$ plane with $r = U$, and $\theta = 2\pi U$, where U is a uniformly distributed random variable;
/* Set initial positions */
Apply the rotation to G_2 giving a new point $G_3 = \mathbf{R}G_2$;
Place particle P_r at point G_3 ;
Place particle P_q at $O = (0,0,0)$;
/* Perform the collision */
while No point of contact do
Translate P_r along a vector parallel to G_1O by distance $R/100$;
Check for contact;
if P_r has passed through the bounding sphere of P_q then
/* This is an unsuccessful collision */
Break;
end
end
if Single point of contact then
/* This is a successful collision */
New particle P_s created by connecting the binary trees of P_q and P_r at a new
head node;
Contacting primaries p_i and p_j connected at the new head node;
$ $ return New particle P_s
end
until Successful collision
end

Algorithm 4: Diffusion limited cluster aggregation algorithm.

Input: Particles P_q and P_r chosen for coagulation. **Output:** Daughter particle P_s . begin Randomly rotate P_q and P_r around their centres of mass (using [8]) Calculate the bounding spheres $r_b(P_q)$ and $r_b(P_r)$ (using [146]) Centre the bounding spheres at the origin repeat /* Determine random trajectory */ Uniformly select a point on a sphere $G_1(R, \theta, \phi)$ (using [179]), with: $\phi = 2\pi U$ and $\theta = \arccos(2U-1)$, where U is a uniformly distributed random variable; and $R = r_{\rm b}(P_q) + r_{\rm b}(P_r)$; /* Set initial position of P_r */ Place P_r at $G_1(R, \theta, \phi)$; /* Brownian steps of size $\overline{d}_{p}(P_{r})$ while No point of contact do Generate a random trajectory $G_2(\Delta x, \Delta y, \Delta z)$: $\Delta x = \overline{d}_{p} \cos \phi \sin \theta, \quad \Delta y = \overline{d}_{p} \sin \phi \sin \theta, \quad \Delta z = \overline{d}_{p} \cos \theta,$ with $\phi = 2\pi U$ and $\theta = \arccos(2U-1);$ Translate P_r along the random trajectory G_2 ; Check for contact; if Separation of P_r and P_q is greater than 2R then /* This is an unsuccessful collision */ Break; end end if Single point of contact then /* This is a successful collision */ New particle P_s created by connecting the binary trees of P_q and P_r at a new head node: Contacting primaries p_i and p_j connected at the new head node; return New particle Ps end until Successful collision end

Algorithm 5: Surface growth

Input: Particle P_q ; Number of units of TiO₂ added $\Delta \eta$ **Output:** Particle *P_q* begin Select a primary p_i in particle P_q with probability $P(p_i) = \frac{A_i}{\sum_{i=1}^{n_p(P_q)} A_i};$ Save old volume and radius: $v_{i,old} \leftarrow v_i$ and $r_{i,old} \leftarrow r_i$; Update primary composition: $\eta_i \leftarrow \eta_i + \Delta \eta$; Calculate new volume, v_i ; while $v_{i,old} < v_i$ do /* Primary radius increased in 1% increments */ $\Delta r \leftarrow r_i/100;$ $\Delta v \leftarrow A_i \Delta r;$ if $v_{i,old} + \Delta v > v_i$ then $\Delta r \leftarrow \frac{(v_i - v_{i,\text{old}})}{\Delta v} \Delta r;$ end Increase radius: $r_i \leftarrow r_i + \Delta r$; Update free surface area, A_i ; $v_{i,\text{old}} \leftarrow v_{i,\text{old}} + \Delta v;$ end /* Redistribution of composition between neighbours */ foreach Neighbour p_i of p_i do Estimate change in volume of p_i : $\Delta v_j \leftarrow -A_{\mathrm{n},ij} \frac{r_{i,\mathrm{old}}}{d_{i\,i}} \left(r_i - r_{i,\mathrm{old}}\right);$ Calculate (integer) change in composition of p_i : $\Delta \eta_j \leftarrow \frac{\Delta v_j}{M_{\rm TiO_2}/(\rho_{\rm TiO_2}N_{\rm A})},$ rounded down to the nearest integer; if $|\Delta \eta_i| > 0$ then Update the composition of p_i : $\eta_i \leftarrow \eta_i + \Delta \eta_i$; Update the composition of p_i : $\eta_i \leftarrow \eta_i - \Delta \eta_j$; end end return P_q end

Algorithm 6: Sintering

Input: Particle P_q ; Time to sinter particle t_s **Output:** Particle P_q begin **foreach** Neck between two primaries p_i and p_j in particle P_q do $\Delta d_{ij,\max} \leftarrow d_{ij}/100;$ $t \leftarrow 0$; while $t < t_s$ do Calculate sintering rate: $\frac{dd_{ij}}{dt}$ (Eq. (4.26)); Calculate time step: $\Delta t \leftarrow \frac{\Delta d_{ij,\max}}{\frac{\mathrm{d}d_{ij}}{\mathrm{d}t}};$ if $t_s > t + \Delta t$ then $\lambda \leftarrow 100;$ else $\lambda \leftarrow 100 \frac{(t_{\text{sint}} - t)}{\Delta d_{ii} \max} \frac{\mathrm{d} d_{ij}}{\mathrm{d} t};$ end Generate a Poisson random variate *X* with mean λ ; Calculate change in separation: $\Delta d_{ij} = -\frac{X}{100} \Delta d_{ij,\max};$ $\Delta \mathbf{d}_{ij} = -\Delta d_{ij} \frac{\mathbf{x}_j - \mathbf{x}_i}{|\mathbf{x}_i - \mathbf{x}_i|};$ Adjust centre to centre separation: $d_{ij} \leftarrow d_{ij} + \Delta d_{ij}$; /* Only need to adjust the coordinates of primaries on one side of the neck, in this case p_i . */ Translate primary p_i : $\mathbf{x}_i \leftarrow \mathbf{x}_i + \Delta \mathbf{d}_{ii}$; Translate neighbours $(p_i; p_j; \Delta \mathbf{d}_{ij});$ Compute change in radii using Eq. (4.35): Δr_i and Δr_i ; Adjust connectivity $(p_i; p_j; \Delta r_i);$ Adjust connectivity $(p_i; p_i; \Delta r_i);$ Update primary radii: $r_i \leftarrow r_i + \Delta r_i$ $r_j \leftarrow r_j + \Delta r_j$ Update properties of primaries p_i and p_i ; $t \leftarrow t + \Delta t$; if Coalescence condition is met then Merge primaries p_i and p_j ; Break; end end end end

end

Algorithm 6: Sintering Cont.

/* Translates all the neighbours of a primary p_i by Δd_{ii} , except for neighbour p_i */ **Function** Translate neighbours (Primary p_i ; Neighbour p_j ; Translation $\Delta \mathbf{d}$) **foreach** Neighbour p_k of p_i , except for primary p_j **do** Translate p_k by $\Delta \mathbf{d}$; $\mathbf{x}_k \leftarrow \mathbf{x}_k + \Delta \mathbf{d};$ /* Recursively translate the neighbours of p_k , except for primary p_i */ Translate neighbours (Primary p_k ; Neighbour p_i ; Translation $\Delta \mathbf{d}$); end /* Update centre to centre separations and coordinates of neighbours p_k of primary p_i except for neighbour p_i */ **Function** Adjust connectivity (Primary p_i ; Neighbour p_j ; Δr_i) **foreach** Neck between primary p_i and neighbour p_k , except for primary p_j **do** Calculate change in separation (Eq. (4.31)): $\Delta d_{ik} = \frac{r_i}{x_{ik}} \Delta r_i;$ $\Delta \mathbf{d}_{ik} = \Delta d_{ik} \frac{\mathbf{x}_k - \mathbf{x}_i}{|\mathbf{x}_k - \mathbf{x}_i|};$ Translate neighbour to update centre to centre separation: $d_{ik} \leftarrow d_{ik} + \Delta d_{ik};$ $\mathbf{x}_k \leftarrow \mathbf{x}_k + \Delta \mathbf{d}_{ik};$ Translate neighbours (Primary p_k ; Neighbour p_i ; Translation $\Delta \mathbf{d}_{ik}$);

Algorithm 7: Merger

Input: Particle P_q ; Primaries p_i and p_j to merge **Output:** Particle P_q with merged primary $p_{i,\text{new}}$ /* We assume that p_i is the larger primary: $r_i > r_j$ */ begin Solve Eq. (4.38) for the new merge primary radius of $r_{i,\text{new}}$; Update the composition of p_i : $\eta_{i,\text{new}} = \eta_i + \eta_j$; **foreach** Neck between p_i and neighbour p_k except p_j **do** $x_{ki} = \frac{d_{ik}^2 - r_i^2 + r_k^2}{2d_{ik}};$ $\Delta d_{ik} = \max\left(x_{ki} \pm \sqrt{x_{ki}^2 - r_k^2 + r_{i,\text{new}}}\right) - d_{ik};$ $\Delta \mathbf{d}_{ik} = \Delta d_{ik} \frac{\mathbf{x}_k - \mathbf{x}_i}{|\mathbf{x}_k - \mathbf{x}_i|};$ Translate neighbour p_k : $d_{ik} \leftarrow d_{ik} + \Delta d_{ik};$ $\mathbf{x}_k \leftarrow \mathbf{x}_k + \Delta \mathbf{d}_{ik};$ Translate neighbours (Primary p_k ; Neighbour p_i ; Translation $\Delta \mathbf{d}_{ik}$); /* The function Translate neighbours is defined in Algorithm 6 */ end **foreach** Neck between p_i and neighbour p_l except p_i **do** $x_{lj} = \frac{d_{jl}^2 - r_j^2 + r_k^2}{2d_{jl}};$ $\Delta d_{il} = \max\left(x_{lj} \pm \sqrt{x_{lj}^2 - r_l^2 + r_{i,\text{new}}}\right) - d_{il};$ $\Delta \mathbf{d}_{il} = \Delta d_{il} \frac{\mathbf{x}_l - \mathbf{x}_i}{|\mathbf{x}_l - \mathbf{x}_i|};$ Translate neighbour p_l : $d_{il} \leftarrow d_{il} + \Delta d_{il};$ $\mathbf{x}_l \leftarrow \mathbf{x}_l + \Delta \mathbf{d}_{il};$ Translate neighbours (Primary p_l ; Neighbour p_j ; Translation $\Delta \mathbf{d}_{il}$); end $r_i \leftarrow r_{i,\text{new}};$ Remove primary p_i and restructure binary tree ; Update particle properties;

return P_q

B.3 TEM images

A simulated TEM-style image is produced using Algorithm 8.

Algorithm 8: TEM images

```
Input: Ensemble Q; Frame size 2x_{max} \times 2y_{max}; Particles per frame N; Number of
        images n_{\rm f}
Output: n<sub>f</sub> TEM images
begin
    for n<sub>f</sub> frames do
        for N particles do
            Uniformly select a particle P_q from ensemble Q;
            Randomly rotate P_q around its centres of mass using the method described by
             Arvo [8];
            Generate (x, y) coordinates uniformly in the image plane with
              -x_{\max} \le x \le x_{\max} and -y_{\max} \le y \le y_{\max};
            Position P_q in the image plane with its centre of mass at (x, y);
            Project P_q into the image plane;
            Remove P_q from the ensemble;
        end
    end
end
```

Appendix C

Appendix to Chapter 4

C.1 BCCA with uniform particle selection

A test case was created in which particles are uniformly selected for collision from the particle ensemble. The test case was initialised with a population of 4096 monodisperse spherical particles with diameter $d_p = 1.81$ nm. The simulation was repeated 8 times producing a total of 16667 particles with a median of 172 primaries per particle.

The data and a least squares fit to a subset of the data with $n_p \ge 16$ are shown in Fig. C.1a. Figure C.1b shows how the fitted values of D_f and k_f vary as function of the minimum number of primaries per aggregate $n_{p,min}$. Both D_f and k_f display similar behaviour with respect to $n_{p,min}$ as the free-molecular case.

The fractal dimension D_f obtained in Fig. C.1a ($D_f = 1.91 \pm 0.01$) is in good agreement with the value obtained by free-molecular collisions and the values reported by Jullien [81] and Eggersdorfer and Pratsinis [42]. The fractal prefactor, however, is lower ($k_f = 1.19 \pm 0.03$) than that obtained by selection based on the free-molecular kernel in Section 4.4.1.

C.2 Diffusion Limited Cluster Aggregation

Diffusion limited cluster aggregation is simulated using the algorithm described in Appendix B.2.2. A simple test case was created to determine the average fractal dimension generated by the algorithm. A zero-dimensional batch reactor was simulated with an initial population of 4096 monodisperse spherical particles with diameter $d_p = 1.81$ nm (corresponding to 100 units of rutile). Particles were allowed to coagulate in the slip-flow regime with no other processes turned on and the simulation was repeated 8 times.



Fig. C.1 BCCA with uniform selection of particles for collision. (a): estimate of fractal dimension and prefactor by least squares fit to aggregates with $n_p \ge 16$; the result reported by Eggersdorfer and Pratsinis [42] is included for reference; error bars indicate the confidence interval with P = 0.999. (b): fractal dimension and prefactor as a function of $n_{p,min}$ with P = 0.999 confidence intervals. The error bars increase with increasing $n_{p,min}$ due to the smaller sample size.



Fig. C.2 DLCA with particle selection based on the slip-flow kernel. (a) estimate of fractal dimension and prefactor by least squares fit to aggregates with $n_p \ge 16$; the result reported by Eggersdorfer and Pratsinis [42] is included for reference; error bars indicate the confidence interval with P = 0.999. (b) fractal dimension and prefactor as a function of $n_{p,min}$ with P = 0.999 confidence intervals. The error bars increase with increasing $n_{p,min}$ due to the smaller sample size.

The fractal dimension D_f and pre-factor k_f were estimated by fitting the standard fractal relationship to the data as described for BCCA in Section 4.4.1. The data and a least squares fit to a subset of the data (particles with $n_p \ge 16$) are shown in Fig. C.2a. Figure C.2b shows how the fitted values of D_f and k_f vary as function of the minimum number of primaries per aggregate $n_{p,min}$ included in the fit. Sensitivity to $n_{p,min}$ is not observed in Fig. C.2b due to the tighter clustering of the simulation data compared to the BCCA case. Very few particles with $n_p < 16$ are observed.

The values obtained in Fig. C.2a ($D_f = 1.81 \pm 0.02$ and $k_f = 1.29 \pm 0.07$) are in good agreement with the results reported by Eggersdorfer and Pratsinis [42] ($D_f = 1.79 \pm 0.03$ and $k_f = 1.40 \pm 0.12$) and Jullien et al. [82] ($D_f = 1.78 \pm 0.05$, k_f not reported).

C.3 Growth model equations for 1D and 2D particle models

C.3.1 Constant growth

Spherical particle

For a constant rate of growth β , the time evolution of the particle volume is

$$V(t) = \beta t + V_0, \tag{C.1}$$

and the surface area and radius of a single sphere are:

$$S(t) = 4\pi \left(\frac{3}{4\pi} \left(\beta t + V_0\right)\right)^{2/3},$$
 (C.2)

$$r(t) = \left(\frac{3}{4\pi}(\beta t + V_0)\right)^{1/3}.$$
 (C.3)

Spherical primaries in point contact

 $n_{p,0}$ primaries of radius $r_{p,0}$ are assumed to remain in point contact during growth. The surface area and primary radius evolve according to:

$$S(t) = 4\pi n_{\rm p,0} \left(\frac{3}{4\pi n_{\rm p,0}} \left(\beta t + V_0\right)\right)^{2/3},\tag{C.4}$$

$$r_{\rm p}(t) = \left(\frac{3}{4\pi n_{\rm p,0}} \left(\beta t + V_0\right)\right)^{1/5},\tag{C.5}$$

where the initial aggregate volume and surface area are:

$$V_0 = \frac{4}{3}\pi r_{\rm p,0}^3 n_{\rm p,0},\tag{C.6}$$

$$S_0 = 4\pi r_{\rm p,0}^2 n_{\rm p,0}.$$
 (C.7)

C.3.2 Collision limited growth

Assuming a collision limited, condensation-like growth process in the free-molecular regime, the growth rate is (*cf.* Eq. (4.17))

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \beta r_{\mathrm{c}}^2,\tag{C.8}$$

for some constant β and where r_c is the collision radius.

The model equations for three simple models are given below: a spherical particle model, and a surface-volume model with and without particle rounding. The latter case corresponds to $n_{p,0}$ primary particles that remain in point contact.

Spherical particle

A spherical particle with collision radius equal to the spherical radius grows as

$$r = r_0 + \frac{\beta}{4\pi}t,\tag{C.9}$$

where r_0 is the initial radius of the spherical particle.

Surface-volume model without rounding

The initial volume and surface area are given by Eqs. (C.6) and (C.7), and the collision radius [114] is

$$r_{\rm c} = r_{\rm p} n_{\rm p}^{1/D_{\rm f}}.$$
 (C.10)

Equation C.8 is integrated to give the time evolution of the primary diameter

$$r_{\rm p} = r_{\rm p,0} + \frac{\beta}{4\pi} n_{\rm p}^{2/D_{\rm f}-1} t,$$
 (C.11)

from which the surface area and volume can be derived.

Surface-volume model with rounding

A two-dimensional surface-volume model is considered. The average primary radius and number of primaries are [136]:

$$r_{\rm p} = \frac{3V}{S},\tag{C.12}$$

$$n_{\rm p} = \frac{S^3}{36\pi V^2},\tag{C.13}$$

and the collision radius is given by Eq. C.10, which is expressed in terms of the surface area and volume: 1/p

$$r_{\rm c} = \frac{3V}{S} \left(\frac{S^3}{36\pi V^2}\right)^{1/D_{\rm f}}.$$
 (C.14)

Rounding is treated as per Patterson and Kraft [136]:

$$\frac{\mathrm{d}S}{\mathrm{d}V} = 4\left(\frac{\pi}{S}\right)^{1/2}.\tag{C.15}$$

Finally, the model equations for the particle volume and surface area can be expressed as

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \beta \left(\frac{3V}{S} \left(\frac{S^3}{36\pi V^2}\right)^{1/D_{\mathrm{f}}}\right)^2,\tag{C.16}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}S}{\mathrm{d}V}\frac{\mathrm{d}V}{\mathrm{d}t},\tag{C.17}$$

$$=4\beta \left(\frac{\pi}{S}\right)^{1/2} \left(\frac{3V}{S} \left(\frac{S^3}{36\pi V^2}\right)^{1/D_{\rm f}}\right)^2.$$
(C.18)

C.3.3 Surface area dependent growth

A growth rate proportional to the particle surface area is assumed:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \beta S,\tag{C.19}$$

for some constant β . The model equations are given for the same three particle models as in the previous case of collision limited growth.

Single sphere

The radius of single spherical particle evolves as

$$r = r_0 + \beta t, \tag{C.20}$$

where r_0 is the initial particle radius.

Surface-volume model without rounding

For primary particles in point contact the primary radius evolves as

$$r_{\rm p} = r_{\rm p,0} + \beta t. \tag{C.21}$$

Surface-volume model with rounding

The average primary radius and number of primaries are given by Eqs. (C.12) and (C.13). The model equations are

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \beta S,\tag{C.22}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = 4\beta\sqrt{\pi S},.\tag{C.23}$$

These equations can be solved analytically:

$$V = \frac{1}{6\sqrt{\pi}} \left(2\sqrt{\pi}\beta t + 2\sqrt{\pi n_{\rm p,0}}r_{\rm p,0} \right)^3 + \frac{4}{3}\pi r_{\rm p,0}^3 \left(n_{\rm p,0} - n_{\rm p,0}^{3/2} \right), \tag{C.24}$$

$$S = \left(2\sqrt{\pi}\beta t + 2\sqrt{\pi n_{\rm p,0}}r_{\rm p,0}\right)^2.$$
 (C.25)

C.4 Sintering model equations for a 2D particle model

The model of Koch and Friedlander [89] describes the decay in excess surface area over that of a sphere of the same mass:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{1}{\tau_{\mathrm{s}}} \left(S - S_{\mathrm{sph}} \right),\tag{C.26}$$

where S is the surface area of the particle, S_{sph} is the surface area of a sphere with same mass, and τ_s is the characteristic sintering time. The equations for implementation in a surface-volume particle model are given below. Two variations are considered: a constant and a time dependent characteristic sintering time. Sintering is assumed to progress by grain boundary diffusion with characteristic sintering time

$$\tau_{\rm s} = \kappa r_{\rm p}^4. \tag{C.27}$$

In the time dependent case, the primary radius is allowed to evolve in time.

C.4.1 Surface-volume model with constant characteristic time

If the characteristic sintering time is kept constant $\tau_s = \kappa r_{p,0}^4$, where the radius is taken as the initial primary radius $r_{p,0}$, the surface area evolution is simply an exponential decay

$$S(t) = (S_0 - S_{\rm sph}) \exp\left(-\frac{t}{\tau_{\rm s}}\right) + S_{\rm sph}.$$
 (C.28)

The initial surface area and volume are

$$S_0 = 4\pi r_{\rm p,0}^2 n_{\rm p},\tag{C.29}$$

$$V_0 = \frac{4}{3}\pi r_{\rm p,0}^3 n_{\rm p},\tag{C.30}$$

and the final surface area is the area of a single sphere with the same volume

$$S_{\rm sph} = 4\pi \left(\frac{3V_0}{4\pi}\right)^{2/3}$$
. (C.31)

C.4.2 Surface-volume model with time dependent characteristic time

If the particle radius term in the characteristic time is allowed to evolve in time, $\tau_s = \kappa r_p^4(t)$, Eq. (C.26) is expressed as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{S^4}{81\kappa V_0^4} \left(S - S_{\mathrm{sph}}\right),\tag{C.32}$$

where we have used the relationship

$$r_{\rm p} = \frac{3V_0}{S},\tag{C.33}$$

to determine the primary radius [95]. Equation (C.32) is integrated numerically and the characteristic time is updated each time step.

C.5 Hot wall reactor simulations: comparison between BCCA and DLCA

Figure C.3 shows a comparison of the mobility diameter distributions obtained with a BCCA (coloured lines) and a DLCA (coloured open squares) collision model in simulations of the hot wall reactor experiment of Nakaso et al. [131]. Model parameters are the same as those presented in Section 4.6.2. Note the experimental (closed circles) and simulation results (black dotted line) from the original work of Nakaso et al. [131] are not relevant to the comparison made here. Figure C.3 shows no appreciable difference in the mobility diameter distributions obtained by BCCA and DLCA.



Fig. C.3 Aggregate mobility diameters obtained from projected area analysis of particles from simulations of the hot wall reactor experiment of Nakaso et al. [131]. Aggregate structures were formed by either DLCA (coloured open squares) or BCCA (coloured lines). The experimental (closed circles) and simulation results (black dotted line) from [131] are also shown.
Appendix D

Appendix to Chapter 6

D.1 Comparing characteristic sintering times



Fig. D.1 The normalised excess surface area as a function of dimensionless time for the sintering of two equal sized primaries evolving according to Eq. (D.1). An exponential decay is plotted for reference.

The sintering model equation (Eq. (6.11)) is expressed in terms of the dimensionless time:

$$\frac{\mathrm{d}x_{ij}}{\mathrm{d}t^*} = -\frac{d_{\rm p}^4}{16A_{{\rm n},ij}} \left(\frac{1}{r_i - x_{ij}} - \frac{1}{a_{ij}}\right),\tag{D.1}$$

where

$$t^* = \frac{t}{\theta}.\tag{D.2}$$

The evolution of the normalised excess surface area of two equal sized particles sintering according to Eq. (D.1) is plotted in Fig. D.1 as a function of t^* . Equation (D.1) was solved using the Euler method. The solution was found to be insensitive to the choice of initial primary diameter. An exponential decay, the solution to Eq. (6.6) assuming a constant characteristic time, is plotted for reference. The two models show quite different behaviour, particularly at early times. The primary separation based model used in this work predicts a reduction in excess surface area of 87% over its characteristic time θ compared to the 63% reduction of an exponential decay.

To facilitate comparison of characteristic sintering times typically used in surface area based models [89] with the primary separation based model used in this work, a consistent definition of the characteristic sintering time is needed. In this case, we extract a value for τ_s from Fig. D.1 for the sintering model used here. τ_s is defined as the time needed for the excess surface area of two equal sized primaries to decrease by 63% – consistent with Eqs. (6.7)–(6.9) [25, 88, 153]. For the primary separation based model used in this work,

$$\tau_{\rm s} = 0.14\theta. \tag{D.3}$$

D.2 Simulated flame profiles¹

A full description of the temperature measurements and simulated flame profiles is provided in [105]. In brief, the temperature measurements were used to estimate the point at which the temperature rises sharply for the lean ($\phi = 0.35$) flame and to adjust the boundary conditions in the first simulation (with the energy equation solved) to reproduce this. The comparison between the simulated temperature profile for this flame and the flame image showed that the simulated H peak coincides with the point at which the flame intensity is half of the maximum intensity. An arbitrary assumption is then made to use the same criteria to define the flame standing distance and to adjust the boundary conditions for all other cases because no temperature measurements for these cases are available. Furthermore, it is assumed that the addition of TTIP does not affect the flame standing distance due to the relatively small amount of TTIP used.



Fig. D.2 Calculated and imposed temperature profiles for $\phi = 0.35$ flames (a: 4 ml/h, b: 12 ml/h, c: 30 ml/h TTIP loading). The imposed temperature profile for 4 ml/h case is taken from experimental measurement (with no TTIP) while those for 12 ml/h and 30 ml/h cases are shifted by 70 and 200 K, respectively, similar to the shifts in the calculated maximum temperature profiles (arrows) to account for the additional heat release from TTIP combustion.

D.2.1 Temperature profile shape

Figure D.2 shows the measured and simulated temperature profiles for the lean flame ($\phi = 0.35$). A significant difference is observed in the profile shape and the maximum temperature. The origin of the discrepancy in the temperature profiles is unclear but a possible reason is the deviation from the one-dimensional stagnation flow solution. Another possible source of error in the temperature measurements is the catalytic reaction on the uncoated thermocouple surface. Catalytic heating is expected to affect the region near the flame front where there is more unreacted premixed gas [154]. This will result in artificially higher temperature estimates at the flame front. This can also explain the measured temperature that is slightly higher than the calculated adiabatic flame temperature.

D.2.2 Sensitivity to temperature profile and flame location

In order to understand the effect of the temperature profile uncertainties on the simulated particle properties, three parameters related to the experimental measurements are investigated in this work. These are the profile shape, flame standing distance, and surface temperature.

¹The temperature measurements and temperature profile simulations were performed by Manoel Manuputty and are described in [105]. Post-processing of the simulation results was performed by the author. A summary is given here due to its relevance in the quantification of the simulation uncertainties associated with the modelling work.

First, the effect of the temperature profile shape is assessed by comparing simulations with the calculated and the imposed temperature profiles. Figure D.2 shows the temperature profiles for the lean flames with varying TTIP loading rate. For the 4 ml/h TTIP loading rate case, the imposed temperature profile is assumed to be the same as the measured profile for the undoped flame (symbols in Fig. D.2). For the 12 and 30 ml/h cases, the temperature profiles are shifted upwards by 70 and 200 K, respectively, to account for the effect of TTIP combustion. These amounts of shift are approximately consistent with the shifts in the corresponding calculated temperature cases. The temperature profile shape does not seem to affect the flame standing distance. The imposed temperature simulations are only attempted for the lean flames ($\phi = 0.35$) because no temperature profile is available for the experimental profile in which the peak temperature is reached near the upstream edge of the flame.

Second, the effect of the flame distance is assessed by comparing simulations with varying flame distance (i.e. peak H concentration) by ± 0.2 mm. This is approximately the same as the experimentally observed fluctuation in the flame front. Finally, the effect of the surface temperature is assessed by comparing simulations with varying stagnation temperature by ± 50 K ($T_s = 503$ K for $\phi = 0.35$ and $T_s = 580$ K for $\phi = 1.67$ [110]). This uncertainty in the stagnation plate temperature comes from the fluctuation during experiment as well as a typical uncertainty for a K-type thermocouple.

Figure D.3 presents the changes in primary particle and aggregate properties for all conditions tested in this work with respect to the uncertainties in the three temperature profile parameters discussed above. The model parameters used in the simulation will be discussed further in Section 6.4.2. Several observations are made here. First, all of the particle properties are insensitive to the shape of the temperature profile (imposed *T* vs. calculated *T*). Second, the mean primary and aggregate diameters are only sensitive to the flame distance – primarily the lean flame with high TTIP loading. Meanwhile, the coefficients of variation show very little sensitivity in all cases. f_{α} shows the greatest degree of sensitivity across the temperature profile parameters F_d and T_s . Overall, the changes in particle sizes are less than 1 nm, except for the lean flame with 30 ml/h TTIP loading (less than 2 nm). The maximum changes for CV and f_{α} are 1% and 3%, respectively. This suggests that the particle properties are relatively insensitive to the temperature profile parameters. More importantly, the changes in Fig. D.3 give an indication of the degree of model prediction uncertainties carried forward from the uncertainties in experimental measurements feeding into the simulation, i.e. temperature and flame distance. These are referred to as the "simulation uncertainties".



Fig. D.3 The changes in particle descriptors as the temperature profile shape (refer to text), flame distance, F_d , and surface temperature, T_s , are varied against the base case (calculated temperature, flame distance z_0 , and surface temperature T_0) for all cases studied here. The particle descriptors are: (1) primary mean diameter, Δd_p , (2) primary coefficient of variation, ΔCV_p , (3) aggregate mean diameter Δd_a , (4) aggregate coefficient of variation, ΔCV_a , and (5) fraction of particles with circular projection, Δf_{α} . The perturbations Δ_z and Δ_T are 0.2 mm and 50 K, respectively.

D.3 Sensitivity to particle model parameters

D.3.1 Collision enhancement factor

The sensitivities of the primary and aggregate mean diameter and coefficient of variation (CV) to the collision enhancement factor ε are shown in Fig. D.4. ε is applied as a multiplicative factor to the free molecular kernels for all collision processes in the particle model; namely, inception, surface growth and coagulation. The enhancement factor is varied in the range: $\varepsilon = 2.2 - 3.0$. The base case value is taken as $\varepsilon = 2.64$ as per Manuputty et al. [108], based on the value calculated by Zhang et al. [196]. $\varepsilon = 2.2$ is the size-independent enhancement factor due to van der Waals forces calculated by Harris and Kennedy [66] for spherical soot particles. The morphological descriptors are not particularly sensitive over the range of ε studied. The mean primary and aggregate diameters show a slight increase with increasing ε , as would be expected from larger collision rates. The primary and aggregate CVs are largely insensitive to ε .



Fig. D.4 Sensitivity of the primary and aggregate mean diameter and coefficient of variation (CV) to the molecular enhancement factor ε for lean ($\phi = 0.35$, left panels) and rich ($\phi = 1.67$, right panels) flames. The shaded areas indicate estimated uncertainty bounds of the experimental measurements.

D.3.2 Titania density

Figure D.5 shows the sensitivity of the primary and aggregate mean diameter and coefficient of variation (CV) to the particle density: $\rho_{TiO_2} = 3.84 \text{ g/cm}^3$ (anatase) and $\rho_{TiO_2} = 4.25 \text{ g/cm}^3$ (rutile). It is important to note that we are actually imposing an effective ρ_{TiO_2} for particles of all sizes at all stages of evolution. Although the particles collected are anatase and rutile in the lean and rich flames respectively, the incipient particles are likely to have significantly lower density, which might affect the results. Overall, the descriptors are not very sensitive to the choice of density. As expected, a lower density (anatase) yields larger mean diameters.



Fig. D.5 Sensitivity of the primary and aggregate mean diameter and coefficient of variation to the particle density $\rho_{\text{TiO}_2} = 3.84 \text{ g/cm}^3$ (anatase, base case), 4.25 g/cm³ (rutile) for lean ($\phi = 0.35$, left panels) and rich ($\phi = 1.67$, right panels) flames. The shaded areas indicate estimated uncertainty bounds of the experimental measurements.

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