

Imperial College London
Department of Mechanical Engineering
Division of Thermofluids

Population Balance Modelling of Nanoparticle Formation in Laminar and Turbulent Flows

by
Malamas Tsagkaridis

Submitted for the degree of
Doctor of Philosophy
in Mechanical Engineering at Imperial College London

October 2022

Abstract

Nanoparticle formation in reacting flows involves many complex phenomena such as turbulence, chemical kinetics, aerosol processes, particle size distribution (PSD) evolution, etc. Simulations of such processes should incorporate several models and solution methods, while the quality of such simulations is subject to the uncertainties and assumptions involved in all of these elements. The main objective of the present work is to develop and employ accurate and comprehensive methodologies for simulating particle formation and flame synthesis in laminar and turbulent flows. While the applications of the proposed methodologies in the present study were primarily concerned with silica nanoparticles, they can easily be extended for the study of other nanomaterials.

In the first part of the present thesis, we propose a novel extended population balance equation (PBE) model for aggregation and sintering and couple it with computational fluid dynamics (CFD) to investigate synthesis of silica nanoparticles in a laminar diffusion flame. The extended PBE includes finite-rate sintering of primary particles by solving the PBE together with a transport equation for the number concentration of primary particles. In the process simulated, the particles are formed via the oxidation of a vapour precursor, HMDSO, and the aerosol processes include nucleation, condensation, aggregation and sintering. The model is validated with the detailed experimental *in-situ* SAXS data of Camenzind et al. (2008) for the S-2 flame and is also compared with a monodisperse and a two-PBE approach. Good agreement is found between the extended one-PBE and two-PBE models, while both of them provide a substantial improvement over the monodisperse one. Furthermore, the coupled CFD-PBE simulation with the extended one-PBE model reduces substantially the computational time as compared with the two-PBE model and requires less than twice the time needed for the monodisperse model. A very good agreement is found between numerical predictions and experimental data for temperature along the centreline and a reasonably good agreement is found between numerical predictions and SAXS data for primary particle diameters.

In the second part, the extended one-PBE model is incorporated into the Large-Eddy Simulation - Probability Density Function (LES-PDF) modelling framework to investigate synthesis of silica nanoparticles in a turbulent diffusion flame. The Eulerian stochastic field method is employed for solving the LES-PBE-PDF equations, characterising the influence of the unresolved sub-grid scale motions, and accounting for the complex interaction between turbulence, chemistry and particle dynamics. A different sub-grid mixing time scale is introduced to the

model to account for the low diffusivity of nanoparticles. The models for gas-phase chemistry and aerosol dynamics were the same as those used in the laminar-flame simulation. Thus, by maintaining the same kinetics without any adjustments, we focus on the modelling issues arising in silica synthesis in turbulent flames. Numerical predictions are compared with the detailed experimental *in-situ* SAXS data of Camenzind et al. (2008) for the S-10 flame. Good agreement is found between numerical predictions and experimental data for temperature along the centreline. However, the LES-PBE-PDF model underestimated the SAXS data for primary particle diameters by a factor of two. Possible reasons for this discrepancy are examined by leveraging knowledge acquired from our laminar-flame simulations. An investigation of the effect of particle sub-grid mixing is also conducted.

Finally, an investigation of turbulence-coagulation interaction via DNS coupled with PBE is presented in the third part of the thesis. Coagulation is an important process in several environmental and engineering applications involving turbulent flow, including soot formation and flame synthesis of nanoparticles, but its interaction with turbulence is not yet fully understood. Particle dynamics can be described by the PBE, whose Reynolds decomposition leads to unclosed terms involving correlations of number density fluctuations. In this work, we employ a discretisation (sectional) method for the solution of the PBE, which is free of *a priori* assumptions regarding the PSD, and couple it with a DNS for the flow field in order to study the behaviour and significance of the unknown correlations. At present, it is not feasible to resolve the Batchelor scales that result from diffusion at high Schmidt numbers; hence a unity Schmidt number is employed. The investigation is conducted on a 3-D planar jet laden with monodisperse nanoparticles, and coagulation in the free-molecule regime is considered. The correlations due to turbulent fluctuations of the particle number density are calculated at several points in the domain and found to be positive in most cases, except close to the jet break-up. The transport equation for the moments of the PSD is also studied, and it is found that the correlations make a considerable contribution to the time-averaged coagulation source term, up to 20% on the jet centreline and 40% close to the edges.

Acknowledgements

I would like to express my deepest appreciation to my supervisors, Dr Stelios Rigopoulos and Prof. George Papadakis, for supporting me throughout my PhD studies and offering me the opportunity to undertake this project. Their guidance, patience, and trust have been invaluable to me. I also wish to express my gratitude to Prof. William Jones for always being willing to share kindly his thoughts and experience. I gratefully acknowledge Prof. Sotiris E. Pratsinis for his help on the interpretation of the experimental results of Camenzind et al. (2008) and for insightful discussions on silica synthesis, as well as Dr Eirini Goudeli for her help on the verification of the monodisperse model.

Furthermore, I am grateful to my colleagues and friends at Imperial: Larry, Sun, Hin Yan, Tom, Tianjie, Danny, Stratos, Daniel, Andrea, and Nav (in the order we met) and all my other friends in London for the great time and discussions we had and for making the past few years so memorable. I am also thankful to my family for their love and support, especially during the COVID-19 pandemic.

I am grateful to the Leverhulme Trust for financial support (grant reference RPG-2018-101). This work used the ARCHER and ARCHER2 UK National Supercomputing Services (<https://www.archer2.ac.uk>) and I wish to acknowledge the UK Consortium on Turbulent Reacting Flows (www.ukctrf.com) for providing access to these facilities through EPSRC grant EP/R029369/1. I also acknowledge the UK Materials and Molecular Modelling Hub for computational resources on THOMAS and YOUNG, which is partially funded by EPSRC (EP/P020194/1 and EP/T022213/1).

Preface

Statement of originality

I hereby declare that the content of this thesis is original and constitutes the product of my own research unless otherwise acknowledged or referenced as appropriate. The work was conducted at Imperial College London from September 2018 to October 2022. This thesis has not been submitted in whole or in part for consideration for any other degree or qualification other than that of Doctor of Philosophy in Mechanical Engineering at Imperial College London.

Copyright declaration

The copyright of this thesis rests with the author. Unless otherwise indicated, its contents are licensed under a Creative Commons Attribution-Non Commercial 4.0 International Licence (CC BY-NC). Under this licence, you may copy and redistribute the material in any medium or format. You may also create and distribute modified versions of the work. This is on the condition that: you credit the author and do not use it, or any derivative works, for a commercial purpose. When reusing or sharing this work, ensure you make the licence terms clear to others by naming the licence and linking to the licence text. Where a work has been adapted, you should indicate that the work has been changed and describe those changes. Please seek permission from the copyright holder for uses of this work that are not included in this licence or permitted under UK Copyright Law.

Publications

Parts of this work have been published or submitted for publication:

- M. Tsagkaridis, S. Rigopoulos, and G. Papadakis. Analysis of turbulent coagulation in a jet with discretised population balance and DNS. *Journal of Fluid Mechanics*, 937(A25), 2022a.
- M. Tsagkaridis, S. Rigopoulos, and G. Papadakis. Modelling of silica synthesis in a laminar flame by coupling an extended population balance model with computational fluid dynamics. *Aerosol Science & Technology*, 57(4):296-317, 2023.
- M. Tsagkaridis, G. Papadakis, W. P. Jones, and S. Rigopoulos. Large-eddy simulation of turbulent flame synthesis of silica nanoparticles with an extended population balance model. *Flow, Turbulence and Combustion*, (in review), 2023.

Contents

Abstract	i
Acknowledgements	iii
Preface	v
1 Introduction	1
1.1 Background	1
1.2 Objectives and contributions	6
2 Modelling of aerosol synthesis in a laminar flame	9
2.1 Introduction	9
2.1.1 Literature review	9
2.1.2 Present investigation	13
2.2 Mathematical formulation	14
2.2.1 Reacting flow	14
2.2.2 Population balance	15
2.2.3 The monodisperse model	16
2.2.4 The two-PBE model for aggregation and sintering	17
2.2.5 A novel extended one-PBE model for aggregation and sintering	20
2.3 Numerical Methods	21
2.4 Gas-phase and aerosol kinetics	22
2.4.1 Gas-phase kinetics and radiation	22
2.4.2 Nucleation	22
2.4.3 Condensation	23
2.4.4 Sintering	24

2.4.5	Aggregation	25
2.4.6	Thermal radiation from particles	25
2.5	Simulation parameters	26
2.5.1	Flame configuration	26
2.5.2	Computational setup	27
2.6	Results and discussion	28
2.6.1	Flow field and temperature	28
2.6.2	Comparison with experimental SAXS data	32
2.6.3	Timescale analysis	36
2.6.4	Investigation of alternative model choices	38
2.6.5	Analysis of computational performance	39
2.7	Summary	40
3	Modelling of aerosol synthesis in a turbulent flame	43
3.1	Introduction	43
3.1.1	Literature review	43
3.1.2	Present investigation	48
3.2	Methodology	49
3.2.1	Governing equations	49
3.2.2	Models for chemical kinetics and aerosol dynamics	52
3.2.3	Large-eddy simulation	54
3.2.4	Joint sub-grid probability density function	55
3.2.5	Stochastic field method	57
3.2.6	Numerical methods	58
3.3	Simulation parameters	59
3.3.1	Flame configuration	59
3.3.2	Computational setup	59
3.4	Results and discussion	61
3.4.1	Flow field and temperature	61
3.4.2	Comparison with experimental SAXS data	63
3.4.3	Effect of particle sub-grid mixing	68
3.4.4	Effect of the number of stochastic fields	70
3.4.5	Investigation of gas-to-particle conversion	70

3.5	Summary	72
4	Analysis of coagulation in turbulent flow	75
4.1	Introduction	75
4.1.1	Literature review	76
4.1.2	Present investigation	78
4.2	Methodology	79
4.2.1	Governing equations	79
4.2.2	Numerical methods	83
4.2.3	Flow configuration and computational setup	85
4.3	Comparison with reference data	88
4.3.1	Flow field validation	88
4.3.2	Particle size distribution	94
4.4	Results and discussion	95
4.4.1	Effect of coagulation and mixing on the moments	95
4.4.2	Reynolds decomposition of the PBE	98
4.4.3	Number density fluctuation correlations	99
4.4.4	Effect of fluctuations on the zeroth moment	103
4.4.5	Effect of fluctuations on the second moment	106
4.5	Summary	109
5	Conclusions and future work	111
5.1	Conclusions	111
5.2	Future work	115
A	The Camenzind et al. experiment	117
A.1	On the selection of the Camenzind et al. experiment	117
B	Supplementary information of the laminar-flame simulation	120
B.1	Validation of the monodisperse model	120
B.2	Inlet velocity profile	121
B.3	Effect of air co-flow velocity	122
B.4	Computational domain and grid	123
B.5	Grid independence	125

C Scalability analysis of code PANTARHEI **128**

 C.1 Introduction 128

 C.1.1 Flow-solver description 128

 C.2 Test case: Kolmogorov fow 130

 C.3 Performance analysis 133

Bibliography **135**

List of Tables

2.1	Comparison of reported flame-made silica characteristics found in selected studies in literature measured with <i>in-situ</i> techniques. The data presented in the table correspond to: experimental technique (SAXS: small-angle X-ray scattering, USAXS: untra small-angle X-ray scattering, TS: thermophoretic sampling, LS: light scattering), method of synthesis (LF: laminar flow, TF: turbulent flow, CF: counterflow, DF: diffusion flame, PM: premixed flame), material used as a precursor, primary particle d_p and aggregate R_g sizes, fractal dimension D_f , particle volume fraction f_v and number concentration of primary particles N_p . The asterisk denotes that the number concentrations of aggregates N were reported instead of N_p	10
2.2	Global two-step reaction mechanism for HMDSO combustion (Feroughi et al., 2017). The reaction rate constant is given in the form $k = AT^n \exp[-E_a/(RT)]$, where T stands for temperature, R for the gas constant, and E_a for the activation energy. The units of the parameter A are expressed in terms of cm, s, and mol, while E_a is given in cal/mol.	22
2.3	Characteristic sintering times for silica nanoparticles tested in the current study. The critical particle diameter in Tsantilis et al. (2001) expression is $d_{p,0} = 1 \cdot 10^{-9}$ m; r_s in Kirchhof et al. (2012) expression denotes the radius of a completely coalesced spherical particle. The units are: m for d_p , $d_{p,0}$ and r_s , K for T and s for τ_s	25
2.4	Inlet boundary conditions, where u_{inlet} denotes the stream bulk inlet velocity in the streamwise direction. The inlet velocity profile at the inflow is presented in Appendix B.2, Fig. B.2.	27
2.5	Definition of timescales for processes encountered in silica flame synthesis. . . .	36

2.6	Comparison of PBE models for describing aerosol dynamics and particle morphology. The total CPU time per timestep includes all processes (flow field, scalar convection/diffusion, gas phase reaction, and PBE solution). Tabulation of the aggregation kernel was employed for the one-PBE model.	41
3.1	Selected CFD-based studies of flame synthesis of silica nanoparticles found in the literature. The relevant studies are presented in chronological order, focusing on the modelling approach adopted in each case. The information presented in the table corresponds to: the reactor type (DF: diffusion flame, PM: premixed flame, TML: temporal mixing layer, FSP: flame spray pyrolysis), the precursor, the CFD approach for the flow simulation (Lam: laminar flow), the combustion model (FRC: finite-rate-chemistry, ED: eddy dissipation model, SE: species equilibrium approach), models for describing particle dynamics, whether turbulence-chemistry and turbulence-particle dynamics interaction were considered in the model or not, whether a comparison with experimental data was attempted or not, and a comment.	47
3.2	Inlet boundary conditions for the S-10 turbulent-flame simulation, where u_{inlet} denotes the stream bulk inlet velocity in the streamwise direction.	59
4.1	Computational parameters of the simulations.	87

List of Figures

1.1	Schematic diagram of nanoparticle synthesis in flames. Reprinted from Raman and Fox (2016).	3
2.1	Contour plots of (a) velocity and (b) temperature fields.	29
2.2	Contour plots of (a) silica volume fraction and (b) primary particle diameter fields.	30
2.3	Comparison of numerical predictions (two-PBE model) with the experimental FTIR data of Camenzind et al. (2008) for flame temperature along the centreline and effect of radial averaging. An average experimental error of ± 60 K given by Kammler et al. (2002) was used in the figure for the FTIR data.	31
2.4	Comparison of numerical predictions (two-PBE model) with experimental data for flame temperature and effect of emission of thermal radiation from gas species and from particles. Results of the radial maximum temperature for each case are compared with the experimental FTIR data of Camenzind et al. (2008). An average experimental error of ± 60 K given by Kammler et al. (2002) was used in the figure for the FTIR data.	32
2.5	Comparison of the experimental SAXS data of Camenzind et al. (2008) with numerical predictions for (a) primary particle diameter, (b) radius of gyration of aggregates, (c) primary particle number concentration and (d) average number of primary particles per aggregate along the pathline of maximum silica volume fraction. Results were obtained with the two-PBE, the extended one-PBE, and the monodisperse model (described in Section 2.2). A logarithmic scale was used for the vertical axes of figures (c) and (d).	33

2.6	Comparison of the experimental SAXS data of Camenzind et al. (2008) with numerical predictions for the geometric standard deviation of aggregate (“agg”) and primary particle (“pp”) size distributions along the pathline of maximum silica volume fraction.	35
2.7	Rates of kinetic processes (absolute values) and timescales along the pathline of maximum silica volume fraction. Results were obtained with the two-PBE model. Note that, for the sintering process in (a), the rate refers to the number concentration of primary particles, N_p . A logarithmic scale was used for the vertical axes.	37
2.8	Effect of sintering time on (a) primary particle diameter, (b) aggregate radius of gyration. Results were obtained with the two-PBE model. Comparison is also made with the experimental data of Camenzind et al. (2008).	39
2.9	Effect of nucleation model on (a) primary particle diameter and (b) aggregate radius of gyration. Three models are compared: instantaneous nucleation (“InstNuc”), classical nucleation theory (CNT) and the dimers-based approach that was used for the rest of the results. Results were obtained with the two-PBE model. Comparison is also made with the experimental data of Camenzind et al. (2008).	40
3.1	Contour plots of the instantaneous (left) and time-averaged (right) fields for (a) streamwise velocity, (b) temperature and (b) silica volume fraction. HAB stands for height above burner.	62
3.2	Comparison of numerical predictions with the experimental FTIR data of Camenzind et al. (2008) for flame temperature along the centreline. An average experimental error of ± 60 K given by Kammler et al. (2002) was used in the figure for the FTIR data.	63
3.3	Comparison of the experimental SAXS data of Camenzind et al. (2008) with numerical predictions for (a) primary particle diameter and (b) radius of gyration of aggregates along the pathline of maximum silica volume fraction. Results were obtained with the extended one-PBE model described in Section 3.2.1.	64

- 3.4 Comparison of the experimental data of Camenzind et al. (2008) with numerical predictions for (a) primary particle number concentration and (b) silica volume fraction along the pathline of maximum silica volume fraction. Results were obtained with the extended one-PBE model (described in Section 3.2.1). A logarithmic scale was used for the vertical axes. 67
- 3.5 Comparison of numerical predictions obtained with two different values of the micromixing constant for number densities, i.e. $C_{d,p} = 0.002$ and $C_{d,p} = 2$: (a) flame temperature; (b) primary particle diameter; (c) primary particle number concentration; (d) particle volume fraction. In both cases, the micromixing constant for the gas-phase species and enthalpy was $C_{d,s} = 2$. Comparison is also made with the experimental data of Camenzind et al. (2008). 69
- 3.6 Comparison of numerical predictions obtained with eight and sixteen stochastic fields: (a) flame temperature; (b) primary particle diameter; (c) primary particle number concentration. For both cases, the micromixing constants were $C_{d,s} = 2$ and $C_{d,p} = 0.002$. Comparison is also made with the experimental data of Camenzind et al. (2008). 70
- 3.7 (a) Formation rate of $\text{SiO}_2(\text{g})$ species, R_{G2} , along the pathline of maximum silica volume fraction; (b) Rate of change of particle number concentration due to kinetic processes (absolute values) along the pathline of maximum silica volume fraction. Note that, for the sintering process in (b), the rate refers to the number concentration of primary particles, N_p . A logarithmic scale was used for the vertical axis of figure (b). 71
- 3.8 Rate of change of silica volume fraction due to nucleation and condensation. (a) Contour plots; (b) results along the pathline of maximum silica volume fraction. 71
- 4.1 Flow field data: (a) turbulent kinetic energy (TKE) k ; (b) 3-D view of the instantaneous spanwise vorticity field ω_z ; (c) instantaneous contours of the passive scalar on (x-y) plane $z = 0$ 89
- 4.2 Growth of the jet half-width based on the velocity (a) and centreline mean velocity excess decay (b). — Present results; $\square$ (Thomas and Chu, 1989); $\diamond$ (Browne et al., 1983); $\cdots$ DNS (Stanley et al., 2002). 90

4.3	Downstream growth of the jet half-width based on the passive scalar (a) and decay of the mean scalar on the jet centreline (b). — Present results; $\diamond$ (Browne et al., 1983); $\square$ (Davies et al., 1975); $\cdots$ DNS (Stanley et al., 2002).	90
4.4	Self-similar profiles of mean velocity and mean passive scalar for three axial positions. (a) Mean velocity. — Present results; $\square$ (Gutmark and Wygnanski, 1976); $\circ$ (Ramaprian and Chandrasekhara, 1985); $\cdots$ DNS (Stanley et al., 2002). (b) Mean scalar. — Present results; $\square$ (Davies et al., 1975); $\circ$ (Jenkins and Goldschmidt, 1973); $\cdots$ DNS (Stanley et al., 2002).	91
4.5	Variation of turbulent kinetic energy budgets along the jet centreline (all terms are non-dimensionalised with the variables defined in equation (4.3)).	92
4.6	One-dimensional power spectra $E_{11}(\kappa_1)$ (a) and $E_{22}(\kappa_1)$ (b) obtained from the frequency spectra of the streamwise and cross-stream velocity fluctuations at the probe point $(x, y, z) = (20, 1.5, 0)$. Kolmogorov's universal scaling was used. The dashed red lines represent the one-dimensional wavenumber spectra (a) $E_{11}(\kappa_1) = C_1 \epsilon^{2/3} \kappa_1^{-5/3}$ (b) and $E_{22}(\kappa_1) = C'_1 \epsilon^{2/3} \kappa_1^{-5/3}$. Logarithmic scales were used for both axes.	93
4.7	Normalised time-averaged PSDs at several probe points along the centreline. The results are compared with reference data for the self-preserving distribution (Vemury and Pratsinis, 1995). A logarithmic scale was used for the horizontal axes. (a) $Da_{coag} = 1$; (b) $Da_{coag} = 1/3$	94
4.8	Instantaneous contour plots of M_0 on (x-y) plane $z = 0$. (a) $Da_{coag} = 1$; (b) $Da_{coag} = 1/3$. A logarithmic scale colourbar is used.	96
4.9	Instantaneous contour plots of M_2 on (x-y) plane $z = 0$. (a) $Da_{coag} = 1$; (b) $Da_{coag} = 1/3$	97
4.10	Centreline variation of time-averaged M_0 (a) and M_2 (b) for the two Da_{coag} cases. The red dashed-dotted line indicates the jet break-up location. A logarithmic scale was used for the vertical axis in (a). A black dashed-dotted line is used for $\overline{M_1}$ in (a).	98
4.11	Map of number density fluctuation correlations $\overline{n'(v)n'(w)}$: (a) for $Da_{coag} = 1$ at probe point $(10, 0, 0)$; (b) for $Da_{coag} = 1$ at probe point $(17.5, 0.5, 0)$; (c) for $Da_{coag} = 1/3$ at probe point $(10, 0, 0)$; (d) for $Da_{coag} = 1/3$ at probe point $(17.5, 0.5, 0)$	100

4.12	(a) Map of time-averaged number density combinations $\overline{n(v)} \overline{n(w)}$, and (b) time-averaged PSD for $Da_{coag} = 1$ at probe point $(10, 0, 0)$	100
4.13	Intensity of correlations of number density fluctuations I_n at probe point $(10, 0, 0)$: (a) $Da_{coag} = 1$; (b) $Da_{coag} = 1/3$. Results are normalised by $I_\phi = 0.156$. The black dashed line indicates the location where the fluctuation intensities are equal, i.e. $I_n = I_\phi$	102
4.14	Contour plots of $ A_0 $ (a) and C_0 (b) for $Da_{coag} = 1/3$. A logarithmic scale colourbar was used in (a).	104
4.15	Coagulation source terms for the zeroth moment (see (4.28)). (a) Centreline values of A_0 ; the red dashed-dotted line indicates the jet break-up location. (b) Cross-stream profiles of A_0 , B_0 and C_0 at the axial position $x = 20$. A logarithmic scale was used for the vertical axis in (a). The horizontal axis in (b) was normalised by $\delta_\phi = 2.362$. Note the different horizontal axes in (a) and (b).	104
4.16	C_0/A_0 ratio (see (4.28)). (a) Centreline values of C_0/A_0 . (b) Cross-stream profiles of C_0/A_0 at the axial position $x = 20$. The horizontal axis in (b) was normalised by $\delta_\phi = 2.362$. Note the different horizontal axes in (a) and (b).	105
4.17	Contour plots of A_2 (a) and C_2 (b) for $Da_{coag} = 1/3$	107
4.18	Coagulation source terms of the second moment equation (see (4.30)). (a) Centreline values of A_2 , B_2 and C_2 ; the red dashed-dotted line jet break-up location. (b) Centreline values of ratio C_2/A_2	108
A.1	Experimental setup for the synthesis of the SiO_2 nanoparticles with a co-flow diffusion flame burner. Reprinted from Camenzind et al. (2008).	118
B.1	Validation of the monodisperse model presented in Section 2.2.3. Aggregation and sintering of nanoparticles at conditions described in Goudeli et al. (2015) were simulated with the monodisperse model “Mono” (see Section 2.2.3). Results were in excellent agreement with the data of Goudeli et al. (2015).	120

B.2	Inlet velocity profiles in the streamwise direction. The stream bulk velocities u_{inlet} of the jets coming from the inner tube, the first and second annulus were $U = 6.715$ m/s, $U_1 = 2.057$ m/s and $U_2 = 8.57$ m/s, respectively. The inlet velocities were estimated based on the given mass flow rates (Camenzind et al., 2008) and by assuming that the temperature of the streams was 75°C. A parabolic laminar flow velocity profile was employed for the inner jet and Poiseuille laminar profiles through annulus sections were employed for the other two jet streams. A uniform velocity $U_{air} = 0.4$ m/s was used for the air co-flow stream at the inlet. See also Table 2.4 in Section 2.5.2.	121
B.3	Numerical predictions for flame temperature and primary particle diameter for different values of air co-flow velocity U_{air} . Results were obtained with the monodisperse model. Comparison is also made with the experimental data of Camenzind et al. (2008).	122
B.4	Computational domain/grid (top) and computational grid focussing in the region above the burner (bottom).	124
B.5	Effect of the computational grid on the flame temperature. Results were obtained with the one-PBE model. Comparison is also made with the experimental data of Camenzind et al. (2008).	126
B.6	Effect of computational grid on (a) primary particle diameter, (b) radius of gyration of aggregates, (c) primary particle number concentration and (d) average number of primary particles per aggregate Data are plotted along the pathline of maximum silica volume fraction. Results were obtained with the one-PBE model. Comparison is also made with the experimental data of Camenzind et al. (2008).	127
C.1	Three-dimensional Kolmogorov flow in a triply periodic domain driven by a large-scale steady sinusoidal force. The size of the computational domain is $-\pi \geq x, y, z, \geq \pi$. Sustainable turbulence is reached by forcing the Navier-Stokes equations with Eq. (C.3). The Reynolds number based on Eq. (C.4) is 490.	131

C.2	(a) Time-averaged velocity profile in the forced direction. (b) Turbulent rms velocity fluctuations in the forced direction. The reference data were found in (Borue and Orszag, 1996). The discrepancy in (b) is expected since Borue and Orszag (1996) solved the hyperviscosity-modified Navier-Stokes equations. . . .	132
C.3	(a) Ratio of cell size, defined as $\Delta_{cell} = (\Delta x \Delta y \Delta z)^{1/3}$, to the Kolmogorov length scale $\eta = (\nu^3/\epsilon)^{1/4}$. (b) Reynolds number $Re_\lambda = \sqrt{ \mathbf{u}' ^2} \lambda / \nu$, based on the Taylor micro-scale $\lambda = \sqrt{\nu \mathbf{u}' ^2} / \epsilon$	133
C.4	Relative speedup for the three cases. The solid black line indicates the theoretical linear scaling. The speedup is evaluated with Eq. (C.5).	135
C.5	Parallel efficiency for the three cases. The efficiency is evaluated with Eq. (C.6).	135
C.6	Wall time per timestep T_n (in seconds) for the three cases. A logarithmic scale was used for both axes in (b).	136
C.7	CPU hours per timestep (in hours) for the three cases. The CPU hours per timestep are evaluated with Eq. (C.7).	136
C.8	Strong-scaling analysis of code PANTARHEI on ARCHER2. Each node on ARCHER2 has 128 CPUs (processors). The one-node case was selected as the reference case. Results are presented in table format. “Uniformity” refers to whether the cells are distributed evenly amongst processors.	137

List of Acronyms

ATF	Artificial flame thickening
BDF	Backward differentiation formula
CFD	Computational fluid dynamics
CFL	Courant-Friedrichs-Levy number
CNT	Classical nucleation theory
DNS	Direct numerical simulation
EDC	Eddy dissipation concept
FSP	Flame spray pyrolysis
FTIR	Fourier transform infrared spectroscopy
GDE	General dynamic equation
HAB	Height above burner
HMDSO	Hexamethyldisiloxane
LES	Large eddy simulation
MMC	Multiple mapping conditioning
PBE	Population balance equation
PDF	Probability density function
PFGM	Premixed flamelet generated manifold
PSD	Particle size distribution
PSR	Perfectly stirred reactor
QMOM	Quadrature method of moments
RANS	Reynolds-averaged Navier-Stokes equations
rms	Root mean square
SAXS	Small-angle X-ray scattering
SDE	Stochastic differential equations
SGS	Sub-grid scale

SPSD	Self-preserving particle size distribution
STP	Standard temperature and pressure
TEOS	Tetraethylorthosilicate
TKE	Turbulent kinetic energy
TVD	Total variation diminishing

Chapter 1

Introduction

1.1 Background

Aerosols constitute dispersions of fine particles or droplets in gases and are encountered in many natural and engineering processes. Examples include soot or carbon black formation (Rigopoulos, 2010, 2019; Raman and Fox, 2016), flame synthesis of nanoparticles (Buesser and Pratsinis, 2012; Goudeli and Pratsinis, 2016), sulphur-driven particle formation in exhaust systems (Olin et al., 2015), and atmospheric processes (Kulmala et al., 2004).

Aerosol flame synthesis is one of the main methods for the industrial production of nanomaterials and has received increased attention over the last few decades. Flame reactors are simple, scalable, and most favourable in terms of energy since fuel energy is used directly to synthesise nanopowders and films (Buesser and Pratsinis, 2012). Today, 80 – 90% of the commercially available flame-made nanomaterials are manufactured in diffusion or spray flame reactors (Wegner and Pratsinis, 2003b). Examples of such nanoparticles are carbon blacks, fumed silica (SiO_2), pigmentary titania (TiO_2), zirconia (ZnO_2) and alumina (Al_2O_3) (Rosner, 2005; Buesser and Pratsinis, 2012; Park and Park, 2015) and they find a wide range of applications in gas sensors, energy storage materials, nanotoxicity studies, catalysts, biomaterials, and electroceramics (Meierhofer and Fritsching, 2021) amongst others. It is thus desirable to develop models that can aid the production of tailor-made nanoparticles by predicting the particle size and morphology and linking them to process design and operating conditions.

The proposed methodologies and models in the present work have been applied to flame synthesis of silica nanoparticles, although they can be extended for the study of other nanomaterials. Fumed silica, also known as “pyrogenic silica” or its commercial name “Aerosil”, is one of the most widely produced flame-made commodities by value and volume (Pratsinis, 2011). It is frequently used as a filler in silicon rubber and as a flowing agent to enhance the rheological

properties of paints, resins, and inks (Friedlander, 2000). It also serves as an ingredient for the manufacturing of nanocomposites with enhanced properties, e.g. elastic modulus (Mueller et al., 2004), and is encountered in pharmaceutical and cosmetical products (Pratsinis, 2011; Meierhofer and Fritsching, 2021).

A number of complex transport and kinetic processes take place in flame synthesis of nanoparticles. These processes are illustrated in Fig. 1.1. Fluid mechanics “set the stage” by establishing the temperature and reactant distribution in the domain. In typical aerosol flame synthesis, a precursor, which is a chemical compound containing molecules of interest, is introduced into the flame reactor. Gas-phase chemical kinetics governs fuel combustion and precursor decomposition and oxidation. Usually, fuel-combustion reactions are weakly coupled to the precursor’s chemical reactions (Roth, 2007). Rapid decomposition and oxidation of the precursor occur due to the high flame temperatures, leading to the formation of monomers (product molecules) and highly-supersaturated concentrations. Due to the supersaturated conditions, stable nuclei (newly-formed particles consisting of a few molecules) are formed, a process known as nucleation or particle inception. After that, particles grow in size either by coagulation, when particles collide with each other and form larger particles, or by condensation of gas species onto the particles. In some cases, particles can also grow by surface reactions. Particles in contact tend to reduce their surface free energy (Koch and Friedlander, 1990) by sintering (partial coalescence). Competition between aggregation and sintering can lead to either spherical or fractal-like structures.

For reference purposes, the term coagulation is used to describe particle collision processes in general, coalescence is defined as the particle collision process that leads to fully fused particles, while aggregation is defined as the collision process that results in aggregated particles. Clusters of chemically-bonded primary particles are known as aggregates, while clusters of physically-bonded primary particles are known as agglomerates (Buesser and Pratsinis, 2012).

Flame-made nanoparticles are polydisperse in terms of particle sizes, and their polydispersity is characterised by the particle size distribution (PSD). The PSD is an essential characteristic of nanoparticle products. The spatial and temporal evolution of the PSD can be described by the population balance equation (PBE), also known as the general dynamic equation (GDE) for aerosols, which is a mathematical method for modelling distributed properties, i.e. particle number densities, which are subject to changes due to all the aforementioned physicochemical phenomena encountered in nanoparticle flame synthesis.

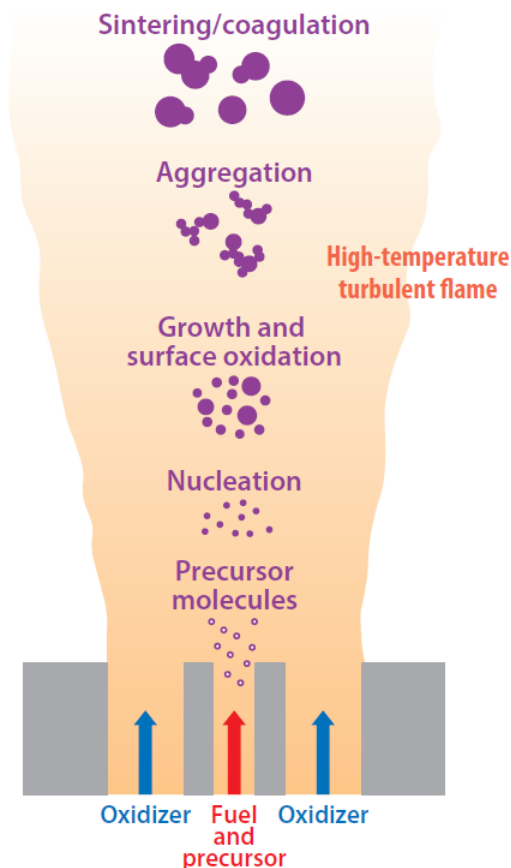


Figure 1.1: Schematic diagram of nanoparticle synthesis in flames. Reprinted from Raman and Fox (2016).

Product characteristics are highly affected by flow configuration, turbulent reactant mixing, flame temperature, precursor loading, etc. (Raman and Fox, 2016). Furthermore, spatial phenomena such as particle convection, diffusion and thermophoresis cause particles to follow different trajectories with different temperature and species-concentration histories, leading to a product with a wide variety in morphology. All the aforementioned processes take place at different time and length scales. In spite of extensive experimental and theoretical research over the last few decades, modelling and simulation of the overall aerosol flame synthesis process remain a challenge (Buesser and Gröhn, 2012). Prediction of particle morphology in different flow regimes, such as laminar or turbulent, is a particularly difficult task (Camenzind et al., 2008).

The comprehensive modelling of flame synthesis requires coupling of PBE with fluid dynamics, species transport and chemical kinetics to predict nanoparticle properties in laminar and turbulent flows. This coupling may be straightforward when laminar flows are considered; however, new modelling challenges are introduced when the coupling is attempted in the con-

text of turbulent flows. The new modelling aspects pertain primarily to the interaction of the different phenomena involved in aerosol flame synthesis with turbulence. The issue is discussed in more detail in the review papers of Rigopoulos (2010) and Raman and Fox (2016).

In most industrial cases, aerosol flame synthesis occurs in high-Reynolds-number turbulent flows (Re number $O(10^6)$) (Buesser and Pratsinis, 2012). Turbulent flows exhibit a wide range of length and time scales. Current methods for describing turbulent reacting flows are based on Reynolds-averaged Navier-Stokes (RANS) equations, large-eddy simulations (LES) and direct numerical simulations (DNS). In the RANS approach, flow variables are decomposed into mean (time-averaged) and fluctuating parts and equations for the mean quantities are solved. These equations include unclosed terms involving turbulent fluctuations correlation and sophisticated models must be introduced to account for their effect. In the same way, Reynolds decomposition of the PBE leads to unclosed terms involving correlations of number density fluctuations (Rigopoulos, 2007). The advantage of RANS models is their low computational cost; however, the quality of simulations relies heavily on modelling choices.

On the other hand, in DNS, the governing equations are solved directly without any modification, and all length and time scales of fluid motion are explicitly resolved. DNS studies are usually restricted to low-Reynolds-number flows (Moin and Mahesh, 1998), while the increased computational cost of DNS has limited its application in aerosol flame synthesis studies. In turn, in LES, the large more-energy-containing scales are resolved directly by spatially filtering the governing equations, while the effect of small unresolved scales needs to be modelled. LES provides a higher level of fidelity compared to RANS (Pitsch, 2006), while the modelling impact is diminished. Therefore, LES is probably the most promising and favourable approach for predicting aerosol flame synthesis in turbulent flows with an affordable computational cost.

The PBE is a nonlinear partial integrodifferential equation, and several methods have been developed for its numerical solution. The methods can be divided into three categories: Monte Carlo, moment, and discretisation/sectional methods. The use of the Monte Carlo approach has been employed by researchers to solve multidimensional population balances and investigate the formation of SiO_2 (Shekar et al., 2012b) and TiO_2 (Lindberg et al., 2019) nanoparticles, amongst others. However, the increased computational cost restricts this methodology only to 0-D or 1-D simulations. More details on the Monte Carlo approach can be found in the papers of Fichthorn and Weinberg (1991); Gillespie (1975) and Ramkrishna (1981). Moment methods compose a large collection of methods for solving equations for the moments of the PSD and, therefore,

solving the PBE indirectly (Frenklach and Harris, 1987; Frenklach, 2002; Marchisio and Fox, 2005; Nguyen et al., 2016). They have been used widely in CFD investigations of aerosol flame synthesis due to their low computational cost. However, they require closure assumptions. Recent advances in computational power rendered discretisation/sectional methods attractive for coupling with CFD. In discretisation/sectional methods, the domain of the independent variable (usually particle volume) is discretised into sections allowing for an accurate description of the PSD (Gelbard et al., 1980; Rigopoulos, 2010; Liu and Rigopoulos, 2019).

In light of the preceding remarks, it is clear that there is a need for the development of models for describing aerosol flame synthesis that are able to give reliable predictions. The role of coupled CFD-population balance models (denoted as CFD-PBE) is threefold: 1) comparisons of numerical predictions with experimental data can reveal sources of uncertainties and, thus, guide theoretical and experimental research, 2) CFD-PBE models predict the particle properties (primary particle and aggregate sizes, number concentrations, etc.) in the whole reactor domain and thus could facilitate the design and scale-up of reactors, and 3) comprehensive CFD-PBE models can help in gaining physical insight into the underlying phenomena.

1.2 Objectives and contributions

Simulations of nanoparticle formation in laminar and turbulent reacting flows should incorporate several models and solution methods. Particularly, the individual model components for the entire synthesis process include: 1) the description of laminar or turbulent flow, 2) detailed gas-phase chemical kinetics, 3) population balance modelling, 4) kinetic models for aerosol processes, 5) the interactions between all these elements. The quality of the simulations is subject to the uncertainties and assumptions involved in all of these elements. The use of simplified models for the reaction kinetics, aerosol dynamics, and their interaction due to turbulent flow may lead to compensation of errors and complicate the validation efforts. The main objective of the present research is to develop and employ accurate and comprehensive methodologies for simulating particle formation and flame synthesis in laminar and turbulent flows. By comparing with experimental data, we hope to shed light on the nature of the discrepancies and identify possible sources of uncertainties. The particular contributions of the thesis are detailed below.

- Development of a novel extended population balance model for simulating aerosol flame synthesis. The new model is termed “extended one-PBE” and has three key characteristics: 1) it can describe the evolution of primary particle sizes, thus particle morphology, 2) it accounts for finite-rate sintering and 3) it is more computationally efficient (especially with respect to coupling with CFD) than a two-dimensional or a two-equation PBE. This is accomplished by solving the PBE together with a transport equation for the number concentration of primary particles. A sectional method is employed for the numerical solution of the PBE, meaning that the model can predict the evolution of the PSD.
- The extended one-PBE model is employed to simulate synthesis of silica nanoparticles in a laminar flame and predict the detailed experimental *in-situ* SAXS measurements of Camenzind et al. (2008)¹ for the S-2 flame. For this purpose, the extended one-PBE model is coupled with an in-house CFD code, BOFFIN (staggered version), and aerosol kinetics associated with silica, i.e. nucleation, condensation and sintering, is implemented in the code. The S-2 flame of Camenzind et al. (2008) is selected for the validation strategy for two main reasons. The first reason is that the S-2 flame is laminar and laminar flame simulations are free of the impediments found in RANS and LES simulations, where

¹Camenzind et al. (2008) used the notation “S-y” to refer to a series of SiO₂-producing flames with different O₂ flow rates “y” [L/min]. In this series, the S-2 flame was laminar, while the S-10 flame was turbulent. More information on the selection of the Camenzind experiment is given in Appendix A.1.

“closure” models are needed to account for the turbulence-chemistry and turbulence-particle dynamics interaction. The second reason is that Camenzind et al. (2008) provided a plethora of particle data for several heights above the burner (HAB) allowing us to validate specific components of our methodology. Simulations with a monodisperse and a two-PBE model are also conducted and the results are compared with those obtained with the extended one-PBE model.

- The extended one-PBE model is introduced into the filtered probability density function/stochastic field modelling framework (denoted as LES-PBE-PDF) and coupled with an in-house LES code, BOFFIN-LES. The advantage of this methodology, as compared to other modelling strategies for nanoparticle flame synthesis found in the literature, is that 1) it accounts for a comprehensive aerosol dynamics description, 2) it accounts for the complex interaction between turbulence, chemistry and particle dynamics, and 3) it can predict the evolution of particle morphology, i.e. primary particle sizes.
- The extended one-PBE model (within the LES-PBE-PDF framework) is employed to simulate synthesis of silica nanoparticles in a turbulent flame and predict the detailed experimental *in-situ* SAXS measurements of Camenzind et al. (2008) for the S-10 flame. For this purpose, we employ the same set of models for gas-phase chemistry and aerosol dynamics without any adjustments in parameters which is employed for the simulation of the S-2 flame. Thus, by maintaining the same kinetics, we focus on the modelling issues arising in silica flame synthesis. Furthermore, by comparing numerical predictions with *in-situ* experimental data and by leveraging knowledge obtained from the laminar-flame simulation, we attempt to identify possible sources of uncertainties in the model and shed light on the nature of the discrepancies between predictions and experimental results.
- Investigation of the effect of particle sub-grid mixing. The model parameter that directly affects the sub-grid contribution in the LES-PBE-PDF methodology is the micromixing constant. While the sensitivity of the LES results on the micromixing constant for the gas-phase species has been examined previously by researchers, the impact of the micromixing constant for particle number densities is more questionable due to the very low diffusivity of nanoparticles. To investigate the effect of particle sub-grid mixing, simulations with different values of the micromixing constant for particle number densities are performed and results are analysed.

- Investigation of turbulence–coagulation interaction via DNS and PBE. Coagulation is an important process in several environmental and engineering applications involving turbulent flow, including soot formation and flame synthesis of nanoparticles. In particular, coagulation is considered to be the dominant mechanism in nanomaterial flame synthesis (Buesser and Pratsinis, 2012). However, its interaction with turbulence is not yet fully understood. To investigate this effect, a computational experiment that isolates the effect of turbulence–coagulation interaction is designed. Specifically, DNS simulations of a 3-D spatially developing planar jet laden with coagulating nanoparticles are performed. For this purpose, a discretisation (sectional) model for the solution of the PBE is coupled with an in-house DNS code, PANTARHEI². This methodology is free of *a priori* assumptions regarding the turbulent motions and the shape of the PSD, allowing us to study turbulence-coagulation interaction. In the analysis, particular focus is given to the behaviour and significance of the unknown correlations that arise in the Reynolds decomposition of the PBE, a long-standing problem in the literature.

The outcome of the present research is organised into three main parts. The first part incorporates a study of aerosol synthesis in a laminar diffusion flame and is presented in Chapter 2. The second part comprises an LES investigation of aerosol synthesis in a turbulent diffusion flame and is reported in Chapter 3. The final part of the present research is presented in Chapter 4 and comprises a DNS analysis of turbulence-coagulation interaction in a planar jet. The literature review specifically associated with each of these parts is presented in the introduction of each chapter.

²A performance analysis for the scalability of code PANTARHEI has been conducted and results are discussed in Appendix C.1.

Chapter 2

Modelling of aerosol synthesis in a laminar flame

2.1 Introduction

In the present chapter, we propose a novel extended PBE model for aggregation and sintering and couple it with CFD to investigate synthesis of silica nanoparticles in a laminar diffusion flame. A discretised/sectional method is employed to describe the aerosol dynamics and numerically solve the PBE. The extended PBE includes finite-rate sintering of primary particles by solving the PBE together with a transport equation for the number concentration of primary particles. In the process simulated, the particles are formed via the oxidation of a vapour precursor, hexamethyldisiloxane (HMDSO), and the aerosol processes include nucleation, condensation, aggregation and sintering. The model is validated with the detailed experimental *in-situ* SAXS data of Camenzind et al. (2008) and is also compared with a monodisperse and a two-PBE approach.

2.1.1 Literature review

A number of CFD-based studies of flame synthesis of nanoparticles have been reported in the literature. In the present work, the proposed methodology is applied to silica synthesis; hence we survey the relevant studies in chronological order, focussing on the modelling approach adopted in each case. For studies on other inorganic nanoparticles, we refer to the review papers of Buesser and Pratsinis (2012); Buesser and Gröhn (2012), Meierhofer and Fritsching (2021) and Raman and Fox (2016). Furthermore, a review of experimental studies including *in-situ* measurements of silica nanoparticle synthesis in flames has been conducted, and the studies are summarised in Table 2.1.

Reference	Experimental technique	Synthesis method	Precursor	Silica production rate $[g/h]$	d_p $[nm]$	R_g $[nm]$	D_f	$\max f_v \times 10^6$ $[-]$	$\max N_p$ $[\#/cm^3]$
(Scheckman et al., 2009)	Mass-Mobility	DF	HMDSO	0.7 – 10.8	12 – 93	n/a	1.7 – 2.4	n/a	n/a
(Camenzind et al., 2008) “S-2”	SAXS + TS	LF DF	HMDSO	4.8	5 – 90	52 – 121	1.7 – 2.9	0.25	8×10^{11}
(Camenzind et al., 2008) “S-10”	SAXS + TS	TF DF	HMDSO	4.8	9 – 12	45 – 93	1.75 – 2.13	0.053	4.5×10^{12}
(Kammler et al., 2005) “Cold”	USAXS	TF PM	HMDSO	14	5 – 11	65 – 135	2.1 – 2.35	1.7	7×10^{13}
(Kammler et al., 2005) “Hot”	USAXS	TF PM	HMDSO	38	8 – 27	40 – 170	1.95 – 2.58	2.1	6×10^{13}
(Kim and Choi, 2003)	plane laser LS	flat PM	SiCl ₄	n/a	n/a	50 – 220	1.3 – 2	n/a	n/a
(Cho and Choi, 2000)	LS + TS	H ₂ DF	SiCl ₄	2.08 – 24.26	15 – 50	25 – 140	1.62 – 1.76	30	8×10^{13}
(Choi et al., 1999)	LS + TS	H ₂ DF	SiCl ₄	3.46	19 – 49	55 – 110	1.35 – 1.85	50	1.1×10^{13}
(Chang and Biswas, 1992)	LS	DF	SiCl ₄	3.62	n/a	292 – 303	2.17 – 2.8	14	$6.7 \times 10^{11*}$
(Chung et al., 1992)	laser LS	CF DF	SiCl ₄	n/a	20 – 30	50 – 200	n/a	n/a	$3 \times 10^{10*}$
(Zachariah et al., 1989)	dynamic LS	CF DF	SiH ₄	n/a	20 – 30	n/a	n/a	0.6	$2 \times 10^9*$
(Ulrich and Rieh, 1982)	laser LS	PM	SiCl ₄	n/a	7.6 – 18	n/a	n/a	n/a	n/a

Table 2.1: Comparison of reported flame-made silica characteristics found in selected studies in literature measured with *in-situ* techniques. The data presented in the table correspond to: experimental technique (SAXS: small-angle X-ray scattering, USAXS: ultra small-angle X-ray scattering, TS: thermophoretic sampling, LS: light scattering), method of synthesis (LF: laminar flow, TF: turbulent flow, CF: counterflow, DF: diffusion flame, PM: premixed flame), material used as a precursor, primary particle d_p and aggregate R_g sizes, fractal dimension D_f , particle volume fraction f_v and number concentration of primary particles N_p . The asterisk denotes that the number concentrations of aggregates N were reported instead of N_p .

The coupling of aerosol and fluid dynamics for modelling silica nanoparticle formation in laminar flows was explored in the studies of Kim and Pratsinis (1988), Pratsinis and Kim (1989) and Kim and Pratsinis (1989). A method of moments, where the PSD was assumed to adopt a lognormal shape, was employed to describe aerosol dynamics, while only spherical particles were considered.

Lee et al. (2001) investigated flame synthesis of silica non-spherical nanoparticles in a laminar flat flame. A one-dimensional flame model was employed, together with the sectional two-dimensional PBE model of Xiong and Pratsinis (1993), which accounts for the evolution of aggregate structure. Different expressions for the sintering characteristic time were tested, including a hybrid model between viscous flow and atomistic diffusion sintering models (Ehrman, 1999). Numerical predictions for number concentrations and particle volume fractions were compared with the *in-situ* experimental data of Chang and Biswas (1992). Later, Kim et al. (2003) performed two-dimensional CFD simulations to investigate flame synthesis of silica nanoparticles by oxidation of silicon tetrachloride (SiCl_4) in a co-flow diffusion laminar flame. A two-PBE sectional model was coupled with CFD and the hybrid sintering model was employed. Their model slightly underestimated the primary particle sizes.

Subsequently, Ji et al. (2007) investigated flame synthesis of silica nanoparticles via CFD. They implemented a moment model and coupled it with commercial CFD software to simulate synthesis of silica nanoparticles through oxidation of tetraethylorthosilicate (TEOS) in a hydrogen diffusion flame reactor. Good agreement with the experimental *ex-situ* data of Jang (2001) was achieved by performing a parametric analysis and adjusting the particle formation and growth rate constants. However, their model did not distinguish between primary particles and aggregates. Buddhiraju and Runkana (2012) advanced the analysis of Ji et al. (2007) by using a monodisperse population balance model that accounts for fractal aggregates. Results were compared again with the *ex-situ* experimental data of Jang (2001) and were in close agreement.

Gröhn et al. (2011) incorporated a monodisperse moment model that accounts for fractal aggregates within CFD. They used the RANS approach with a realisable k - ϵ turbulence model to model flame synthesis of silica nanoparticles through oxidation of hexamethyldisiloxane (HMDSO) vapour in turbulent methane/oxygen diffusion flames. Furthermore, they investigated different sintering-time expressions, and the results were compared with experimental *ex-situ* particle size data. Their model underpredicted the primary particle sizes at high oxygen flow rates and at high silica production rates. Olivas-Martinez et al. (2015) used a commercial CFD

software to model flame spray pyrolysis (FSP) for synthesis of silica nanopowder and demonstrated the capability of CFD models to be used in the design process of FSP reactors. The standard k - ϵ turbulence model was employed to describe fluid dynamics, spray droplet evolution was described from the Lagrangian point of view and the quadrature method of moments (QMOM) was used to solve the PBE. Their model incorporated nucleation and coagulation of nanoparticles. However, finite-rate sintering was not considered and, therefore, primary particle and aggregate sizes were not distinguished. Instead, the particles were assumed to be spherical, and a finite value of a sticking coefficient was incorporated in the coagulation kernel.

Vo et al. (2017) developed a sparse-Lagrangian multiple mapping conditioning (MMC) model in the context of large eddy simulation (LES), thus accounting for turbulence-chemistry interaction. This model was applied to describe silica nucleation in a temporal mixing layer and the results were validated against data obtained via direct numerical simulations (DNS). Subsequently, this approach was employed by Neuber et al. (2019) who presented a joint experimental and numerical study of flame synthesis of silica nanoparticles. They showed the modelling capabilities of the PBE-MMC-LES approach by simulating flame synthesis of silica nanoparticles in a turbulent reacting jet. This approach was based on a sectional model for aerosol dynamics and also considered the interaction between turbulence, chemistry and particle dynamics. Aggregation of non-spherical particles was considered by assuming a constant primary particle diameter of 0.98 nm. To an extent, a fair agreement was found with the experimental data, while discrepancies were attributed to uncertainties in the precursor-decomposition reaction mechanism.

Feroughi et al. (2017) studied experimentally and numerically a premixed laminar low-pressure flame seeded with low concentrations of HMDSO, and they proposed a reaction scheme for the decomposition and combustion of HMDSO. This scheme was incorporated, along with a monodisperse moment model, into CFD to simulate flame synthesis of nanoparticles. A fair agreement between numerical predictions and experimental particle sizes was found, while the model slightly underpredicted the primary particle sizes at high precursor concentrations. The proposed reaction mechanism was utilised by (Rittler et al., 2017) where they developed and presented a model within the LES framework for describing flame spray pyrolysis for synthesis of nanoparticles; however, a comparison with experimental data was not attempted. Recently, Dasgupta et al. (2022) used a commercial CFD software to perform unsteady RANS and study silica nanoparticle synthesis from flame spray pyrolysis. Nanoparticle dynamics was described

with the hybrid method of moments while the model of Tsantilis et al. (2001) for sintering time was employed. Different operating conditions of a complex geometry reactor were investigated, and mean particle diameters were compared with *ex-situ* experimental data.

2.1.2 Present investigation

Several points can be concluded from the preceding literature review. First, there is a need to develop models capable of predicting the change in particle morphology at different flow regimes. Second, most of the reported CFD studies on turbulent flames were within the context of RANS, which adds extra uncertainty due to the need for modelling turbulent flow, turbulence-chemistry interaction and turbulence-particle interaction where extra terms arise from the Reynolds averaging of the PBE (Rigopoulos, 2007). The modelling challenges arising in turbulent-flow simulations are discussed in more detail in the review papers of Rigopoulos (2010) and Raman and Fox (2016). The extra uncertainty introduced by turbulence closure models could lead to compensation of modelling errors and this complicates the efforts in identifying the precise sources of discrepancies when comparing with experiments. Furthermore, in most of the studies, a monodisperse or moment method was employed for the solution of PBE, which involves further modelling assumptions and does not predict the evolution of the PSD directly. Finally, in most cases, the validation of previous CFD models was done by comparing final primary particle sizes with *ex-situ* experimental data for particles, while comparison with *in-situ* data focussing on the evolution of particle growth has been overlooked.

In light of the aforementioned points, the purpose of the present chapter is twofold. First, we propose a novel extended population balance model for simulating aerosol flame synthesis with the following key characteristics: it distinguishes between primary particles and aggregates, accounts for finite-rate sintering and is computationally efficient. To accomplish this, a sectional method is employed to solve the PBE, which is solved together with a transport equation for the number concentration of primary particles. This approach is more computationally efficient (especially with respect to coupling with CFD) than a two-dimensional or a two-equation PBE while still being able to predict the evolution of primary particle sizes. Second, the aforementioned PBE is coupled with a detailed CFD model and employed to predict the detailed experimental *in-situ* small-angle X-ray scattering (SAXS) measurements of Camenzind et al. (2008) in a laminar silica synthesis diffusion flame. The quality of CFD simulations is subject to the uncertainties and assumptions involved in the mathematical model. Laminar flames do

not pose the complications of turbulence and turbulence-kinetics interaction, and furthermore, the sectional approach employed is free of the closure models required by monodisperse and moment methods. By employing an approach with minimum assumptions with respect to fluid dynamics and population balance modelling, we aim to limit the modelling uncertainties to the selection of aerosol kinetic models and, therefore, shed light on the nature of discrepancies between predictions and experimental results.

The rest of the chapter is organised as follows. First, the governing equations and population balance models employed in this study are introduced. The subsequent sections describe the numerical solution method, the kinetic models employed and the flame configuration and computational setup. Results are then presented and discussed, and the chapter concludes with a summary of the main findings.

2.2 Mathematical formulation

2.2.1 Reacting flow

The variable density and low Mach number formulation of the conservation equations for mass, momentum, species and energy is employed for the gas phase and is summarised below. As discussed in the next paragraph, the interaction between the gas and particle phases is described by a one-way coupling approach. This means that sink terms in Eq. (2.1) due to gas-to-particle conversion processes have been neglected. The equations are presented with Cartesian tensor notation. The continuity equation is:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u_i)}{\partial x_i} = 0 \quad (2.1)$$

The momentum equation is:

$$\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial(\rho u_j u_i)}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial \sigma_{ij}}{\partial x_j} + \rho g_i \quad (2.2)$$

where u_i is the velocity component in the i -th direction, p is the pressure, ρ is the density and g_i is the gravitational acceleration. For a Newtonian fluid, the stress tensor is given by $\sigma_{ij} = 2\mu(S_{ij} - \frac{1}{3}S_{kk}\delta_{ij})$, where μ is the dynamic viscosity of the gas mixture, δ_{ij} is the Kronecker delta, and the strain rate is defined by $S_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$. The species transport equation is:

$$\frac{\partial(\rho Y_\alpha)}{\partial t} + \frac{\partial(\rho u_j Y_\alpha)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\rho D_\alpha \frac{\partial Y_\alpha}{\partial x_j} \right) + \rho \dot{\omega}_\alpha \quad (2.3)$$

where Y_α , D_α are the mass fraction and diffusion coefficient of a chemical species into the gas mixture, respectively¹, while the mass source due to chemical reaction is denoted $\dot{\omega}_\alpha$. Fick's diffusion law and the Hirschfelder and Curtiss approximation (Hirschfelder et al., 1955; Poinso and Veynante, 2005) have been employed to calculate D_α . A correction velocity is employed to ensure mass conservation (Poinso and Veynante, 2005). The species transport coefficients are estimated with relationships derived from the kinetic theory of gases. The dynamic viscosity of the mixture is obtained by Wilke's mixing rule (Wilke, 1950). Finally, the energy equation is written in terms of specific enthalpy that includes the thermal and chemical enthalpies, as follows:

$$\frac{\partial(\rho h)}{\partial t} + \frac{\partial(\rho u_j h)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\frac{k}{c_p} \frac{\partial h}{\partial x_j} \right) - \sum_{\alpha=1}^M h_\alpha \frac{\partial}{\partial x_j} \left[\rho \left(\frac{k}{\rho c_p} - D_\alpha \right) \frac{\partial Y_\alpha}{\partial x_j} \right] + \rho \dot{q}_{rad} + \rho \dot{q}_{rad,p} \quad (2.4)$$

where $\dot{q}_{rad}$ and $\dot{q}_{rad,p}$ denote enthalpy losses due to the thermal radiation from gas species and particles, respectively, and M is the number of chemical species. Since both chemical and thermal enthalpies are included in the transported quantity, the interchange between them due to reaction does not appear explicitly. The thermal conductivity, k , is obtained by the averaging formula of Mathur and Saxena (1967). Viscous heating, Soret and Dufour effects have been neglected in the overall formulation.

2.2.2 Population balance

A population balance equation (PBE) is employed to describe aerosol dynamics. As is common practice for dilute particulate flows (with particle volume fraction $\phi < 10^{-6}$), a one-way coupling between the gas and particle phases has been considered to formulate the mathematical model. One-way coupling takes into account the effects of the carrier phase (gas) on the dispersed phase (particles) but not vice versa (Michaelides et al., 2016). In other words, it has been assumed that the particles have a negligible effect on the gas properties and motion. Therefore, sink terms in Eq. (2.1) due to gas-to-particle conversion processes have been neglected.

Particle morphology is an important factor and its prediction is one of the objectives of the present study. A two-dimensional formulation (Koch and Friedlander, 1990; Xiong and Pratsinis, 1993) introduces an additional dimension such as particle surface area, but its discretised form is too expensive for coupling with CFD. A two-PBE formulation employs two sets of PBEs, one for the number density of particles and another one for number of primary

¹Chemical species are denoted with the subscript α and no summation is implied by repeated Greek subscripts.

particles (Rogak, 1997) or particle surface area (Tsantilis and Pratsinis, 2000); such an approach is computationally feasible and able to incorporate morphology effects, but still requires twice the number of equations as compared with the one-PBE approach. A monodisperse model (Kruis et al., 1993) has also been proposed, although this entails several assumptions. In the present section, we first describe the monodisperse and two-PBE approaches as employed in our study. Subsequently, a new formulation is proposed that, while employing one PBE, incorporates elements of the two-PBE approach with respect to the description of morphology.

Before proceeding, we first summarise the description of particle morphology adopted in the present study. Coalescence and sintering give rise to fractal aggregates, which are clusters of primary particles. The aggregation kernel must, therefore, be formulated in terms of the aggregate collision diameter, d_g . Fractal-like aggregates follow a power-law relationship that relates their collision diameter with the number of primary particles per aggregate n_p and their average diameter d_p (Friedlander, 2000; Buesser and Pratsinis, 2012) and assumes the following form:

$$d_g = d_p \left(\frac{n_p}{k_f} \right)^{1/D_f} \quad (2.5)$$

where k_f is a prefactor associated with the aggregate anisotropy (Heinson et al., 2010) and D_f is the fractal dimension, which has values close to 3 for compacted aggregates and close to 1 for chain-like structures (Friedlander, 2000). The evolution of D_f has little effect on final particle characteristics (Goudeli et al., 2015). In the present simulations, the values $k_f = 1.4$ and $D_f = 1.91$ were employed corresponding to ballistic cluster-cluster aggregation in the free molecule regime (Ball and Jullien, 1984; Friedlander, 2000).

2.2.3 The monodisperse model

The simplest and probably the most widely used model for describing aerosol dynamics in flame-synthesis studies is the monodisperse model of Kruis et al. (1993). In this model, only transport equations for the moments of the PSD are solved, while both aggregate and primary particle size distributions are assumed to be monodisperse. Its success in describing relatively well average particle properties can be attributed to some unique features of nanoparticle flame synthesis, in particular the rapid attainment of the self-preserving aerosol size distribution (SPSD) by coagulation, which simplifies the modelling strategy Buesser and Pratsinis (2012). While the monodispersed model was initially formulated in terms of surface area, in the present work we reformulate it in terms of the number concentration of primary particles for consistency

with the detailed PBE models to be discussed later. Specifically, transport equations for the number concentration of aggregates, N , and particle volume fraction, V , are solved along with a transport equation for the number concentration of primary particles, N_p . This formulation is equivalent to that of (Kruis et al., 1993; Gröhn et al., 2011) and the model implementation is validated with the data of Goudeli et al. (2015) (see Fig. B.1 in B.1). The equations to be solved are:

$$\frac{\partial N}{\partial t} + \frac{\partial(U_j N)}{\partial x_j} - \frac{\partial}{\partial x_j} \left(D_p(v, T) \frac{\partial N}{\partial x_j} \right) = J(\mathbf{Y}, T) - \frac{1}{2} \beta(v_m, v_m) N^2 \quad (2.6)$$

$$\frac{\partial V}{\partial t} + \frac{\partial(U_j V)}{\partial x_j} - \frac{\partial}{\partial x_j} \left(D_p(v, T) \frac{\partial V}{\partial x_j} \right) = J(\mathbf{Y}, T) v_{nuc} + \beta(v_m, v_o) N \frac{p_{\text{SiO}_2}}{k_B T} v_o \quad (2.7)$$

$$\frac{\partial N_p}{\partial t} + \frac{\partial(U_j N_p)}{\partial x_j} - \frac{\partial}{\partial x_j} \left(D_p(v, T) \frac{\partial N_p}{\partial x_j} \right) = J(\mathbf{Y}, T) - \frac{3}{\tau_s} \left(\frac{V}{v_{p,av}} - \frac{M_{23}}{v_{p,av}^{2/3}} \right) \quad (2.8)$$

where v_o is the volume of a SiO_2 monomer, the particle mean size is given by $v_m = V/N$, v_{nuc} is the volume of a nucleus particle, D_p is the diffusion coefficient of particles of volume v estimated by the Stokes-Einstein equation (Friedlander, 2000), J is the nucleation rate, β is the aggregation kernel and τ_s is the sintering characteristic time. The kinetic expressions employed will be shown in Section 2.4. The last term in Eq. (2.7) represents the condensation process, where p_{SiO_2} is the partial pressure of the SiO_2 gas species and k_b is the Boltzmann constant. In the monodisperse model, the $2/3$ fractional moment of the PSD is given by $M_{23} = v_m^{2/3} N = V^{2/3} N^{1/3}$. The velocity, U_j , is equal to the sum of the flow velocity, u_j , and the thermophoretic velocity, $u_{j,th}$, and the latter can be estimated from the following relationship (Friedlander, 2000):

$$u_{j,th} = -0.55 \frac{\mu}{\rho T} \frac{\partial T}{\partial x_j} \quad (2.9)$$

where T is the local temperature of the gas mixture. The average primary particle size, $v_{p,av}$, and the average number of primary particles per aggregate, $n_{p,av}$, can be calculated as follows:

$$v_{p,av} = \frac{V}{N_p} \quad (2.10)$$

$$n_{p,av} = \frac{N_p}{N} \quad (2.11)$$

2.2.4 The two-PBE model for aggregation and sintering

A more comprehensive approach to the prediction of the PSD constitutes the direct use of the PBE and its solution by discretisation (the so-called sectional approach). Three main augmentations to the basic PBE have been proposed to account for particle morphology: the

two-dimensional PBE, the modified one-dimensional PBE and the coupled two-PBE approach. The two-dimensional approach is too expensive for coupling with a CFD simulation; hence CFD-based efforts have employed the other two methods, a comparison between which can be found in Sun et al. (2021) in the context of soot formation. In the present work, the two-PBE approach will be used, and its equations are briefly summarised below. The PBE for the aggregates is (Friedlander, 2000):

$$\begin{aligned} \frac{\partial n}{\partial t} + \frac{\partial(U_j n)}{\partial x_j} = & \frac{\partial}{\partial x_j} \left(D_p(v, T) \frac{\partial n}{\partial x_j} \right) + B(\mathbf{Y}, T) \delta(v - v_{nuc}) + C(\mathbf{Y}, v) \\ & + \frac{1}{2} \int_0^v \beta(w, v-w) n(w) n(v-w) dw - \int_0^\infty \beta(v, w) n(v) n(w) dw \end{aligned} \quad (2.12)$$

where v and w express volume of aggregates, while $n = n(\mathbf{x}, t, v)$ is the particle number density concentration (denoting number of particles per unit of particle volume and mixture volume). B and C denote the nucleation² and condensation rates, respectively, while $\delta(v - v_{nuc})$ is the Dirac delta function. In the two-PBE approach, an additional PBE must be solved to account for particle morphology. In the present formulation, this is an equation for the number density of primary particles and takes the following form (Sun et al., 2021):

$$\begin{aligned} \frac{\partial n_p}{\partial t} + \frac{\partial(U_j n_p)}{\partial x_j} = & \frac{\partial}{\partial x_j} \left(n_{av} D_p(v, T) \frac{\partial n}{\partial x_j} \right) + B(\mathbf{Y}, T) \delta(v - v_{nuc}) + C_p(\mathbf{Y}, v) - \frac{3}{\tau_s} \left[\frac{n_p}{n} - \left(\frac{n_p}{n} \right)^{2/3} \right] n \\ & + \frac{1}{2} \int_0^v \beta(w, v-w) n(w) n(v-w) (n_{av}(w) + n_{av}(v-w)) dw - \int_0^\infty \beta(v, w) n(v) n(w) n_{av}(v) dw \end{aligned} \quad (2.13)$$

where $n_p = n_p(\mathbf{x}, t, v)$ is the number density function of primary particles that form an aggregate of volume v per unit volume and $n_{av}(\mathbf{x}, t, v)$ is the average number of primary particles per aggregate of volume v . By definition, the n_{av} is given by:

$$n_{av}(v, t) = \frac{n_p(v, t)}{n(v, t)} \quad (2.14)$$

Note that, unlike n and n_p , n_{av} is not a distribution. It is also worth mentioning that the integration of Eqs. (2.12) and (2.13) over v results in transport equations for the number concentration of aggregates, N , and the number concentration of primary particles, N_p , which are the variables solved for in the monodisperse model discussed earlier.

Sintering of incipient particles smaller than a minimum particle diameter can be considered instantaneous (Tsantilis et al., 2001). A critical diameter $d_{p,min}$ that distinguishes particles

²Unlike J in Eqs. 2.6-2.8, B is a source of particle number density rather than particle number.

that coalesce instantaneously from those that fuse with a finite rate can be introduced in the two-PBE model. This way, particles smaller than the critical diameter are assumed to be spherical, while the number of equations to be solved in discretisation methods is reduced since $n_p(v < v_{p,min}) \equiv n(v < v_{p,min})$, where $v_{p,min} = \pi d_{p,min}^3/6$. This value was selected to be 1 nm in the present study.

From knowledge of $n(v)$ and $n_p(v)$, we estimate the number concentration of primary particles, N_p , the average primary particle diameter, $d_{p,av}$, the average number of primary particles per aggregate, $n_{p,av}$, and the average radius of gyration of aggregates as follows:

$$N_p = \int_{v_d}^{\infty} n_p(v) dv \quad (2.15)$$

$$d_{p,av} = \frac{\int_{v_d}^{\infty} d_p(v) n_p(v) dv}{N_p} \quad (2.16)$$

$$n_{p,av} = \frac{N_p}{N} \quad (2.17)$$

$$R_{g,av} = \frac{1}{2} \frac{\int_{v_d}^{\infty} d_g(v) n(v) dv}{N} \quad (2.18)$$

where $d_p(v)$ is the diameter of the primary particles in an aggregate of volume v , which can be estimated as $v_p(v) = v/n_{av}(v)$ assuming spherical primary particles, $d_g(v)$ is the aggregate diameter given by Eq. (2.5), and v_d is the volume of the smallest detectable particles (1 nm) by SAXS measurements (Camenzind et al., 2008).

The assumption inherent in the two-PBE model is that all aggregates of particle volume v consist of equally-sized spherical primary particles. While this is not strictly true, similar assumptions have been used in experimental techniques (Iyer et al., 2007), while transmission electron microscope (TEM) images of aggregates have repeatedly shown that the distribution of primary particles within an aggregate is relatively uniform (Kammler et al., 2005), supporting the assumptions adopted here. The two-PBE model is a comprehensive approach that yields information for both aggregate and primary particle size distributions and their evolution at a reduced cost as compared with a two-dimensional PBE, but the number of equations to be solved is still twice that of a one-PBE approach, which is significant when it comes to coupling with CFD.

2.2.5 A novel extended one-PBE model for aggregation and sintering

In the present section, we propose an extended one-PBE model that captures aggregation dynamics and can describe particle-morphology evolution while maintaining computational cost to a level commensurable with other one-PBE approaches. One-PBE models have been employed in the modelling of soot formation in laminar and turbulent flows by simply introducing a pre-defined cut-off size (e.g. Netzell et al., 2007; Rodrigues et al., 2018) separating primary particles and aggregates that corresponds to the average primary particle size observed experimentally. This approach does not include a finite-rate sintering model, and a detailed discussion of its shortcomings can be found in Sun et al. (2021). Here, we overcome this problem by solving the PBE together with a transport equation for the number concentration of primary particles, N_p . In this way, the sintering process is incorporated into the model and the one-PBE model can predict the evolution of primary particle size.

The evolution of the PSD of aggregates is described by the same equation (Eq. (2.12)) as in the two-PBE model and it is repeated here for completeness:

$$\begin{aligned} \frac{\partial n}{\partial t} + \frac{\partial(U_j n)}{\partial x_j} = & \frac{\partial}{\partial x_j} \left(D_p(v, T) \frac{\partial n}{\partial x_j} \right) + B(\mathbf{Y}, T) \delta(v - v_{nuc}) + C(\mathbf{Y}, v) \\ & + \frac{1}{2} \int_0^v \beta(w, v-w) n(w) n(v-w) dw - \int_0^\infty \beta(v, w) n(v) n(w) dw \end{aligned} \quad (2.19)$$

To obtain the additional equation, we assume that the primary particle size is monodisperse (i.e. it is the same for aggregates of all sizes, unlike in the case of the two-PBE model). Based on this assumption, n_{av} can be expressed as:

$$n_{av}(v, t) = \frac{v}{v_{p,av}(t)} \quad (2.20)$$

where v is the volume of an aggregate and $v_{p,av} = \pi d_{p,av}^3/6$ is the volume of the primary particles. By substituting Eq. (2.20) into Eq. (2.13) and integrating both sides of (2.13) over v , we derive a transport equation for the number concentration of primary particles:

$$\frac{\partial N_p}{\partial t} + \frac{\partial(U_j N_p)}{\partial x_j} - \frac{\partial}{\partial x_j} \left(D_p(v, T) \frac{\partial N_p}{\partial x_j} \right) = J(\mathbf{Y}, T) - \frac{3}{\tau_s} \left(\frac{V}{v_{p,av}} - \frac{M_{23}}{v_{p,av}^{2/3}} \right) \quad (2.21)$$

where $v_{p,av}$ is the average primary particle volume, V the particle volume fraction and M_{23} is the $2/3$ fractional moment of the PSD. The condensation term is absent since it does not alter the number concentration of primary particles, while the aggregation terms cancel out after the integration of (2.13) over v . Eq. (2.21) is solved along with (2.12) but, unlike the second

equation in the two-PBE model, *does not require discretisation in the particle volume domain*. The $v_{p,av}$ and $n_{p,av}$ are then estimated by Eqs. (2.10) and (2.11). The major advantage of Eq. (2.21) over the conventional one-PBE model is that it brings a finite-rate sintering model into the PBE. Compared with the two-PBE model, the drawback is the assumption of monodisperse primary particle size. The importance of this assumption will be discussed in Section 2.6, where results from both models will be compared with experimental data.

2.3 Numerical Methods

A sectional method is employed for the numerical solution of the PBE (Liu and Rigopoulos, 2019). It is a conservative finite volume method that was recently extended to the two-PBE formulation by Sun et al. (2021). The method provides an accurate prediction of the distribution with a small number of sections while conserving the first moment (with respect to volume) during the aggregation process, which is important for satisfying the mass balance. The method can employ an arbitrary non-uniform grid for discretisation along the particle volume domain and has also been shown to be robust and efficient when incorporated within a CFD framework (Liu and Rigopoulos, 2019; Sun et al., 2021; Sun and Rigopoulos, 2022). This approach is used for both the one- and two-PBE formulations.

The PBE models have been implemented in our in-house CFD code BOFFIN, which is based on the variable-density low Mach number formulation of the Navier-Stokes equations and has been used to simulate laminar and turbulent flames with soot formation that have similar features to the problem considered here (Sun et al., 2021; Sun and Rigopoulos, 2022). The Navier-Stokes equations are discretised by applying the finite volume method on a staggered grid. A second-order central discretisation scheme is employed for the convection and viscous terms, while a second-order accurate Crank-Nicolson method is employed for the temporal integration. The convection and viscous terms are treated implicitly. The pressure-velocity coupling is dealt with an iterative SIMPLE-type scheme. The transport equations for the reactive scalars and discretised PBE are solved with a fractional step method, where separate fractional steps were employed for convection-diffusion, chemical reaction and PBE integration. A backward Euler scheme is used for the integration of the chemical reaction step, while the explicit Euler scheme was selected for the PBE step since the discretised PBE is not stiff. The convection-diffusion term is solved as described above with the addition that van Leer's TVD scheme was employed for the convection terms to ensure boundedness for the reactive scalars.

2.4 Gas-phase and aerosol kinetics

2.4.1 Gas-phase kinetics and radiation

The reaction mechanism for methane combustion used in the present study is the Gas Research Institute (GRI) 1.2 mechanism (Frenklach et al., 1995b,a), containing 175 steps and 31 species. The reduced two-step mechanism proposed by Feroughi et al. (2017) is employed for the HMDSO (precursor) decomposition and oxidation and is shown in Table 2.2. This global two-step HMDSO mechanism has been used previously in the literature to study the synthesis of silica nanoparticles via flame spray pyrolysis (Rittler et al., 2017).

Step	Reaction	A	n	E_a
G1	$\text{HMDSO} + \text{OH} \longrightarrow 2 \text{SiO} + 6 \text{CH}_3 + \text{H}$	6×10^{12}	0.46	15000
G2	$\text{SiO} + \text{H}_2\text{O} \longrightarrow \text{SiO}_2(\text{g}) + \text{H}_2$	8.5×10^{10}	0	5650

Table 2.2: Global two-step reaction mechanism for HMDSO combustion (Feroughi et al., 2017). The reaction rate constant is given in the form $k = AT^n \exp[-E_a/(RT)]$, where T stands for temperature, R for the gas constant, and E_a for the activation energy. The units of the parameter A are expressed in terms of cm, s, and mol, while E_a is given in cal/mol.

Following Barlow et al. (2001), the optically thin hypothesis is invoked in the present study to model thermal radiation from gas species. The radiative loss term in the enthalpy h equation due to the radiation of the most abundant species H_2O , CO_2 , CH_4 and CO can be computed according to:

$$\dot{q}_{rad} = -\frac{4\sigma}{\rho}(T^4 - T_b^4) \sum_i a_{p,i} p_i \quad (2.22)$$

where $\sigma = 5.669 \cdot 10^{-8} \text{ W/m}^2/\text{K}^4$ is the Stefan-Boltzmann constant, $T_b = 295 \text{ K}$ is the ambient background temperature, i -index indicates summation over the four major radiating species, p_i is the partial pressure of species i and $a_{p,i}$ is the Planck mean absorption coefficients expressed as polynomials in temperature (Barlow et al., 2001; Grosshandler, 1993).

2.4.2 Nucleation

We follow an approach similar to that described in Shekar et al. (2012b) to describe the nucleation process. We assume that two molecules (monomers of SiO_2) in the gas phase collide to form a dimer. The dimers are considered to be the first primary particles in the simulation.

The free molecule regime kernel is used to describe the self-collision frequency of the monomers. Based on these considerations, the nucleation rate is given by:

$$J = \frac{1}{2} K_{fm} N_A^2 C_{\text{SiO}_2}^2 \quad (2.23)$$

where N_A is Avogadro's number, C_{SiO_2} is the gas-phase concentration of SiO_2 monomers and K_{fm} is the free molecule coagulation kernel given by:

$$K_{fm} = E_F \cdot 4 \sqrt{\frac{\pi k_b T}{m_{\text{SiO}_2}}} d_o^2 \quad (2.24)$$

where E_F is the Van der Waals enhancement factor whose value is approximated to 1.88 based on the observations of Kennedy and Harris (1990), k_b is the Boltzmann constant, and m_{SiO_2} and d_o are the mass and diameter of a $\text{SiO}_2(\text{g})$ molecule, respectively. It is assumed that $\text{SiO}_2(\text{g})$ molecules have diameter $d_o = 0.44$ nm and that the density of silica particles is $\rho_p = 2196$ kg/m³. After discretisation of the PBE, the nucleation source term in Eq. (2.13) takes the form:

$$B = J \frac{v_{nuc}}{dv_{nuc} v_{m,nuc}} \quad (2.25)$$

where v_{nuc} is the volume of dimers (volume of nuclei), $v_{m,nuc}$ is the representative volume (midpoint) in the section that covers the volume of nuclei and dv_{nuc} is the interval of that section, respectively.

The approach described above will be used for the results in Section 2.6, except for Section 2.6.4 where some alternative nucleation models will be explored in order to investigate the sensitivity of the simulation to the choice of nucleation model.

2.4.3 Condensation

Condensation is considered as a collision process between silica monomers and particles. Let section i denote the range (v_{i-1}, v_i) . In the discretised PBE, three different condensation scenarios are considered that can change the number density, n_i , within section i : a) condensation of monomers on particles of section i , $\omega_{cond,0 \rightarrow i}$, b) condensation of monomers on particles of section $i - 1$ that will enter into section i , $\omega_{cond,i-1 \rightarrow i}$, and c) condensation of monomers on particles of section i that will go to section $i + 1$, $\omega_{cond,i \rightarrow i+1}$. The condensation rate for each of the scenarios mentioned above is evaluated according to (Sun et al., 2021; Rodrigues et al., 2018):

$$\omega_{cond,0 \rightarrow i} = C_{\text{SiO}_2} N_A \int_{v_{i-1}}^{v_i - v_o} \beta_{0,i} n(w) dw \quad (2.26)$$

$$\omega_{cond, i-1 \rightarrow i} = C_{SiO_2} N_A \int_{v_{i-1}-v_o}^{v_{i-1}} \beta_{0,i-1} n(w) dw \quad (2.27)$$

$$\omega_{cond, i \rightarrow i+1} = C_{SiO_2} N_A \int_{v_i-v_o}^{v_i} \beta_{0,i} n(w) dw \quad (2.28)$$

where the collision frequency of a monomer and a particle in section i is evaluated as follows:

$$\beta_{0,i} = 1.28 \sqrt{\frac{\pi k_B T}{2\rho_p}} (d_o + d_{g,i})^2 \sqrt{\frac{1}{v_o} + \frac{1}{v_{m,i}}} \quad (2.29)$$

where $v_{m,i}$ is the volume at the middle of section i , $d_{g,i}$ is the collision diameter of the particles at section i evaluated according to Eq. (2.5). The amplification factor of 1.28 is due to Van der Waals interactions and its value was approximated based on the observations of Kennedy and Harris (1990). Following Sun et al. (2021), in terms of discretised PBE, the condensation source terms in Eqs. (2.12) and (2.13) in section i can be evaluated as:

$$C_i(\mathbf{Y}, v) = (\omega_{cond, 0 \rightarrow i} + \omega_{cond, i-1 \rightarrow i} - \omega_{cond, i \rightarrow i+1}) \frac{v_o}{v_{m,i} dv_i} \quad (2.30)$$

$$C_{p,i}(\mathbf{Y}, v) = (\omega_{cond, 0 \rightarrow i} n_{av,i} + \omega_{cond, i-1 \rightarrow i} n_{av,i-1} - \omega_{cond, i \rightarrow i+1} n_{av,i}) \frac{v_o}{v_{m,i} dv_i} \quad (2.31)$$

where $n_{av,i}$ is the average number of primary particles per aggregate for particles in section i and dv_i is the particle volume range for that section.

2.4.4 Sintering

Sintering of two particles in contact is driven by the tendency of the system to reduce its surface free energy (Koch and Friedlander, 1990). The sintering term in (Eq. (2.13)) thus reduces the number of primary particles. Silica nanoparticles are amorphous materials with low viscosity, and viscous flow (Frenkel, 1945) is considered the dominant mechanism when sintering takes place (Friedlander, 2000). Many different expressions for the sintering characteristic time, τ_s , of silica nanoparticles appear in literature without a consensus on which τ_s is more suitable for flame synthesis modelling (Park and Park, 2015). Goudeli et al. (2015) discussed different sintering times of silica found in literature and tested them in a perfectly stirred reactor (PSR).

In the present study, all four expressions shown in Table 2.3 were tested. The Tsantilis et al. expression provided the best results and was thus employed for all the results shown in Section 2.6, except for Section 2.6.4 where results with all four expressions are compared.

Reference	Characteristic sintering time, τ_s
Tsantilis et al. (2001)	$6.5 \cdot 10^{-13} d_p \exp \left[\frac{8.3 \cdot 10^4}{T} \left(1 - \frac{d_{p,0}}{d_p} \right) \right]$
Ehrman et al. (1998)	$6.3 \cdot 10^{-8} d_p \exp \left[\frac{6.1 \cdot 10^4}{T} \right]$
Kirchhof et al. (2012)	$\frac{(1-1/e)r_s^2}{2^{2/3}(3.5 \cdot 10^{-4})} \exp \left[\frac{4.4 \cdot 10^4}{T} \right]$
Shekar et al. (2012b)	$3.49 \cdot 10^{-14} d_p \exp \left[\frac{11.44 \cdot 10^4}{T} \left(1 - \frac{5.76 \cdot 10^{-9}}{d_p} \right) \right]$

Table 2.3: Characteristic sintering times for silica nanoparticles tested in the current study. The critical particle diameter in Tsantilis et al. (2001) expression is $d_{p,0} = 1 \cdot 10^{-9}$ m; r_s in Kirchhof et al. (2012) expression denotes the radius of a completely coalesced spherical particle. The units are: m for d_p , $d_{p,0}$ and r_s , K for T and s for τ_s .

2.4.5 Aggregation

Expressions for the aggregation kernel, $\beta(v, w)$, depend on the Knudsen number, $Kn = 2\lambda_f/d_g$, where λ_f is the mean free path of the gas estimated by Willeke's formula (Willeke, 1976). The expressions for the free molecule particle size regime ($Kn < 0.1$) and the continuum regime ($Kn > 10$) are (Friedlander, 2000):

$$\beta_{fm}(v, w) = E_f \sqrt{\frac{\pi k_B T}{2\rho_s}} \left(\frac{1}{v} + \frac{1}{w} \right)^{1/2} (d_{g,v} + d_{g,w})^2 \quad (2.32)$$

$$\beta_c(v, w) = \frac{2k_B T}{3\mu} \left(\frac{C_c(v)}{d_{g,v}} + \frac{C_c(w)}{d_{g,w}} \right) (d_{g,v} + d_{g,w}) \quad (2.33)$$

where $C_c(v) = 1 + 1.257Kn$ is the Cunningham slip correction factor. A harmonic mean of the two expressions (Pratsinis, 1988) is employed for the transition regime ($0.1 < Kn < 10$):

$$\beta_{tr}(v, w) = \frac{\beta_{fm}(v, w)\beta_c(v, w)}{\beta_{fm}(v, w) + \beta_c(v, w)} \quad (2.34)$$

2.4.6 Thermal radiation from particles

In heavily particle-laden flames, thermal losses due to the radiation from nanoparticles need to be accounted for in the model (Modest, 2003). The radiative loss term due to the radiation from the nanoparticles is expressed as:

$$\dot{q}_{rad,p} = -\frac{4\sigma}{\rho} C_s f_v (T^5 - T_{amb}^5) \quad (2.35)$$

where f_v is the silica volume fraction and C_s is a proportionality constant. It can be shown that, in the optically thin limit, the heat loss due to emission of thermal radiation from a

spherical object surrounded by a vacuum is proportional to the object's volume (Modest, 2003). Therefore, it is reasonable that $\dot{q}_{rad,p}$ is proportional to f_v in Eq. (2.35). Furthermore, Lee (2011) studied the emission properties of silica aggregates at high temperatures and employed the below expression for the spectral radiant intensity E_λ from the particles in a flame:

$$E_\lambda = \frac{A \cdot 2\pi h c^2 \epsilon(\lambda, T) f_v}{\lambda^5 \left[\exp\left(\frac{hc}{\lambda k_b T}\right) - 1 \right]} \quad (2.36)$$

where h is Planck's constant, c the speed of light in the medium, λ the wavelength, $\epsilon(\lambda, T)$ the emissivity of silica and A is an arbitrary constant. Lee (2011) observed that ϵ is a linear increasing function of temperature, while $\epsilon(\lambda, T)$ is expected to be a weak function of λ at the wavelengths of interest; therefore, the emissivity of silica is assumed to follow the relationship $\epsilon \propto (C_s/A)T$. Based on these considerations, integration of Eq. (2.36) over λ and all possible directions results in an expression for the radiative heat flux similar to Eq. (2.35), giving support to the radiation model adopted here. In the absence of any information for the value of A , the value $C_s = 1100 \text{ m}^{-1}\text{K}^{-1}$ was selected in the present study, which is lower than the value of $1307 \text{ m}^{-1}\text{K}^{-1}$ used in sooting flame simulations and gave good agreement with the experimental results, as will be shown in Section 2.6.1.

2.5 Simulation parameters

2.5.1 Flame configuration

The flame under investigation is the “S-2” laminar case of Camenzind et al. (2008) and, to the best of our knowledge, the present work is the first simulation of this experiment. The synthesis of silica nanoparticles takes place by oxidation of HMDSO in oxygen/methane diffusion flames. This flame was selected because it is one of the few laminar flames for which *in-situ* experimental data for the particles are available in the literature (see Table 2.1); Camenzind et al. (2008) provided a plethora of particle data for several heights above the burner (HAB) obtained via *in-situ* SAXS measurements. More information on the selection of the Camenzind experiment is given in Appendix A. The experimental setup is shown in Fig. A.1 and more information on the geometric characteristics of the co-flow diffusion flame reactor and the experimental conditions employed in the experiment of Camenzind et al. (2008) are given in Appendix A.1. The Reynolds number of S-2 flame, based on the bulk velocity and the outer diameter of the reactor, was $Re \approx 1414$.

Stream	Profile	u_{inlet} [m/s]	T [°C]	Mole fractions [%]
Inner	Laminar	$U = 6.715$	75	$X_{CH_4} = 61.338$; $X_{N_2} = 36.803$; $X_{HMDSO} = 1.859$
1st annulus	Laminar	$U_1 = 2.057$	75	$X_{N_2} = 100$
2nd annulus	Laminar	$U_2 = 8.57$	75	$X_{O_2} = 100$
Co-flow air	Uniform	$U_{air} = 0.4$	20	$X_{N_2} = 76.83$; $X_{O_2} = 23.17$

Table 2.4: Inlet boundary conditions, where u_{inlet} denotes the stream bulk inlet velocity in the streamwise direction. The inlet velocity profile at the inflow is presented in Appendix B.2, Fig. B.2.

2.5.2 Computational setup

Two-dimensional axisymmetric simulations were performed, with an axisymmetric boundary condition being applied along the centreline and a symmetry boundary condition being applied at the opposite side. A zero-gradient boundary condition was applied at the outlet boundary in the streamwise direction. In the plots, the r coordinate is defined to denote the cross-stream direction. The stream bulk velocities u_{inlet} of the jets coming from the inner tube, the first and second annulus were $U = 6.715$ m/s, $U_1 = 2.057$ m/s and $U_2 = 8.57$ m/s, respectively. The inlet velocities were estimated based on the given mass flow rates reported earlier and by assuming that the temperature of the streams was 75°C. At the inflow, laminar flow velocity profiles were employed for the inner jet as well as through the annular sections for the other two jet streams. The inlet velocity profiles are shown in Appendix B.2, Fig. B.2. In the absence of any information for the entrainment velocity, a uniform velocity $U_{air} = 0.4$ m/s was used for the air co-flow stream at the inlet and the ambient temperature was set to $T_{amb} = 20^\circ\text{C}$. Test cases showed that U_{air} has a minor effect on the results (see Appendix B.3, Fig. B.3). The mole fractions of the species for the inner stream were set to $X_{CH_4} = 61.338\%$, $X_{N_2} = 36.803\%$ and $X_{HMDSO} = 1.859\%$. The thickness of the burner tubes was 0.3 mm, which was taken into account in the simulation by applying a no-slip boundary condition at these radii. The inlet boundary conditions employed in this study are summarised in Table 2.4.

The size of the computational domain is $60D \times 15D$, where $D = 1.8$ mm is the inner tube diameter. A computational grid with 264×162 cells with spacing increasing exponentially by factors 1.0132 and 1.03 in the axial and radial directions, respectively, was employed. Images of the computational domain and grid are shown in Appendix B.4, Fig. B.4. Grid refinement was employed at the height of the second annulus to ensure that at least ten cells were used to

capture the inlet velocity profile. Tests with a finer grid comprising about 4.5 times more cells showed that grid independence had been achieved, and the results are shown in Appendix B.5, Fig. B.5. The time step was $\Delta t = 10^{-7}$ s, resulting in a maximum Courant-Friedrichs-Levy (CFL) number of 0.03. Each simulation was run until the solution reached a steady state independent of the initial conditions. Following this, the simulations were run for more than 3 million time steps, corresponding roughly to 0.4 seconds of the simulated process.

Regarding the discretisation of the PBE, the particle volume domain covered particle sizes from 0.44 nm to 1 μ m in diameter and was discretised with an exponential grid comprising 60 intervals. Convergence studies with a perfectly stirred reactor showed that this grid sufficed to describe the PSD evolution accurately.

Finally, to ensure that conservation of mass was achieved in the simulation, the silica mass flow rate at the exit of the computational domain was calculated as $\int_{A_{out}} \rho_{SiO_2} f_v \mathbf{u} \cdot d\mathbf{A} = 4.755$ g/h. The relative difference with the reported (Camenzind et al., 2008) silica production rate (4.8 g/h) is less than 1%.

2.6 Results and discussion

In the present section, the results are presented and discussed. Particular emphasis is given to the validation of the modelling strategy adopted in this study by comparing numerical predictions of particle field quantities with reference *in-situ* experimental data. Numerical simulations performed with the three population balance models described in Section 2.2 are referred to as “2PBE”, “1PBE” and “Mono”, while “Exp” refers to experimental results. An analysis of the calculated timescales and rates is presented to draw insight into the model predictions. Results obtained from alternative sintering and nucleation models are also presented in order to demonstrate the sensitivity of the predictions to modelling choices. Finally, the computational performance of the PBE models is analysed.

2.6.1 Flow field and temperature

Contour plots of the velocity and temperature fields are shown in Fig. 2.1. The numerical results from the three models tested in this study were in good agreement with each other in terms of temperature and velocity fields; therefore, contour plots only for the two-PBE model are shown. The simulation was allowed to reach a steady state before the results were extracted. Fig. 2.1 clearly shows that the solution has reached a steady state. Plots of the volume fraction

and primary particle diameter field are shown in Fig. 2.2a and 2.2b, respectively. Particles are formed within the flame reaction zone, which is located approximately 1.4 mm away from the flame centreline. It can be seen that particles stay within this thin layer at all downstream locations. This is reasonable considering the very low diffusivity of particles (estimated from the Stokes-Einstein relation (Friedlander, 2000)) and the laminar flow in the experiment.

A plot of the primary particle diameter field is depicted in Fig. 2.2b. Primary particles have diameters less than 15 nm at low HABs, while they grow in size rapidly at $3.5 < \text{HAB} < 5$ cm at the flame front and eventually reach constant values downstream. It is observed from Fig. 2.2a and 2.2b that the maximum primary particle sizes appear within the thin layer where the maximum silica volume fraction is located. As will be explained later, in the vicinity above the burner, the particle formation rate is comparable to particle aggregation rates, resulting in small average primary particle sizes. After the flame front at $3.5 < \text{HAB} < 5$ cm, conversion of the precursor is almost complete, the effect of particle nucleation is less significant and sintering becomes the dominant mechanism, leading to rapid primary-particle growth. At $\text{HAB} > 5$ cm, sintering ceases, and aggregation becomes the dominant mechanism. This explains why the primary particle size remains almost constant at these locations.

A comparison of numerical results for temperature with the experimental data of Camenzind

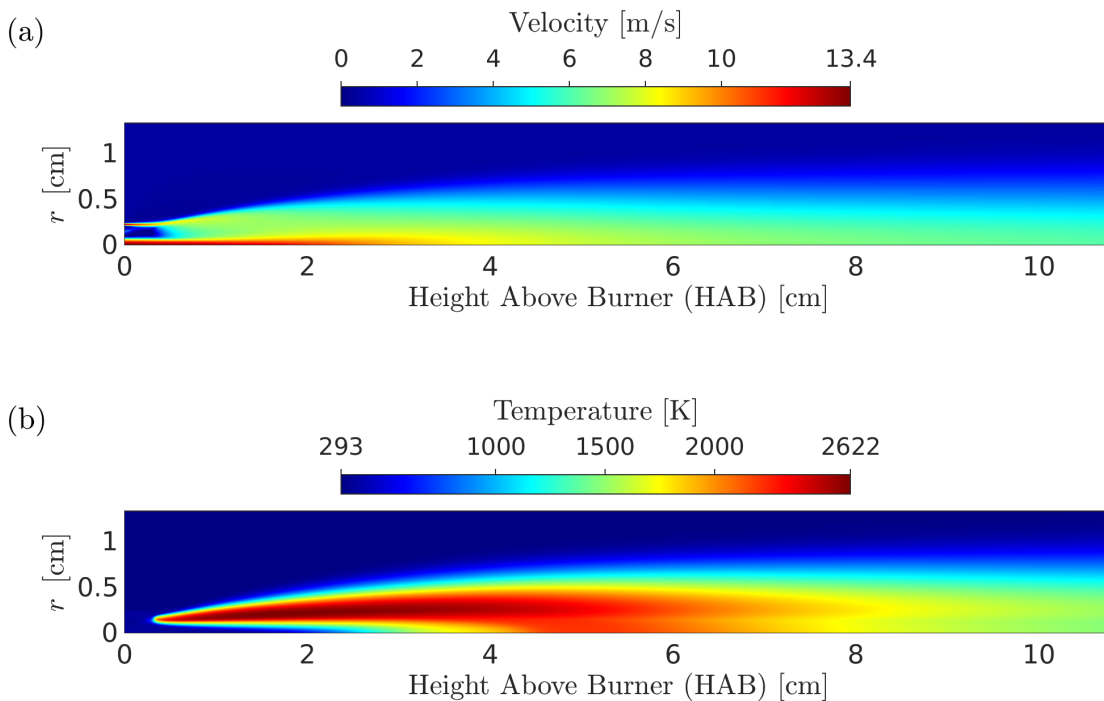


Figure 2.1: Contour plots of (a) velocity and (b) temperature fields.

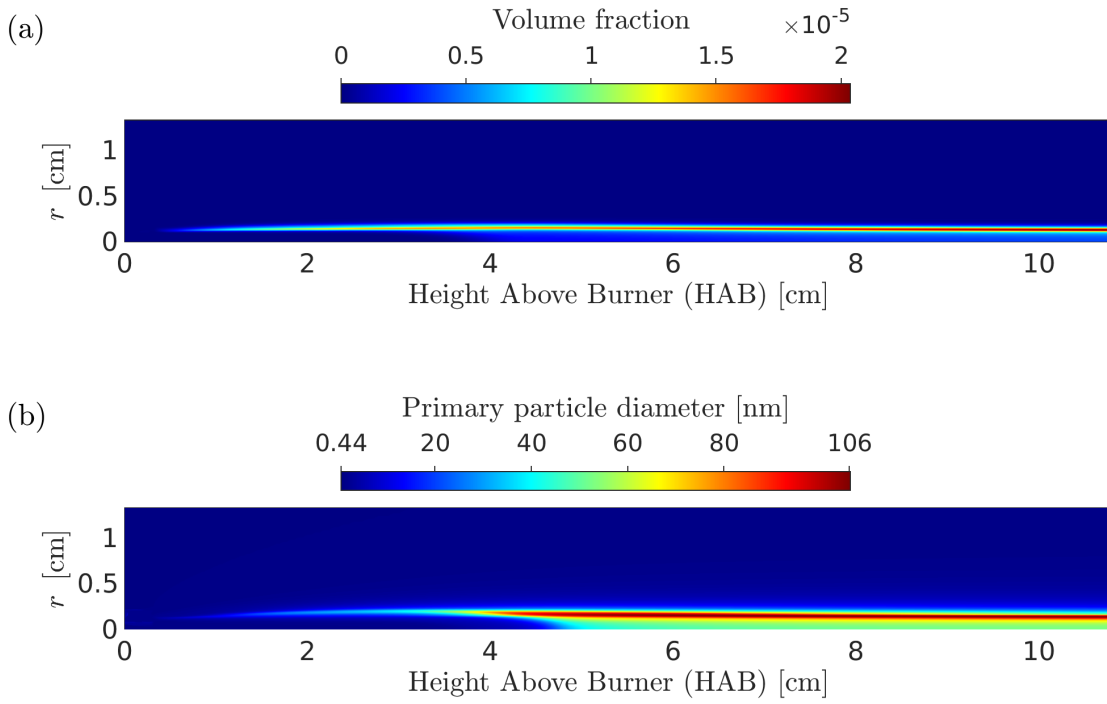


Figure 2.2: Contour plots of (a) silica volume fraction and (b) primary particle diameter fields.

et al. (2008) is shown in Figure 2.3. As before, only results with the two-PBE model are shown in Fig. 2.3 and Fig. 2.4 since all of the three PBE models resulted in similar temperature distributions. Accurate prediction of temperature is the cornerstone of flame synthesis modelling, as it is driving many of the subsequent processes. In the present study, numerical results for flame temperature are in good agreement with the experimental data, largely due to the direct coupling of detailed chemistry with flow, the absence of modelling uncertainties involved in turbulent flame simulations (turbulence modelling and turbulence-chemistry interaction) and the inclusion of the model for the thermal radiation from particles.

The experimental temperature data were obtained using Fourier transform infrared (FTIR) spectroscopy (Griffiths and De Haseth, 2007; Morrison Jr et al., 1997) which is a line-of-sight technique over the total flame width. It has been documented that the FTIR data represent a radial-average temperature of the diffusion flame in the region close to the burner tip, where reactants are not mixed (Camenzind et al., 2008). In fact, in this region, the temperature on the flame centreline is well below the reported values, which can also be observed in Fig. 2.1b. For this reason, numerical results for the radial maximum value of temperature at each height above the burner are plotted (solid black line) in Fig. 2.3, instead of the centreline values. Radial maximum temperatures are more representative of the experimental data. Emitted

radiation (relevant to FTIR measurements) scales with the fourth power of temperature; thus, it can be expected that regions with the highest temperature would dominate in the FTIR data analysis. Nevertheless, radial averaging of values of cells in the flame reaction zone was performed, and results are also presented in Fig. 2.3 (solid magenta line). The flame reaction zone was approximated with the cells whose value of CO_2 concentration is greater than 80% of the radial maximum value at each height above the burner. However, both lines in Fig. 2.3 lie within an average experimental error of ± 60 K (Kammler et al., 2002) for most HABs, indicating that the flame temperature was predicted accurately by the simulation.

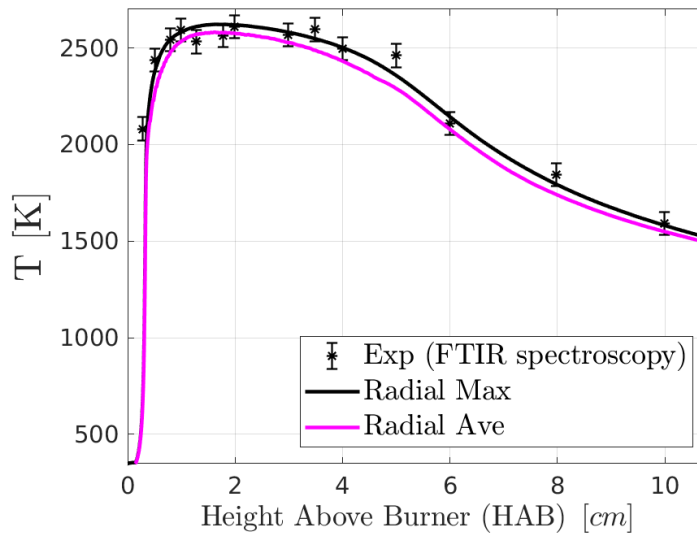


Figure 2.3: Comparison of numerical predictions (two-PBE model) with the experimental FTIR data of Camenzind et al. (2008) for flame temperature along the centreline and effect of radial averaging. An average experimental error of ± 60 K given by Kammler et al. (2002) was used in the figure for the FTIR data.

In order to quantify the effect of thermal radiation from gas species and from particles, two alternative simulations were performed and are compared with the one including radiation in Fig. 2.4. In one case (red line), all radiation thermal losses were neglected, while in another (green line) radiation from gas species only was considered. When only radiation from gas species is considered, then the CFD model considerably overestimates the experimental data at downstream locations. A better agreement with the experimental data is achieved when the emission of radiation from particles is included. These results suggest that thermal losses due to radiation from particles have a non-trivial effect on the evolution of the temperature field.

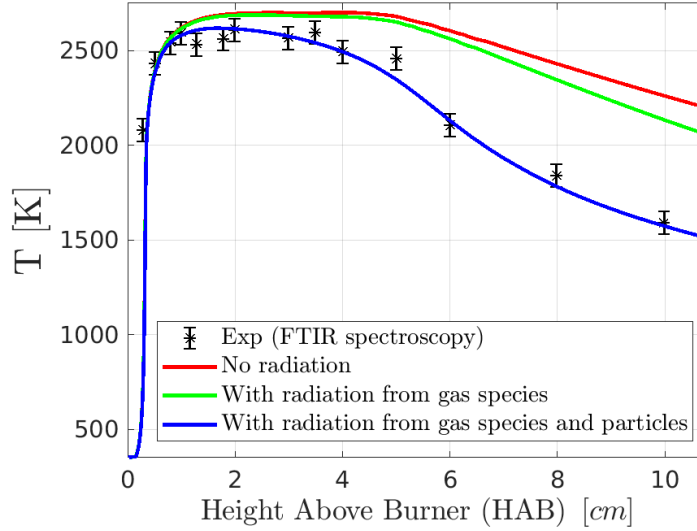


Figure 2.4: Comparison of numerical predictions (two-PBE model) with experimental data for flame temperature and effect of emission of thermal radiation from gas species and from particles. Results of the radial maximum temperature for each case are compared with the experimental FTIR data of Camenzind et al. (2008). An average experimental error of ± 60 K given by Kammler et al. (2002) was used in the figure for the FTIR data.

2.6.2 Comparison with experimental SAXS data

Comparisons of numerical predictions with the experimental SAXS data of Camenzind et al. (2008) will now be shown. In SAXS measurements, a monochromatic X-ray beam penetrates the flame and is collected on a SAXS detector located a few meters away from the flame. However, particle quantities cannot be uniform in the radial direction in the vicinity of the burner tip where reactants are not mixed. As discussed earlier, the flame reaction zone, where particles are formed, is located slightly off the centreline. The experimental particle data refer to the thin flame zone where the scattered intensity (relevant to SAXS measurements) should be maximum. This was also discussed in Sztucki et al. (2007) where it was found that the maximum scattered intensity was achieved when the X-ray beam penetrated the flame in the soot growth zone located slightly off the centreline of the flame. For this reason, we present data along the pathline of maximum silica volume fraction, accounting also for the radius of the beam $r_b = 0.1$ mm. Specifically, we first identify the radial location (r_ϕ) of the maximum silica volume fraction for each axial location. Then we radially average the particle data in the range $r = r_\phi \pm r_b$ (accounting for the beam radius) for each axial location. For clarity, this averaging procedure of the simulation data is not to be confused with the signal processing of the SAXS data performed by Camenzind et al. (2008). The experimental data for particle morphology

quantities were obtained by SAXS data analysis using the unified fit model (Beaucage, 1995, 2004); however, the original SAXS signals are unavailable to the author. It should also be mentioned that the smallest detectable particle size by the SAXS measurements was 1 nm, and this was taken into account in the post-processing of the simulation results by not accounting for particles smaller than that when averaging the PSD.

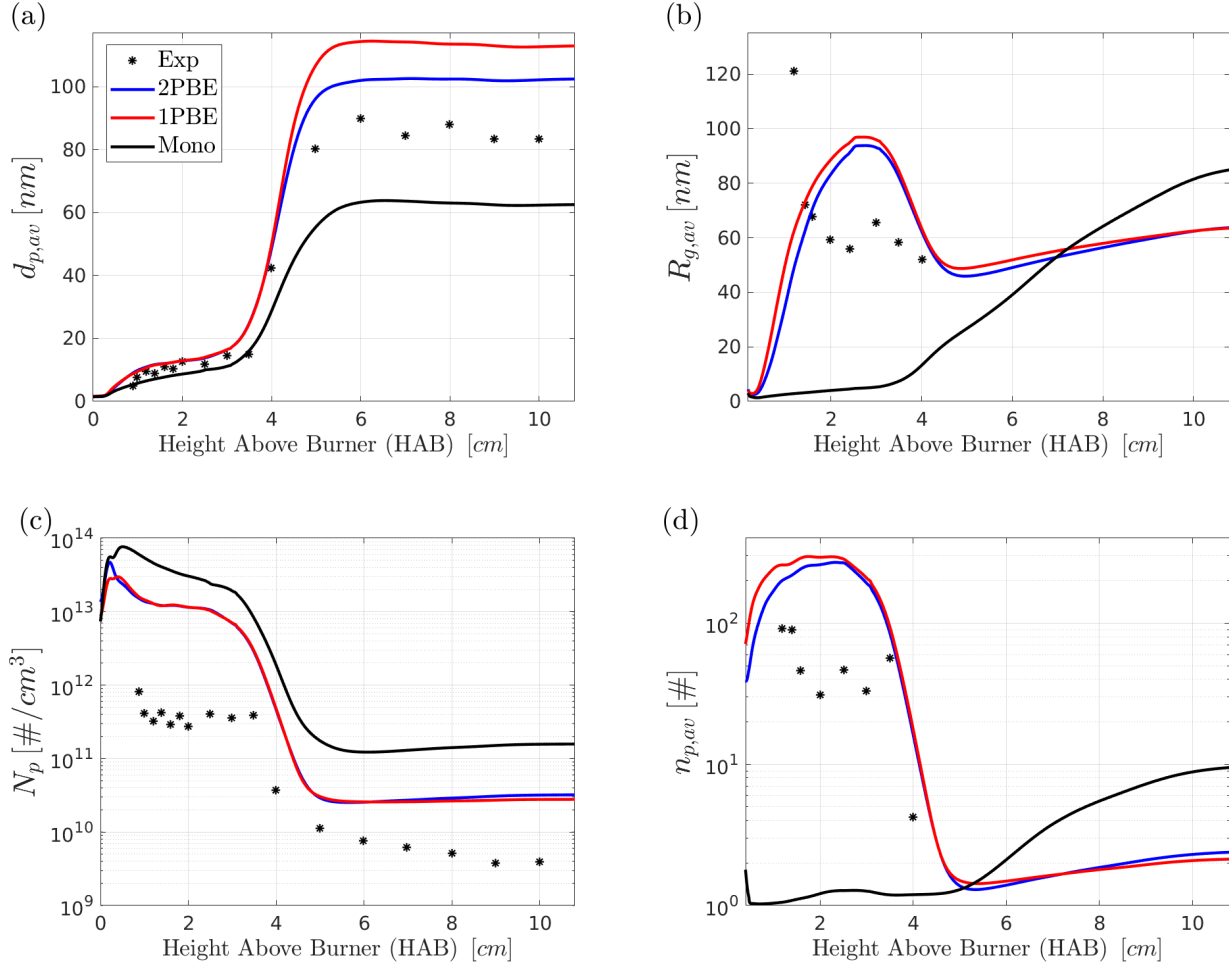


Figure 2.5: Comparison of the experimental SAXS data of Camenzind et al. (2008) with numerical predictions for (a) primary particle diameter, (b) radius of gyration of aggregates, (c) primary particle number concentration and (d) average number of primary particles per aggregate along the pathline of maximum silica volume fraction. Results were obtained with the two-PBE, the extended one-PBE, and the monodisperse model (described in Section 2.2). A logarithmic scale was used for the vertical axes of figures (c) and (d).

The average primary particle diameter, $d_{p,av}$, the average aggregate radius of gyration, $R_{g,av}$, the number concentration of primary particles, N_p , and the average number of primary particles per aggregate, $n_{p,av}$, along the pathline of maximum silica volume fraction are shown in Fig. 2.5a, 2.5b, 2.5c and 2.5d, respectively. The plots show the results from the three PBE models

and the measurements. Focussing initially on the results obtained with the more comprehensive two-PBE model, we can see that good agreement with experiments is found for primary particle diameters. In particular, the model predicts relatively well $d_{p,av}$ at low HABs while overestimating by about 15% the experimental data at downstream locations ($HAB > 5$ cm). This indicates that aggregation and sintering are represented well by the model. Furthermore, fair agreement can be observed for R_g and $n_{p,av}$. In particular, the model slightly overestimates R_g (by about 43% at $HAB = 3$ cm), most likely due to uncertainties involved in the precursor decomposition kinetics/nucleation model and the questionable validity of Eq. (2.5) at the first stages of particle synthesis. Furthermore, $n_{p,av}$ is overestimated, and this is consistent with the overprediction of N_p discussed below.

Numerical predictions for N_p are in qualitative agreement with the SAXS data. However, the particle formation rate is overpredicted, leading to an overestimation of N_p by approximately 1.5 orders of magnitude (Fig. 2.5c). This discrepancy is most likely related to uncertainties involved in the SAXS measurements, precursor decomposition kinetics and the nucleation model. The experimental data for particle morphology quantities were obtained by SAXS data analysis using the unified fit model (Beaucage, 1995, 2004), while information for N_p was extracted by the data (Camenzind et al., 2008). Regarding the precursor decomposition/oxidation reaction mechanism, data obtained with low-pressure flames and low HMDSO concentrations were employed for the development of the two-step chemical reaction mechanism of (Feroughi et al., 2017), while the flame examined here was at atmospheric pressure and the precursor concentration was relatively high. Nevertheless, it should be mentioned that the good agreement with primary particle diameter is more important, as this quantity is of more practical interest.

Aggregates are formed at low HABs where $n_{p,av}$ takes values close to 200, while compact - almost spherical - particles are formed at downstream locations where $n_{p,av}$ declines quickly and reaches values close to 3 (see Fig. 2.5d). The reduction of $n_{p,av}$ is also observed in the SAXS data at $HAB = 4$ cm. Experimental data for downstream locations are unavailable, but the model suggests that the residence time of particles at high temperatures (i.e. at $3.5 < HAB < 5.5$ cm) is large enough for almost complete coalescence of aggregates, leading to compact structures at $HAB > 6$ cm. This can also be seen in Figs. 2.5a and 2.5b by comparing the values of $d_{p,av}$ and $R_{g,av}$ in the two-PBE model predictions at downstream locations; twice $R_{g,av}$ is only slightly greater than $d_{p,av}$.

Results obtained with the extended one-PBE and the monodisperse model are also presented

in Fig. 2.5. Overall, good agreement was found between the two-PBE and the extended one-PBE models. Specifically, the extended one-PBE model somewhat overestimated primary particle sizes at downstream locations (by about 35% relative to the SAXS data and by about 10% relative to the two-PBE results at $HAB = 10$ cm), while an excellent agreement was found between the two models for the rest of the particle quantities. On the other hand, the monodisperse model underestimates $d_{p,av}$ (Fig. 2.5a) (by about 26% relative to the SAXS data and by about 39% relative to the two-PBE results at $HAB = 10$ cm). Furthermore, the monodisperse model underestimates $R_{g,av}$ (Fig. 2.5b) and $n_{p,av}$ (Fig. 2.5c), at the early stages of particle synthesis, i.e. at $HAB < 5$ cm, while the two-PBE and the extended one-PBE models describe the evolution of particle morphology in a more accurate manner (both quantitatively and qualitatively).

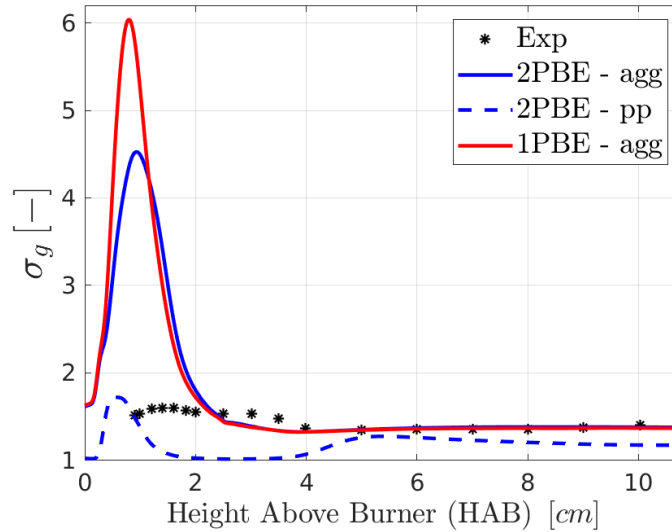


Figure 2.6: Comparison of the experimental SAXS data of Camenzind et al. (2008) with numerical predictions for the geometric standard deviation of aggregate (“agg”) and primary particle (“pp”) size distributions along the pathline of maximum silica volume fraction.

Measurements are also available for the geometric standard deviation, σ_g , of the primary particle size distribution. This quantity can be predicted only by the two-PBE model. However, as explained earlier, aggregates at downstream locations are quite compact and comprise only a few primary particles, most likely connected by sinter bonds; thus, they would be difficult to distinguish by SAXS measurements. It is therefore worth comparing with predictions of σ_g for both primary particles and aggregates. Fig. 2.6 shows the measurements and the predictions by the two-PBE (for both primary particles and aggregates) and the one-PBE (for aggregates only) models; results with the monodisperse model are not included since σ_g in that case is unity by

definition. It can be seen that better agreement is found when comparing with the simulation results for aggregates than for primary particles. In particular, the figure shows good agreement between the numerical predictions of σ_g for aggregates with the SAXS data (approximately 1.4% relative difference at HAB = 10 cm) at downstream locations where aggregation is the dominant mechanism and the PSD attains the self-preserving distribution (the σ_g for aggregates approaches an asymptotic value of ≈ 1.38 at HAB > 7 cm). The two-PBE and one-PBE models agree well with each other except at low HABs, where both overpredict the SAXS data. At that stage, nucleation, condensation and aggregation take place simultaneously and the PSD is far from the self-preserving state. The disagreement can be partly explained by the fact that σ_g was estimated from SAXS measurements based on the measured polydispersity index and assuming a lognormal particle size distribution of spherical primary particles (Kammler et al., 2005), while at these HABs the PSD was far from lognormal.

2.6.3 Timescale analysis

The coupling of CFD with population balance allows the calculation of the timescales of different processes at all points in the domain, which can provide further insight on the results presented so far and furthermore help identify the dominant mechanisms. Timescales are defined for nucleation, aggregation and sintering in a consistent way and summarised in Table 2.5; in all cases, the total number of particles (primary or aggregates, depending on the process) is divided by the rate of the process (or its absolute value when needed). We also define a flow timescale as the residence time, τ_{res} , of particles along the pathline of maximum silica volume fraction.

Process	Nucleation	Aggregation	Sintering	Flow
timescale, τ	$\frac{\int_0^\infty n(v)dv}{J}$	$\frac{\int_0^\infty n(v)dv}{\left -\frac{1}{2} \int_0^\infty \int_0^\infty n(w)n(v)dw dv \right }$	$\frac{\int_0^\infty n_p(v)dv - \int_0^\infty n(v)dv}{\left -\frac{3}{\tau_s} \left(\frac{V}{v_{p,av}} - \frac{M_{23}}{v_{p,av}^{2/3}} \right) \right }$	$\int_0^x \frac{1}{u_x(x')} dx'$

Table 2.5: Definition of timescales for processes encountered in silica flame synthesis.

Results for the nucleation, aggregation and sintering rates along the pathline of maximum silica volume fraction are presented in Fig. 2.7a, while results for the timescales are depicted in Fig. 2.7b. The value of N_p is quite constant at HAB < 3.5 cm, while it starts to drop at downstream locations (see Fig. 2.5c). At low HABs, the flame front is positioned slightly off the centreline and particles are constantly formed within the flame reaction zone. Nucleation and

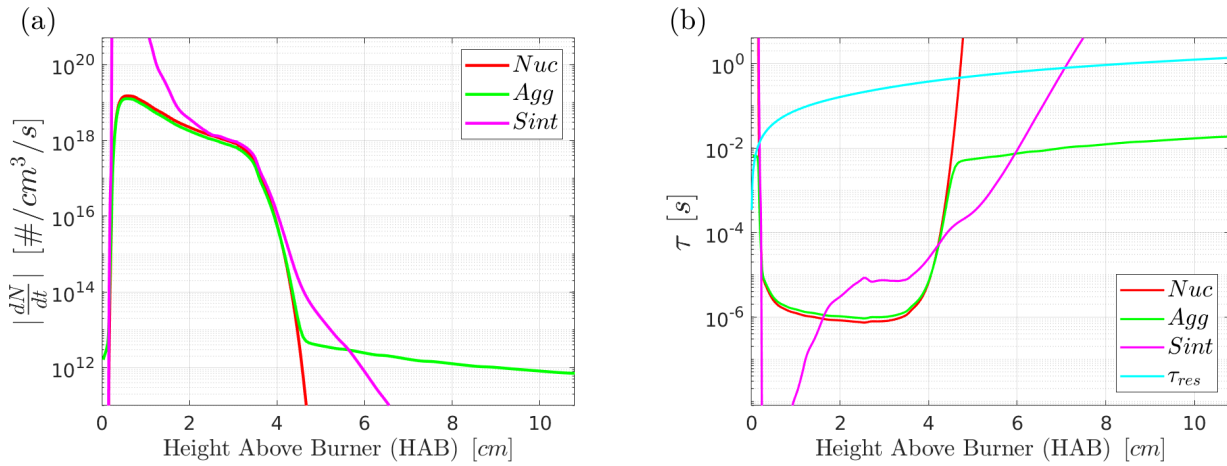


Figure 2.7: Rates of kinetic processes (absolute values) and timescales along the pathline of maximum silica volume fraction. Results were obtained with the two-PBE model. Note that, for the sintering process in (a), the rate refers to the number concentration of primary particles, N_p . A logarithmic scale was used for the vertical axes.

aggregation rates reach comparable values (see Fig. 2.7a) within this zone resulting in constant primary particle number concentrations in this region (Fig. 2.5c) and relatively small average primary particle sizes (Fig. 2.5a). On the other hand, after the flame front on the centreline (HAB $\approx$ 3.5 cm), precursor conversion is almost complete; the nucleation rate decreases by several orders of magnitude and sintering of particles becomes the dominant mechanism. This is demonstrated by Fig. 2.7a, where it can be seen that the sintering rate is higher than the nucleation and aggregation rates at $4 < \text{HAB} < 5.6$ cm. In terms of timescales, the sintering timescale is smaller than (or comparable to) the nucleation and aggregation timescales at $4 < \text{HAB} < 6$ cm (Fig. 2.7b), indicating that the effect of sintering is more profound in this region. This explains the reduction of N_p and the apparent growth of the average primary particle sizes (see Fig. 2.5a) at these HABs. At HAB > 5 cm, the temperature decreases, attenuating the effect of sintering and resulting in constant $d_{p,av}$ values. Aggregation becomes the dominant mechanism at HAB ≈ 6 cm (see the intersection of the lines in Fig. 2.7b). The sintering timescale becomes greater than the residence time of particles in the flow at HAB ≈ 7 cm, signifying that the effect of sintering is negligible at HAB > 7 cm.

2.6.4 Investigation of alternative model choices

Models for the characteristic sintering time

As explained in Section 2.4.4, the results shown so far were obtained with the Tsantilis et al. (2001) expression for the characteristic sintering time, τ_s . Simulations were also performed with the other models shown in Table 2.3, and the results for $d_{p,av}$ and $R_{g,av}$ are shown in Fig. 2.8. The model of Ehrman et al. (1998) predicts greater sintering times (smaller coalescence rates) compared to that of Tsantilis et al. (2001), leading to an underestimation of $d_{p,av}$ for all HABs. The experimentally derived expression of Kirchhof et al. (2012) fails to capture the coalescence of the nucleus-size nanoparticles (it must be noted that particle diameters larger than 10 nm were considered by Kirchhof et al., 2012) and thus does not predict well the particle morphology. Shekar et al. (2012b) proposed an expression where the sintering parameters were acquired by fitting their model to the experimental data of Seto et al. (1997). The resulting sintering time leads to an overestimation of $d_{p,av}$ at low HABs and an underestimation of $d_{p,av}$ at large HABs. The use of the expression of Tsantilis et al. (2001) slightly overpredicts $d_{p,av}$ at the downstream locations. The model of Tsantilis et al. (2001) accounts for the particle-size dependence of the melting point of silica and the parameter $d_{p,0} = 1 \cdot 10^{-9}$ m (see Table 2.3) was proposed as a first approximation. Overall, results obtained with the τ_s of Tsantilis et al. (2001) are in better agreement with the experimental data compared to the other τ_s cases, at least for the flame conditions examined in the present study. Regarding $R_{g,av}$, the sintering models predict similar trends and slightly overestimate the SAXS data, with the exception of the Kirchhof et al. (2012) model, which yields a greater overprediction.

Nucleation models

The reliable prediction of particle nucleation rates remains an unresolved problem in the field of flame synthesis of nanomaterials (Rosner, 2005). In the present section, we investigate some alternatives to the approach described in Section 2.4.2 and used to obtain the results presented so far.

It is customary in flame-synthesis studies to assume that fast precursor oxidation leads to silica monomers (molecules) that serve as the first primary particles (Ulrich, 1971). This approach will be referred to here as the instantaneous nucleation assumption. The reasoning behind this approach is that monomer vapour is usually in a supersaturated state, the nucleation barriers can be neglected (Xiong and Pratsinis, 1991) and, even if the critical clusters (nuclei)

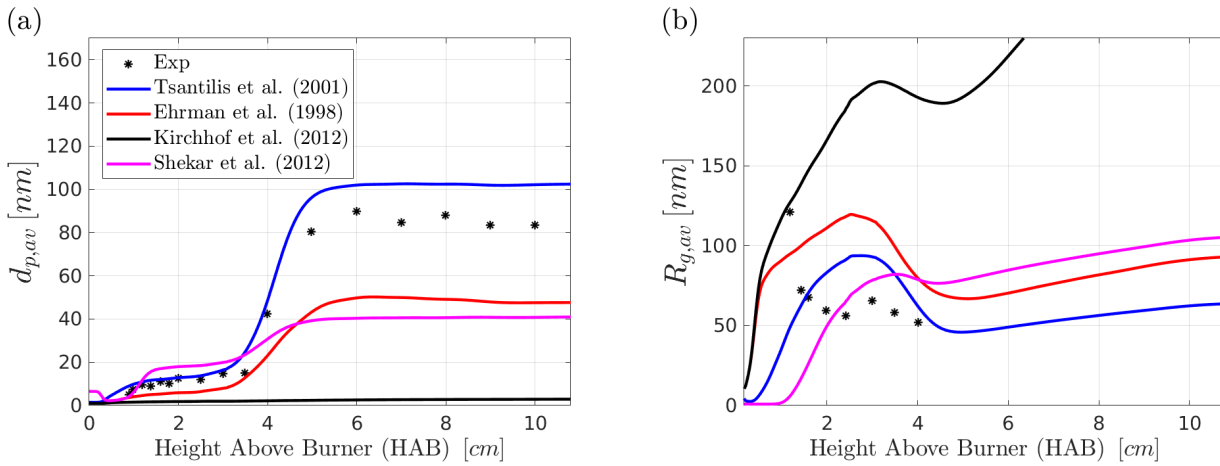


Figure 2.8: Effect of sintering time on (a) primary particle diameter, (b) aggregate radius of gyration. Results were obtained with the two-PBE model. Comparison is also made with the experimental data of Camenzind et al. (2008).

comprise few molecules, coagulation quickly extinguishes initial differences (Gröhn et al., 2011; Tsantilis et al., 2002). Theoretical tools to describe nucleation rate have also been developed, with the most celebrated one being the classical nucleation theory, a discussion of which can be found, for example, in Ford (2004). Here, we compare instantaneous nucleation, the classical nucleation theory as formulated by Girshick and Chiu (1989) and the dimers-based approach that was discussed in Section 2.4 and used for the results presented in Section 2.6. Results obtained with the three nucleation models for $d_{p,av}$ and $R_{g,av}$ along the pathline of maximum silica volume fraction are presented in Fig. 2.9a and 2.9b, respectively. The classical theory overestimates $d_{p,av}$ at low HABs, while the instantaneous model overestimates $R_{g,av}$ at low HABs. The dimers-based approach seems to describe better the evolution of the particle morphology; however, all models predict similar particle sizes at downstream locations.

2.6.5 Analysis of computational performance

The total CPU time per timestep for simulating all processes (including flow field, scalar convection/diffusion, gas phase reaction, and PBE solution) for each of the three models is presented in Table 2.6 and it can be seen that the simulation with the one-PBE model requires about a third of the CPU time spent on the two-PBE model. Remarkably, it is even comparable with the time required by the monodisperse model (less than twice). This difference is much greater than suggested by the number of equations in each model (116 for the two-PBE compared with 61 equations for the extended one-PBE) and is explained by the fact that the discretisation

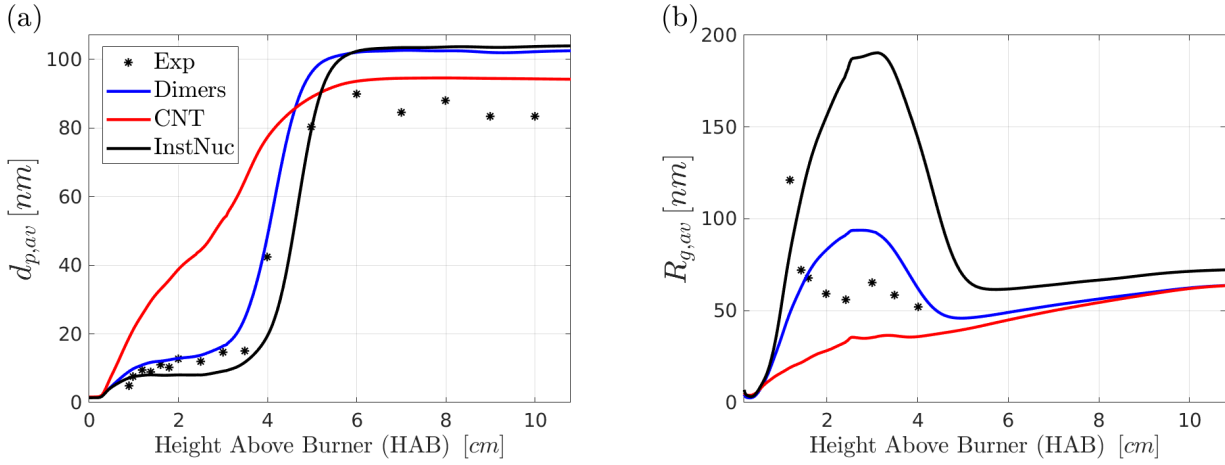


Figure 2.9: Effect of nucleation model on (a) primary particle diameter and (b) aggregate radius of gyration. Three models are compared: instantaneous nucleation (“InstNuc”), classical nucleation theory (CNT) and the dimers-based approach that was used for the rest of the results. Results were obtained with the two-PBE model. Comparison is also made with the experimental data of Camenzind et al. (2008).

of the particle volume domain in the one-PBE model allows for the tabulation of the aggregation kernel. On the other hand, tabulation of the aggregation kernel for the two-PBE was not employed because it would be very memory-intensive; in particular, tabulation of the kernel in the one-PBE requires storing a three-dimensional matrix (for two volumes and d_p) since, at one time instant, d_p is the same for all particle volume pairs, while the two-PBE requires a four-dimensional matrix since every section has a different d_p . This discussion demonstrates that coupling CFD with population balance is computationally feasible, while the extended one-PBE model is a major step forward in terms of balancing accuracy and computational speed. It should be emphasised that, while this reduction in CPU time is not essential for the simulation of the present laminar flame as the total CPU time is manageable with all approaches, the advantages offered by the extended one-PBE model will be crucial when it comes to the coupling of detailed population balance modelling with LES for the simulation of turbulent flame synthesis.

2.7 Summary

In the present work, the synthesis of silica nanoparticles in a laminar diffusion flame was studied via population balance modelling coupled with CFD. Three population balance models were investigated: a monodisperse model, a detailed two-PBE model and an extended one-PBE

Model	two-PBE	Extended one-PBE	Mono
No. of equations	116	61	3
PSD of aggregates	polydisperse	polydisperse	monodisperse
PSD of primary particles	polydisperse	monodisperse	monodisperse
CPU time (s) / timestep	1.14	0.32	0.187

Table 2.6: Comparison of PBE models for describing aerosol dynamics and particle morphology. The total CPU time per timestep includes all processes (flow field, scalar convection/diffusion, gas phase reaction, and PBE solution). Tabulation of the aggregation kernel was employed for the one-PBE model.

model. The last of these constitutes a new development and is an augmentation of the basic PBE with a finite-rate sintering expression, while an additional transport equation is solved for the total number of primary particles. The extended one-PBE model can predict the evolution of particle morphology while reducing substantially the computational cost as compared with the two-PBE model.

The models were coupled with an in-house CFD code in order to conduct two-dimensional simulations of silica synthesis via oxidation of HMDSO in a laminar diffusion jet flame. The methodology was validated against the experimental *in-situ* SAXS data of Camenzind et al. (2008). Results with all models were in good agreement with the experimental data for the temperature. Thermal losses due to radiation from particles were found to have a non-trivial effect on the evolution of the temperature field. The predictions by the two-PBE and extended one-PBE model for primary particle sizes were in good agreement with the SAXS data indicating that aggregation and sintering were described relatively well, while the models slightly overestimated the aggregate sizes and the number of primary particles per aggregate. By contrast, the monodisperse model did not capture particle morphology at the early stages of the synthesis. The particle formation rate was overpredicted by all models, leading to an overestimation of the number concentration of primary particles. This discrepancy is most likely due to uncertainties in the experimental data, precursor decomposition kinetics and the nucleation model. The coupling of CFD and PBE also allowed the calculation of the rates and timescales of all processes along the domain. This analysis shed light on the mechanisms underlying the evolution of particle properties and the dominant mechanisms at different spatial locations. An investigation of alternative nucleation and sintering models was also conducted and the analysis

showed that, overall, results obtained with the dimers-based nucleation model and the sintering characteristic time of Tsantilis et al. (2001) were in better agreement with the experimental data compared to those obtained with the other models.

The one-PBE model yielded results close to those of the two-PBE model at a substantially reduced computational cost, indicating that it provides a good balance of physical detail and speed. Most importantly, the time taken for the CFD-PBE simulation with the one-PBE model was less than twice the time needed for the CFD-monodisperse model, while the former provided a much better description of the evolution of particle morphology. The superior speed of the one-PBE model was largely owing to the tabulation of the aggregation kernel.

Overall, the results showed that the coupling of CFD and detailed PBE is capable of describing the evolution of particle properties during silica flame synthesis. The computational advantage offered by the extended one-PBE model paves the way for its coupling with LES and the comprehensive simulation of aerosol synthesis in turbulent flames, which will be the objective of the next Chapter.

Chapter 3

Modelling of aerosol synthesis in a turbulent flame

3.1 Introduction

In the present chapter, the extended one-PBE model for aggregation and sintering is incorporated into the Large-Eddy Simulation - Probability Density Function (LES-PDF) modelling framework to investigate synthesis of silica nanoparticles in a turbulent diffusion flame. The Eulerian stochastic field method is employed for solving the LES-PBE-PDF equations, characterising the influence of the unresolved sub-grid scale motions, and accounting for the complex interaction between turbulence, chemistry and particle dynamics. A different sub-grid mixing time scale is introduced to the model to account for the low diffusivity of nanoparticles. The set of models for gas-phase chemistry and aerosol dynamics employed for the turbulent-flame simulation is the same as that used for the laminar-flame simulation presented in Chapter 2. Thus, by maintaining the same kinetics without any adjustments in parameters, we focus on the modelling issues arising in silica flame synthesis. The LES results are compared with the detailed experimental *in-situ* SAXS data of Camenzind et al. (2008) and possible reasons for the discrepancies are discussed by also leveraging knowledge acquired from the laminar-flame simulations. An investigation of the effect of the particle sub-grid mixing is also presented.

3.1.1 Literature review

This section reviews existing strategies for CFD modelling of nanoparticle flame synthesis in turbulent flows, focusing on the modelling aspects adopted in each case. Reported CFD-based studies of silica synthesis in both laminar and turbulent flames have been extensively discussed in Chapter 2 and are summarised here in Table 3.1. Meanwhile, we also refer to the review

papers of Buesser and Pratsinis (2012), Buesser and Gröhn (2012), Meierhofer and Fritsching (2021) and Raman and Fox (2016).

In the early CFD studies of flame synthesis of nanoparticles, the particle dynamics were decoupled from equations for fluid flow. CFD models based on the RANS approach (usually with the standard $k-\epsilon$ turbulence model) were employed to yield information for the flow, temperature and chemical species composition fields. Then, equations describing particle dynamics were integrated along characteristic trajectories through the flame reactors. This methodology was employed by researchers to investigate flame synthesis of nanoparticles such as palladium (Tsantilis et al., 1999), alumina (Johannessen et al., 2000) and titania (Johannessen et al., 2001). In these studies, a simple monodisperse model (Kruis et al., 1993), which neglects aerosol polydispersity but can distinguish between primary particles and aggregates, was recruited to describe particle-dynamics evolution along the trajectories. Silica flame synthesis was investigated by Lee et al. (2001); however, in their model, a 1-D laminar flame was considered while particle dynamics were described by a sectional two-dimensional PBE model due to Xiong and Pratsinis (1993).

Probably the first fully coupled fluid and particle dynamics study of flame synthesis via CFD is the work of Schild et al. (1999). The monodisperse model of Kruis et al. (1993) was coupled with an available commercial CFD solver. They simulated TiO_2 nanoparticle formation in a hot-wall reactor by oxidation of TiCl_4 . The flow was laminar, and premixed reactants were considered. Field data for velocity, temperature, and particle quantities were presented and discussed. Afterwards, Mühlenweg et al. (2002) extended this methodology, and CFD was coupled with a sectional PBE model showing the feasibility of this approach. Kim et al. (2003) performed 2-D CFD simulations to investigate flame synthesis of SiO_2 non-spherical nanoparticles in a co-flow diffusion laminar flame. A sectional two-equation PBE model, which accounts for the evolution of aggregate structure, was employed and coupled with CFD to simulate nanoparticle dynamics. A hybrid sintering model (Ehrman, 1999), which uses different expressions for the characteristic sintering time, i.e. viscous flow and atomistic diffusion sintering times, was employed. Numerical predictions for primary particles slightly underpredicted the experimental data.

Fully-coupled CFD models for nanoparticle synthesis in turbulent flames were first developed within the RANS framework. Synthesis of TiO_2 nanoparticles in a turbulent diffusion flame was modelled by Yu et al. (2008a,b). A $k-\epsilon$ turbulence model together with an eddy dissipation

concept (EDC) combustion model was employed, and good agreement was found between numerical predictions for temperature and experimental data. Particle dynamics was described with an efficient quadrature method of moments (QMOM), while sintering was also incorporated into the model. Flame synthesis of SiO_2 nanoparticles in turbulent methane/oxygen diffusion flames was modelled by Gröhn et al. (2011). A realisable k - ϵ model together with a combustion model based on the mixture fraction theory that assumes chemical equilibrium for species were employed to model flame dynamics, while particle dynamics were described by the monodisperse model. Later, Gröhn et al. (2012) extended the methodology to model flame spray pyrolysis (FSP) of ZnO_2 nanoparticles. However, in all these RANS-based models, the interaction of turbulence with particle dynamics was neglected.

A methodology for describing flame synthesis of nanoparticles that also accounts for the turbulence-chemistry and turbulence-nanoparticles interaction (in the context of RANS) was developed by Akroyd et al. (2011). They employed a projected fields method to solve the joint composition probability density function (PDF) transport equation in conjunction with a method of moments with interpolative closure (MoMIC) for aerosol dynamics. Here, it should be mentioned that this combined method was first suggested by Fox (2003) under the name DQMoM-IEM (the direct quadrature method of moments using the interaction by exchange with the mean micromixing model).

One of the first attempts to model the unclosed terms that arise in the Reynolds decomposition of the PBE was made by Rigopoulos (2007). This study proposed a methodology that accounts for the complex interaction between turbulence, chemistry and nanoparticle dynamics based on the transported joint PDF method. This method, later named as PBE-PDF method, has been employed to describe particle formation processes in turbulent reacting flows and also in soot studies both in the context of RANS (Rigopoulos, 2010; Di Veroli and Rigopoulos, 2009, 2010, 2011) and LES (Sewerin and Rigopoulos, 2017, 2018, 2019).

The first (to the best of the author's knowledge) LES of nanoparticle synthesis in non-isothermal turbulent reacting flames was performed by Sung et al. (2011). The authors proposed an LES methodology for describing synthesis of TiO_2 nanoparticle in turbulent flames. Detailed chemical reaction mechanisms for both fuel combustion and precursor oxidation were employed, while turbulence-chemistry interaction was modelled based on a flamelet approach. Aerosol dynamics were described by a univariate quadrature method of moments (QMOM), and sintering was not included in the model. However, the terms associated with the unre-

solved scales arising in the LES-filtering of the PBE equation were neglected in the model. Consequently, Sung et al. (2014) improved on their LES results by using a bivariate conditional quadrature method of moments (CQMOM) that can incorporate the sintering process into the model and thus, can describe aggregate morphology. The prediction of particle surface area was significantly improved compared to the results with the univariate model, while the primary particle sizes were under-predicted. The discrepancies were attributed to uncertainties involved in the turbulent inflow conditions.

An LES methodology for describing flame spray pyrolysis for synthesis of SiO_2 nanoparticles was presented by Rittler et al. (2017). A model based on a premixed flamelet generated manifold approach (PFGM) along with an artificial flame thickening (ATF) method was proposed for the system, and particle-dynamics evolution was modelled with a monodisperse model. Later, this methodology was extended by Wollny et al. (2020), who presented a multiscale model within the LES framework, that incorporated turbulent flow, spray combustion, nanoparticle synthesis, and particle decoration processes. The aerosol dynamics were described by a sectional model. However, in both studies, the effect of the unresolved turbulent scales on aerosol dynamics was neglected.

Vo et al. (2017) presented an LES methodology based on a sparse-Lagrangian multiple mapping conditioning (MMC) model for describing nanoparticle formation in turbulent flows. Their model accounted for the lower diffusion rate of nanoparticles by defining and incorporating in the model a different mixing timescale than that of the gas species. Later, Neuber et al. (2019) extended this methodology and coupled it with a sectional/discretised PBE model. The presented computational approach, called PBE-MMC-LES, accounts for the complex interaction between turbulence, chemistry and particle dynamics by solving the joint scalar PDF of gas species and discretised PBE. They employed this methodology to simulate flame synthesis of SiO_2 nanoparticles in a turbulent reacting jet by oxidation of SiH_4 . However, finite-rate sintering was not included in the model and a constant primary particle diameter of 0.98 nm was considered. Results were compared with experimental data and the discrepancies were attributed to uncertainties involved in the precursor-decomposition reaction mechanism.

Reference	Reactor	Precursor	Flow	Combustion	Particle dynamics	Turbulence-chemistry- particles interaction	Comparison with exp. data	Comment
(Kim and Pratsinis, 1989)	Tube	SiCl ₄	2-D	Lam	moment (lognormal PSD)	n/a	n/a	spherical particles
(Kim et al., 2003)	DF	SiCl ₄	2-D	Lam	two-equation sectional	n/a	<i>in-situ</i>	considered aggregates/ underestimated d_p
(Ji et al., 2007)	H ₂ DF	TEOS	2-D	RANS	moment	neglected	<i>ex-situ</i> (Jang, 2001)	parameter fitting analysis
(Gröhm et al., 2011)	DF	HMDSO	2-D	RANS	monodisperse (Kruis et al., 1993)	neglected	<i>ex-situ</i>	underestimated particle sizes
(Buddhiraju and Runkana, 2012)	DF	TEOS	2-D	RANS	monodisperse	neglected	<i>ex-situ</i> (Jang, 2001)	considered aggregates / fitted parameters
(Olivas-Martinez et al., 2015)	FSP	TEOS	2-D	RANS	QMOM	neglected	<i>ex-situ</i>	no finite-rate sintering
(Vo et al., 2017)	TML	SiH ₄	3-D	LES	n/a	MMC	with DNS data	only particle formation was modeled
(Feroughi et al., 2017)	PM	HMDSO	3-D	Lam	monodisperse	n/a	<i>in-situ</i>	slightly underestimated d_p
(Rittler et al., 2017)	FSP	HMDSO	3-D	LES	monodisperse	neglected	n/a	no comparison with experimental data
(Neuber et al., 2019)	DF	SiH ₄	3-D	LES	one-equation sectional	PBE-MMC-LES	<i>in-situ</i>	discrepancies attributed to precursor chemistry
(Dasgupta et al., 2022)	FSP	TEOS	3-D	RANS	Hybrid moment	neglected	<i>ex-situ</i>	complex geometry
Laminar-flame simulation presented in Chapter 2	DF	HMDSO	2-D	Lam	two-equation sectional	n/a	<i>in-situ</i> (Camenzind et al., 2008)	d_p in good agreement with exp. data

Table 3.1: Selected CFD-based studies of flame synthesis of silica nanoparticles found in the literature. The relevant studies are presented in chronological order, focusing on the modelling approach adopted in each case. The information presented in the table corresponds to: the reactor type (DF: diffusion flame, PM: premixed flame, TML: temporal mixing layer, FSP: flame spray pyrolysis), the precursor, the CFD approach for the flow simulation (Lam: laminar flow), the combustion model (FRC: finite-rate-chemistry, ED: eddy dissipation model, SE: species equilibrium approach), models for describing particle dynamics, whether turbulence-chemistry and turbulence-particle dynamics interaction were considered in the model or not, whether a comparison with experimental data was attempted or not, and a comment.

DNS studies of flame synthesis of nanoparticles have also started emerging in the literature. Abdelsamie et al. (2020) performed 3-D simulations to describe (TiO_2) flame synthesis in conditions mimicking the SpraySyn burner (Schneider et al., 2019). Particle evolution was described with the monodisperse model of Kruis et al. (1993). Flame synthesis of iron oxide nanoparticles was investigated via 2-D DNS and a sectional model by Cifuentes et al. (2020b). Particular emphasis was given to the flame-vortex interactions and the effect of the high particle Schmidt numbers.

3.1.2 Present investigation

From the preceding review, it is seen that in most of the reported CFD studies on turbulent flame synthesis the complex interaction between turbulence, chemistry and particle dynamics was neglected. Furthermore, the method of moments, which requires closure assumptions regarding the PSD, was employed to describe particle morphology. In the present chapter, the main objective is to investigate numerically synthesis of silica nanoparticles in a turbulent flame via a comprehensive LES methodology that also accounts for the turbulence-chemistry and turbulence-particle dynamics interaction. Particle morphology will be described by a novel extended population balance model proposed by the authors in Chapter 2. It comprises a sectional method where the PBE is solved together with a transport equation for the number concentration of primary particles. In the present work, the extended PBE model is introduced into the filtered probability density function/stochastic field modelling framework (denoted as LES-PBE-PDF) to predict the detailed experimental *in-situ* small-angle X-ray scattering (SAXS) measurements of Camenzind et al. (2008) for the "S-10" turbulent diffusion flame. The LES methodology utilises the same models for gas-phase chemistry and aerosol dynamics without any adjustments in parameters as those employed in Chapter 2 to simulate the S-2 laminar diffusion flame of Camenzind et al. (2008). By comparing with *in-situ* experimental data, we hope to shed light on the nature of the discrepancies between predictions and experimental results. Results and possible sources of uncertainties in the model are discussed in light of the aforementioned laminar-flame simulation presented in Chapter 2.

The rest of the chapter is structured as follows. The LES-PBE-PDF formulation is introduced in Section 3.2 together with a summary of the models employed for chemical kinetics and aerosol dynamics. This is followed by a description of the flame configuration, the numerical solution method and the computational details in Section 3.3. Subsequently, the LES results

are presented in Section 3.4 and the discussion focusses on the discrepancies with the experimental SAXS data. An investigation of the effect of the particle sub-grid scale mixing is also presented. Finally, a summary of the main findings is given in Section 3.5.

3.2 Methodology

3.2.1 Governing equations

The equations are presented in a Cartesian frame of reference using tensor notation, where summation over repeated indices is implied. The conservation equations for mass and momentum for low-Mach-number flows are:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u_j)}{\partial x_j} = 0 \quad (3.1)$$

$$\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial(\rho u_i u_j)}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left[\mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \right] + \rho g_i \quad (3.2)$$

where μ is the dynamic viscosity of the gas mixture and g_i is the gravitational acceleration term. The isotropic part of the viscous stress has been adsorbed into the pressure.

The mass conservation equation for the chemical species κ is¹:

$$\frac{\partial(\rho Y_\kappa)}{\partial t} + \frac{\partial(\rho u_j Y_\kappa)}{\partial x_j} = \frac{\partial}{\partial x_j} \left[\frac{\mu}{Sc_\kappa} \frac{\partial Y_\kappa}{\partial x_j} \right] + \rho \dot{\omega}_\kappa(\mathbf{Y}, T, n(v)) \quad (3.3)$$

where Y_κ is the mass fraction of species κ while $\dot{\omega}_\kappa$ is the chemical reaction rate. Unlike in laminar flame simulations, it is customary in turbulent combustion studies (Cant and Matorakos, 2007) to assume equal diffusivity coefficients for all species, $D_\kappa = D$, which can be related to the mixture's dynamic viscosity through the Schmidt number $Sc_\kappa = \frac{\mu}{\rho D}$ and usually the constant value $Sc_\kappa = 0.7$ is assigned for all the gas species.

The energy equation is expressed in terms of specific enthalpy that includes the thermal and chemical enthalpies:

$$\frac{\partial(\rho h)}{\partial t} + \frac{\partial(\rho u_j h)}{\partial x_j} = \frac{\partial}{\partial x_j} \left[\frac{\mu}{Sc_h} \frac{\partial h}{\partial x_j} \right] + \rho \dot{q}_{rad} + \rho \dot{q}_{rad,p} \quad (3.4)$$

where $\dot{q}_{rad}$ and $\dot{q}_{rad,p}$ are the sink terms for enthalpy losses due to the thermal radiation from gas species and particles, respectively. A unit Lewis number has been assumed (Peters, 2000) meaning $Sc_h = Sc_k$, while acoustic interactions and viscous heating have been neglected in the

¹No summation is implied by repeated Greek subscripts.

overall formulation. In the present work, multicomponent ideal gas flow was considered and the mixture density is a function of the local values of the reactive scalars and temperature.

The evolution of the particle size distribution, which changes due to aerosol (gas-to-particle conversion, aggregation, etc.) and particle-transport processes, is described by the PBE (Friedlander, 2000). Anticipating the application of the PBE to variable density flows (Sewerin and Rigopoulos, 2018), we consider the number density of particles per unit of mixture mass and the PBE assumes the following form²:

$$\begin{aligned} \frac{\partial(\rho n(v))}{\partial t} + \frac{\partial(\rho U_j n(v))}{\partial x_j} = & \frac{\partial}{\partial x_j} \left(\frac{\mu}{Sc_p} \frac{\partial n(v)}{\partial x_j} \right) + \rho B \delta(v - v_{nuc}) + \rho C(\mathbf{Y}, v) \\ & + \rho \left(\frac{1}{2} \int_0^v \beta(w, v-w) n(w) n(v-w) dw - \int_0^\infty \beta(v, w) n(v) n(w) dw \right) \end{aligned} \quad (3.5)$$

where v and w designate volume of aggregates, $n = n(\mathbf{x}, t, v)$ is the number density function per unit of mixture mass (denoting number of aggregates per unit of mixture mass and unit of particle volume). The dependence of N on $\mathbf{x}$ and t has been omitted in the formulation of the equations. B and C represent the nucleation³ and condensation rates, respectively, while $\delta(v - v_{nuc})$ is the Dirac delta function and $\beta(v, w)$ is the aggregation kernel. The detailed expressions of the kinetic models employed will be discussed in Section 3.2.2. The velocity, U_j , is equal to the sum of the flow velocity u_j and the thermophoretic velocity $u_{j,th} = -0.55 \frac{\mu}{\rho T} \frac{\partial T}{\partial x_j}$ (Friedlander, 2000). Equal diffusivity coefficients have been assumed for all particle sizes, while a constant value $Sc_p = 1000$ is assigned for the number density to account for the low diffusivity of particles. It is anticipated that particle diffusion will have little effect on the results since turbulent diffusion is usually the dominant mechanism.

Particle-morphology evolution can be described (see Section 2.2.5) by solving the PBE together with a transport equation for the number concentration of primary particles per unit of mixture mass⁴, N_p :

$$\frac{\partial(\rho N_p)}{\partial t} + \frac{\partial(\rho U_j N_p)}{\partial x_j} - \frac{\partial}{\partial x_j} \left(\frac{\mu}{Sc_p} \frac{\partial N_p}{\partial x_j} \right) = \rho J - \rho \frac{3}{\tau_s} \left(\frac{V}{v_{p,av}} - \frac{M_{23}}{v_{p,av}^{2/3}} \right) \quad (3.6)$$

²In the previous study of Sewerin and Rigopoulos (2018), the diffusion term in the PBE was expressed as $\frac{\partial}{\partial x_j} \left(D_p \frac{\partial \rho n(v)}{\partial x_j} \right) = \frac{\partial}{\partial x_j} \left(\rho D_p \frac{\partial n(v)}{\partial x_j} \right) + \frac{\partial}{\partial x_j} \left(D_p n(v) \frac{\partial \rho}{\partial x_j} \right)$. The term $\frac{\partial}{\partial x_j} \left(D_p n(v) \frac{\partial \rho}{\partial x_j} \right)$ has been neglected in the present study. It is expected that the filtered term arising from this term after applying a density-weighted filtering operation in the context of LES will be negligible compared to the turbulent diffusion term.

³ B is a source of particle number density rather than particle number concentration.

⁴Unlike $n(v)$ in Eq. (3.5), N_p is not a function of particle volume v , therefore Eq. (3.6) does not require discretisation in the particle volume domain.

where J is the nucleation rate, $v_{p,av}$ is the average primary particle volume, V the particle volume concentration per unit of mixture mass, $M_{23} = \int_0^\infty v^{2/3} n(v) dv$ is the $2/3$ fractional moment of the PSD and τ_s is a sintering characteristic time. Description of particle morphology can then be obtained from knowledge of $n(v)$ and N_p . In particular, $v_{p,av}$ is approximated as:

$$v_{p,av} = \frac{V}{N_p} \quad (3.7)$$

where a monodisperse size distribution has been assumed for the primary particles. The primary particle diameter $d_{p,av}$ is then obtained from $v_{p,av}$ by assuming spherical particles. Furthermore, fractal-like aggregates follow a power-law relationship (Friedlander, 2000; Buesser and Pratsinis, 2012). The aggregate collision diameter, d_g , of aggregates of volume v is given by:

$$d_g(v) = d_{p,av} \left(\frac{1}{k_f} \frac{v}{v_{p,av}} \right)^{1/D_f} \quad (3.8)$$

where k_f is a prefactor associated with the aggregate anisotropy (Heinson et al., 2010) and D_f is the fractal dimension. The values $k_f = 1.4$ and $D_f = 1.91$ were assigned to the aggregate parameters corresponding to ballistic cluster-cluster aggregation in the free molecule regime (Ball and Jullien, 1984; Friedlander, 2000). The average radius of gyration of aggregates is calculated as:

$$R_{g,av} = \frac{1}{2} \frac{\int_{v_d}^\infty d_g(v) n(v) dv}{N} \quad (3.9)$$

where N is the number concentration of aggregates and v_d is the volume of the smallest detectable particles (1 nm) by SAXS measurements (Camenzind et al., 2008).

As discussed later, a sectional model is employed for the numerical solution of the PBE and therefore, for the purposes of the mathematical formulation, a discretised form of the number density is introduced. The fundamental idea of sectional methods is to discretise a particle size property, i.e. here is particle volume, into discrete sections and evaluate particle quantities at these sections. In this manner, the number density function $n(\mathbf{x}, t, v)$ can be represented by an array of m scalars $n_i(\mathbf{x}, t)$, $i = 1, m$, each of them expressing number density of particles within a section i with volume in the range v_{i-1}, v_i . Based on the above considerations, equations (3.3) to (3.6) can be expressed in terms of a general reactive scalar ϕ_α , $\alpha = 1, N_s$ (Peters, 2000), where N_s is the number of scalars required to describe the system, i.e. the number of species plus enthalpy plus $m + 1$ scalars required after the discretisation in v of the PBE model:

$$\frac{\partial(\rho \phi_\alpha)}{\partial t} + \frac{\partial(\rho u_j \phi_\alpha)}{\partial x_j} = \frac{\partial J_{\alpha,j}}{\partial x_j} + \rho \dot{\omega}_\alpha(\phi) \quad (3.10)$$

where the scalar diffusion flux is $J_{\alpha,j} = \frac{\mu}{Sc_\alpha} \frac{\partial \phi_\alpha}{\partial x_j}$, while Sc_α and $\dot{\omega}_a(\phi)$ stand for the Schmidt/Prandtl number and sink/source terms for Y_κ , h , n_i or N_p , as appropriate.

3.2.2 Models for chemical kinetics and aerosol dynamics

In Chapter 2, we simulated synthesis of silica nanoparticles by oxidation of hexamethyldisiloxane (HMDSO) precursor in an oxygen/methane laminar diffusion flame. The objective of the present chapter is to simulate synthesis of silica nanoparticles in a turbulent flame, rather than laminar, and employ the same set of models for the description of chemistry and aerosol dynamics as in the laminar-flame simulation. For this reason, the details of the models employed are discussed briefly here.

The Gas Research Institute (GRI) 1.2 reaction mechanism (Frenklach et al., 1995b,a) containing 175 steps and 31 species is used to describe methane combustion. The global two-step mechanism proposed by Feroughi et al. (2017) and shown in Table 2.2 is employed to describe HMDSO combustion. The two-step HMDSO mechanism was also employed in our laminar-flame simulation and has been used previously in the literature to study the synthesis of silica nanoparticles via flame spray pyrolysis (Rittler et al., 2017). Thermal radiation from gas species is considered in the simulation by employing the optically thin radiation model of Barlow et al. (2001).

Similarly to Chapter 2 (Section 2.4.2), the nucleation process involves the formation of dimers and the rate is given by:

$$J = \frac{1}{2\rho} K_{fm} N_A^2 C_{\text{SiO}_2}^2 \quad (3.11)$$

$$K_{fm} = E_F \cdot 4 \sqrt{\frac{\pi k_b T}{m_{\text{SiO}_2}}} d_o^2 \quad (3.12)$$

where N_A is Avogadro's number, C_{SiO_2} is the gas-phase concentration of SiO_2 monomers, K_{fm} is the free molecule coagulation kernel, $E_F = 1.88$ is the Van der Waals enhancement factor, k_b is the Boltzmann constant, T is the local gas-mixture temperature, ρ is the local gas-mixture density, and m_{SiO_2} and d_o are the mass and diameter of a $\text{SiO}_2(\text{g})$ molecule, respectively. It is assumed that $\text{SiO}_2(\text{g})$ molecules have diameter $d_o = 0.44 \text{ nm}$ and that the density of silica particles is $\rho_p = 2196 \text{ kg/m}^3$. After discretisation of the PBE in the particle volume domain, the nucleation source term in Eq. (3.5) takes the form:

$$B = J \frac{v_{nuc}}{dv_{nuc} v_{m,nuc}} \quad (3.13)$$

where v_{nuc} is the volume of dimers (volume of nuclei), $v_{m,nuc}$ is the representative volume (midpoint) in the section that covers the volume of nuclei and dv_{nuc} is the volume range of that section.

Condensation is considered as a collision process in the free-molecular regime between silica monomers and particles. The focus, here, is on the physical description of gas-to-particle mass conversion due to condensation. We refer to the papers of Sun et al. (2021) and Section 2.4.3 of the present thesis for the complete details on the implementation of the condensation model into the PBE. The rate of change of the particle volume concentration per unit of mixture mass due to condensation can be evaluated as:

$$\int_{v_{nuc}}^{\infty} v C(\mathbf{Y}, v) dv = v_0 C_{SiO_2} N_A \int_{v_{nuc}}^{\infty} \beta_{cond}(v_0, v) n(v) dv \quad (3.14)$$

$$\beta_{cond}(v_0, v) = 1.28 \sqrt{\frac{\pi k_B T}{2\rho_p}} (d_o + d_g)^2 \sqrt{\frac{1}{v_0} + \frac{1}{v}} \quad (3.15)$$

where $\beta_{cond}(v_0, v)$ is the collision frequency of a monomer of volume v_0 with a particle of volume v and d_g is the collision diameter of particles of volume v evaluated according to Eq. (3.8). The amplification factor of 1.28 is due to Van der Waals interactions.

The expression for the sintering characteristic time of silica nanoparticles given by Tsantilis et al. (2001) is used in the present study:

$$\tau_s = 6.5 \cdot 10^{-13} \cdot d_p \exp \left[\frac{8.3 \cdot 10^4}{T} \left(1 - \frac{d_{p,min}}{d_p} \right) \right] \quad (3.16)$$

where d_p is the primary particle diameter in meters, T the gas temperature in Kelvin and $d_{p,min} = 1 \cdot 10^{-9} m$ is the cut-off size below which particles are assumed to coalesce instantaneously.

Aggregation in the free molecule, transition and continuum regime is considered and appropriate expressions for the aggregation kernel, $\beta(v, w)$, are employed depending on the values of the Knudsen number, $Kn = 2\lambda_f/d_g$, where λ_f is the mean free path. The expressions for the free molecule particle size regime ($Kn < 0.1$) and the continuum regime ($Kn > 10$) are (Friedlander, 2000):

$$\beta_{fm}(v, w) = E_f \rho \sqrt{\frac{\pi k_B T}{2\rho_s}} \left(\frac{1}{v} + \frac{1}{w} \right)^{1/2} (d_{g,v} + d_{g,w})^2 \quad (3.17)$$

$$\beta_c(v, w) = \rho \frac{2k_B T}{3\mu} \left(\frac{C_c(v)}{d_{g,v}} + \frac{C_c(w)}{d_{g,w}} \right) (d_{g,v} + d_{g,w}) \quad (3.18)$$

where $C_c(v) = 1 + 1.257Kn$ is the Cunningham slip correction factor and ρ has been included in the expressions since the number density function has been defined per unit of mixture mass. A harmonic mean of the two expressions (Pratsinis, 1988) is employed for the transition regime ($0.1 < Kn < 10$).

Thermal losses due to the radiation from nanoparticles are included in the model and evaluated as:

$$\dot{q}_{rad,p} = -\frac{4\sigma}{\rho} C_s f_v (T^5 - T_{amb}^5) \quad (3.19)$$

where $\sigma = 5.669 \cdot 10^{-8} \text{ W/m}^2/\text{K}^4$ is the Stefan-Boltzmann constant, $T_b = 295 \text{ K}$ is the ambient background temperature, $f_v \text{ m}^3/\text{m}^3$ is the silica volume fraction and $C_s = 1100 \text{ m}^{-1}\text{K}^{-1}$ is a proportionality constant (see also Section 2.4.6)..

3.2.3 Large-eddy simulation

In LES, the larger energy-containing turbulent motions are resolved directly, whereas the effect of the unresolved sub-grid scale (SGS) motions needs to be modelled. The separation of the scales is achieved through a spatial low-pass filtering operation, which for a function $Q = Q(\mathbf{x}, t)$ is defined as its convolution with a filter function G according to:

$$\overline{Q}(\mathbf{x}, t) = \int_{\Omega} G(\mathbf{x} - \mathbf{x}'; \Delta(\mathbf{x})) Q(\mathbf{x}', t) d\mathbf{x}' \quad (3.20)$$

where integration is defined over the entire flow domain Ω . In the present study, a box or “top hat” filter is employed and Δ is a characteristic filter width which may vary with position:

$$G(\mathbf{x} - \mathbf{x}') = \begin{cases} \frac{1}{\Delta^3}, & \text{if } |\mathbf{x} - \mathbf{x}'| < \frac{\Delta}{2} \\ 0, & \text{otherwise} \end{cases} \quad (3.21)$$

In LES of combusting flows, the use of density-weighted (Favre) filtering, defined by $\tilde{Q} = \overline{\rho Q} / \bar{\rho}$, is usually employed for the treatment of the density variations in the unresolved scales. Applying the density-weighted filtering operation to the governing transport equations results in the following filtered equations (Jones and Navarro-Martinez, 2007; Jones and Prasad, 2010):

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial (\bar{\rho} \tilde{u}_j)}{\partial x_j} = 0 \quad (3.22)$$

$$\frac{\partial (\bar{\rho} \tilde{u}_i)}{\partial t} + \frac{\partial (\bar{\rho} \tilde{u}_i \tilde{u}_j)}{\partial x_j} = -\frac{\partial \tilde{p}}{\partial x_i} + \frac{\partial}{\partial x_j} \left(2\mu \tilde{S}_{ij} \right) - \frac{\partial \tau_{ij}^r}{\partial x_j} \quad (3.23)$$

$$\frac{\partial(\bar{\rho}\tilde{\phi}_\alpha)}{\partial t} + \frac{\partial(\bar{\rho}\tilde{u}_j\tilde{\phi}_\alpha)}{\partial x_j} = \frac{\partial}{\partial x_j} \left[\frac{\mu}{Sc_\alpha} \frac{\partial\tilde{\phi}_\alpha}{\partial x_j} \right] - \frac{\partial J_{\alpha,j}^{sgs}}{\partial x_j} + \overline{\rho\dot{\omega}_\alpha(\phi)} \quad (3.24)$$

where $\tilde{S}_{ij} = \frac{1}{2} \left(\frac{\partial\tilde{u}_i}{\partial x_j} + \frac{\partial\tilde{u}_j}{\partial x_i} \right)$ is the resolved rate of strain tensor and τ_{ij}^r is the anisotropic part of the sub-grid scale stress tensor $\tau_{ij}^{sgs} = \bar{\rho}(\widetilde{u_i u_j} - \tilde{u}_i \tilde{u}_j)$. The isotropic part of the sub-grid stress has been absorbed into the pressure. Following standard methods, τ_{ij}^r is determined via the Smagorinsky model (Smagorinsky, 1963):

$$\tau_{ij}^r = \tau_{ij}^{sgs} - \frac{\delta_{ij}}{3} \tau_{kk}^{sgs} = -2\mu^{sgs} \tilde{S}_{ij} \quad (3.25)$$

where

$$\mu^{sgs} = \bar{\rho} (C_s \Delta)^2 \|\tilde{S}_{ij}\| \quad (3.26)$$

and $\|\tilde{S}_{ij}\| = \sqrt{2\tilde{S}_{ij}\tilde{S}_{ij}}$ is the Frobenius norm of the resolved rate of strain tensor. The filter width Δ is defined as the cube root of the local grid cell volume and the parameter C_s is determined through the dynamic procedure of Piomelli and Liu (1995). In Eq. (3.24), the terms $J_{\alpha,j}^{sgs} = \bar{\rho} \left(\widetilde{u_j \phi_\alpha} - \tilde{u}_j \tilde{\phi}_\alpha \right)$ and $\overline{\rho\dot{\omega}_\alpha(\phi)}$ (filtered net scalar formation/consumption rate) remain unclosed, as for instance $\overline{\rho\dot{\omega}_\alpha(\phi)} \neq \bar{\rho}\dot{\omega}_\alpha(\bar{\phi})$, and require modelling. The former term represents transport due to sub-grid fluctuations, while the latter is related to turbulence-chemistry and turbulence-particle dynamics interaction.

3.2.4 Joint sub-grid probability density function

An approach based on the joint sub-grid probability density function (PDF) method is employed in the present study to take into account the effect of the unresolved scales on the evolution of the scalar quantities. The LES-PDF method for reacting flows was pioneered by Gao and O'Brien (1992) and Gao and O'Brien (1994), while the PBE was incorporated into the LES-PDF framework by Sewerin and Rigopoulos (2017) for constant density flows. A formal introduction of the LES-PBE-PDF approach for variable density flows is given by Sewerin and Rigopoulos (2018). The formulation adopted in the present study is based on that given by Jones and Navarro-Martinez (2007) and Jones and Prasad (2010) and incorporates elements given by Sewerin and Rigopoulos (2018).

Following Gao and O'Brien (1992) and using the filtering operation defined in Eq. (3.20), a joint sub-grid (or filtered) PDF for the N_s scalar quantities is defined as:

$$f(\boldsymbol{\psi}; \mathbf{x}, t) = \int_{\Omega} g(\boldsymbol{\psi}; \mathbf{x}', t) G(\mathbf{x} - \mathbf{x}') d\mathbf{x}' \quad (3.27)$$

where $g(\boldsymbol{\psi}; \mathbf{x}, t) = \prod_{\alpha=1}^{N_s} \delta(\psi_{\alpha} - \phi_{\alpha}(\mathbf{x}, t))$ is a fine-grained PDF (O'Brien, 1980; Pope, 1985), δ is the Dirac delta function, and $\boldsymbol{\psi}$ denotes the phase or sample space of the scalar quantities $\boldsymbol{\phi}$. Based on the definition of $f(\boldsymbol{\psi}; \mathbf{x}, t)$, the probability of observing values of the scalar variable in the range $\psi_{\alpha} < \phi_{\alpha} < \psi_{\alpha} + d\psi_{\alpha}$ within the filter volume is given by $f(\boldsymbol{\psi}; \mathbf{x}, t) d\boldsymbol{\psi}$. For variable density flows, a density-weighted PDF $\tilde{f}(\boldsymbol{\psi}; \mathbf{x}, t)$ is usually introduced, and a transport equation for this quantity can be derived (Gao and O'Brien, 1992; Colucci et al., 1998; Jaberi et al., 1999; Sewerin and Rigopoulos, 2018) from the appropriate conservation equations using standard methods:

$$\bar{\rho} \frac{\partial \tilde{f}}{\partial t} + \bar{\rho} \tilde{u}_j \frac{\partial \tilde{f}}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\frac{\mu^{sgs}}{Sc^{sgs}} \frac{\partial \tilde{f}}{\partial x_j} \right) - \sum_{\alpha=1}^{N_s} \frac{\partial}{\partial \psi_{\alpha}} \left[\bar{\rho} \dot{\omega}_{\alpha}(\boldsymbol{\psi}) \tilde{f} \right] - \sum_{\alpha=1}^{N_s} \frac{\partial}{\partial \psi_{\alpha}} \left[-\frac{\bar{\rho} \tilde{f}}{\rho} \overline{\left(\frac{\partial J_{\alpha,j}}{\partial x_j} \mid \boldsymbol{\psi} \right)} \right] \quad (3.28)$$

where the arguments of $\tilde{f}(\boldsymbol{\psi}; \mathbf{x}, t)$ have been omitted for compactness. The turbulent transport term has been approximated by a simple gradient closure directly analogous to the Smagorinsky model, and a constant turbulent Schmidt/Prandtl number $Sc^{sgs} = 0.7$ is adopted in the present study (Jones and Prasad, 2010). Note that in Eq. (3.28) the scalar formation/consumption term appears in closed form while the last term on the right-hand side in Eq. (3.28) represents sub-grid scale mixing and requires modelling. There are several modelling proposals for closing the micromixing term ((Fox, 2003). Following Jones and Prasad (2010), the linear mean square estimation (LMSE) micromixing model (Dopazo and O'Brien, 1974; Dopazo, 1975, 1979) is adopted in the present study:

$$-\frac{1}{\rho} \overline{\left(\frac{\partial J_{\alpha,j}}{\partial x_j} \mid \boldsymbol{\psi} \right)} = -\frac{1}{2\tau_{\alpha}^{sgs}} \left(\psi_{\alpha} - \tilde{\phi}_{\alpha}(\mathbf{x}, t) \right) + \frac{1}{\bar{\rho}} \frac{\partial}{\partial x_j} \left(\frac{\mu}{Sc_{\alpha}} \frac{\partial \tilde{\phi}_{\alpha}(\mathbf{x}, t)}{\partial x_j} \right) \quad (3.29)$$

where the sub-grid mixing (or micromixing) times scale is:

$$\tau_{\alpha}^{sgs} = \frac{\bar{\rho} \Delta^2}{C_{d,\alpha} \mu^{sgs}} \quad (3.30)$$

The value $C_{d,\alpha} = 2$ is usually assigned to the micromixing constant for the chemical species and enthalpy (Jones and Prasad, 2010). However, the diffusivity of nanoparticles is much lower than that of gas species; the diffusion coefficient of particles can be estimated by the Stokes-Einstein equation (Friedlander, 2000). Therefore, to account for this effect, a simple approach

is adopted here and a different sub-grid mixing time scale is applied for the discretised number densities, $n_i(\mathbf{x}, t)$, which is assumed to scale with the particle Schmidt number $Sc_p = 1000$. A similar approach was employed by Vo et al. (2017) for the definition of a Lagrangian mixing time for the particles. In the present model, the different micromixing time of the particles can be expressed via the micromixing constant $C_{d,\alpha}$. The value $C_{d,\alpha} = 0.002$ is employed for the discretised number densities, while $C_{d,\alpha} = 2$ for the rest of the reactive scalars α . The values of the micromixing constant employed in the present study are:

$$C_{d,\alpha} = \begin{cases} C_{d,s} = 2, & \text{for species and enthalpy} \\ C_{d,p} = 0.002, & \text{for number densities} \end{cases} \quad (3.31)$$

For clarity, the symbol $C_{d,p}$ was introduced to denote the micromixing constant for number densities and distinguish it from the micromixing constant for gas-phase species $C_{d,s}$. The value $C_{d,p} = 2$ for number densities is also explored in order to investigate the effect of the different sub-grid mixing time scale for the particles and results are discussed in Section 3.4.3.

3.2.5 Stochastic field method

The Eulerian stochastic field method is employed to solve Eq. (3.28). The underlying idea of this method is the derivation of a system of stochastic differential equations (SDE) equivalent to the closed form of the filtered PDF transport equation. $\tilde{f}(\boldsymbol{\psi}; \mathbf{x}, t)$ is then represented by an ensemble of N_f stochastic fields $\theta_\alpha^\pi(\mathbf{x}, t)$, $\pi = 1, N_f$ for each of the reactive scalar $\alpha = 1, N_s$. The formulation based on the *Itô* stochastic integral (Valiño, 1998) is adopted in the present study; thus, the evolution of the stochastic fields is described by:

$$\begin{aligned} \bar{\rho} d\theta_\alpha^\pi = & -\bar{\rho}\tilde{u}_j \frac{\partial \theta_\alpha^\pi}{\partial x_j} dt + \frac{\partial}{\partial x_j} \left[\left(\frac{\mu}{Sc_\alpha} + \frac{\mu^{sgs}}{Sc_\alpha^{sgs}} \right) \frac{\partial \theta_\alpha^\pi}{\partial x_j} \right] dt \\ & + \bar{\rho} \dot{\omega}_\alpha^\pi(\boldsymbol{\theta}^\pi, \mathbf{x}) dt - \frac{\bar{\rho}}{2\tau_\alpha^{sgs}} \left(\theta_\alpha^\pi - \tilde{\phi}_\alpha \right) dt + \bar{\rho} \sqrt{2\frac{\mu^{sgs}}{\bar{\rho}}} \frac{\partial \theta_\alpha^\pi}{\partial x_j} dW_j^\pi(t) \end{aligned} \quad (3.32)$$

where $dW_j^\pi(t)$ is the increment of a three-dimensional Wiener process. $dW_j^\pi(t)$ is different for each field π but not a function of the spatial location $\mathbf{x}$ and can be approximated by time-step increments in the j^{th} direction as $\eta_j^\pi \sqrt{dt}$ where η_j^π is a $\{-1, 1\}$ dichotomic random vector. The Favre filtered value of each reactive scalar ϕ_α , represented by the first moment of the scalar fields, can then be computed by averaging over the stochastic field values:

$$\tilde{\phi}_\alpha(\mathbf{x}, t) = \frac{1}{N_f} \sum_{\pi=1}^{N_f} \theta_\alpha^\pi(\mathbf{x}, t) \quad (3.33)$$

3.2.6 Numerical methods

A conservative finite-volume sectional method developed by Liu and Rigopoulos (2019); O’Sullivan and Rigopoulos (2022) was employed for the numerical solution of the PBE. The advantage of the method is that it provides an accurate prediction of the particle size distribution and conserves the first moment (with respect to volume) during the aggregation process, an important feature for mass balance. The method has been shown to be robust and efficient when coupled with CFD (Liu and Rigopoulos, 2019; Sun et al., 2021; Sun and Rigopoulos, 2022).

For the simulation, the PBE model was implemented in an in-house block-structured, boundary conforming coordinate LES code, BOFFIN-LES (Jones et al., 2002). The LES code has been used to simulate a wide range of combustion flows (Jones et al., 2015). It constitutes a second-order-accurate finite volume method based on a low-Mach number pressure-based formulation using a collocated storage arrangement. A second-order central discretisation scheme is employed for the spatial derivatives, while a second-order accurate Crank-Nicolson method is employed for time discretisation. A total variation diminishing (TVD) scheme based on van Leer’s limiter is used for the scalar equation convection terms to avoid unphysical values. The convection and viscous terms are treated implicitly. A two-step approximate factorization (SIMPLE type) method for the pressure-velocity coupling is employed to ensure mass conservation. The stochastic field equations are solved using a weak first-order temporal Euler-Maruyama scheme (Kloeden and Platen, 1992). A stochastic noise reduction procedure given by Prasad (2011) was employed in the present study.

An approximate fractional step method is applied for the solution of the transport equations of the reactive scalars and discretised number densities. Particularly, separate fractional steps are employed for convection-diffusion, chemical reaction and PBE integration. The chemical reaction rate equations are integrated using an implicit backward Euler scheme, while the PBE integration is achieved with an explicit Euler scheme since the discretised PBE is not stiff. The reaction mechanism is hard-coded in order to accelerate the computations. The code is fully parallelized, utilising domain splitting and Message Passing Interface (MPI) routines. The chemical reaction fractional step is additionally parallelized to distribute reaction source computations evenly across all processors.

Stream	Profile	u_{inlet} [m/s]	T [°C]	Mole fractions [%]
inner	Laminar	$U = 6.715$	75	$X_{CH_4} = 61.338$; $X_{N_2} = 36.803$; $X_{HMDSO} = 1.859$
1st annulus	Laminar	$U_1 = 2.057$	75	$X_{N_2} = 100$
2nd annulus	Laminar	$U_2 = 42.85$	75	$X_{O_2} = 100$
co-flow air	Uniform	$U_{air} = 0.8$	20	$X_{N_2} = 76.83$; $X_{O_2} = 23.17$

Table 3.2: Inlet boundary conditions for the S-10 turbulent-flame simulation, where u_{inlet} denotes the stream bulk inlet velocity in the streamwise direction.

3.3 Simulation parameters

3.3.1 Flame configuration

LES calculations were performed for the S-10 turbulent flame of Camenzind et al. (2008). To the best of the authors' knowledge, the present work is the first simulation of this experiment. Silica nanoparticles were synthesised by oxidation of HMDSO in oxygen/methane diffusion flames. The co-flow diffusion flame reactor was used for both the laminar (S-2) and turbulent (S-10) cases and comprised three concentric stainless-steel tubes. The experimental setup is shown in Fig. A.1 and more information on the geometric characteristics of the co-flow diffusion flame reactor and the experimental conditions employed in the experiment of Camenzind et al. (2008) are given in Appendix A.1. The Reynolds number of the S-10 flame, based on the bulk velocity and the outer diameter of the reactor, was $Re \approx 4280$. Here, it should be emphasised that the only difference between the S-2 and S-10 flames is the O_2 flow rate through the 2nd annulus. In the S-2 case, the O_2 flow rate was 2 l/min, while in the S-10 case, the O_2 flow rate was five times larger, resulting in a turbulent flame.

3.3.2 Computational setup

The solution domain is cylindrical with a diameter of $40D$, where $D = 1.8$ mm is the inner tube diameter, that extends $60D$ in the streamwise direction. The simulation was performed on a non-uniform computational grid with approximately 4.65 million cells. The domain was split into 528 blocks (sub-domains) with 8800 cells per block, and a central processing unit (CPU) was assigned to each block. In total, 264 cells were employed for the discretisation of the domain in the streamwise direction and were distributed based on a geometric expansion formula, resulting in a minimum cell width of 8×10^{-5} m in the vicinity of the nozzle. The cell

width was $7.25 \times 10^{-5} \text{ m}$ in the other two directions in the central region of the jet ($r < 1.33D$). Grid refinement was employed at the height of the second annulus in the radial direction to ensure that at least eight cells were used to resolve the strong gradients that arise near the inlet. The cell width expanded smoothly in the radial direction for $r > 1.5D$.

A free slip condition was used for all lateral boundaries and a convective outflow boundary condition was applied at the exit plane. In the simulation, the burner tubes were excluded from the solution domain, while the tube thickness (0.3 mm) was taken into account in the simulation by applying a no-slip boundary condition at these radii. At the inflow, laminar flow velocity profiles were employed for all the jets issuing into the reactor. A laminar flow profile was also employed for the jet coming from the second annulus on the basis that the estimated Reynolds number, Re , was smaller than the critical Re_c number for transition to turbulence in annulus flow (Dou et al., 2010). Therefore, the turbulent flow in the simulation occurred due to shear and not by employing an artificial-turbulence generator. In the absence of any information for the entrainment velocity, a uniform velocity $U_{air} = 0.8 \text{ m/s}$ was used for the air co-flow stream at the inlet. Preliminary test cases showed that U_{air} has a minor effect on the results. The inlet boundary conditions for the bulk streamwise velocity, temperature and mole fractions for all jet streams are shown in Table 3.2.

Following Mustata et al. (2006) and Jones and Navarro-Martinez (2007), eight stochastic fields were employed to approximate the sub-grid PDF introduced in Section 3.2.4. A comparison of results obtained with eight and sixteen stochastic fields will be shown in Section 3.4.4. The time step was fixed at $\Delta t = 5 \times 10^{-7} \text{ s}$, resulting in a maximum Courant-Friedrichs-Levy (CFL) number of 0.4. The initial flow was allowed to reach a statistically steady state. Following this, the simulation was run for a period of at least three flow-through times, based on the bulk velocity, for the collection of the temporal statistics. Azimuthally averaging of statistical quantities was also performed when appropriate. Each simulation required approximately 200000 CPU hours (AMD EPYC 7742, 2.25 GHz, 64-core processor).

Regarding the PBE numerical parameters, an exponential grid with 60 intervals was employed for the discretisation of the particle volume domain and covered a particle size range from 0.554 nm to $1.4 \text{ }\mu\text{m}$ in diameter. Convergence studies with a perfectly stirred reactor showed that this grid was sufficient for an accurate description of the PSD evolution. The discretisation of the particle volume domain allows for the tabulation of the aggregation kernel. Specifically, the aggregation kernel for several particle-volume pairs and primary particle dia-

meters was pre-computed and stored, leading to a substantial reduction in the computational cost (see also the discussion in Section 2.6.5).

3.4 Results and discussion

In the present section, the LES results are presented and discussed. A mass-based definition of the number density function was presented in Section 3.2. However, here, particle concentrations are expressed per unit of mixture volume to make the results consistent with the experimental data and also allow for a direct comparison with the simulation data presented in our laminar-flame simulation. Comparisons of numerical predictions with the experimental SAXS data of Camenzind et al. (2008) are also presented. Time-averaged quantities are presented in all figures unless specified.

3.4.1 Flow field and temperature

The instantaneous and time-averaged fields for streamwise velocity and for temperature are presented in Fig. 3.1a and Fig. 3.1b, respectively. It is observed that the flame is slightly lifted and not attached to the burner nozzle. In the experiment, N_2 was delivered into the reactor through the 1st annulus in order to slightly lift the flame and prevent the deposition of particles on the nozzle tips, and this is captured well by the simulation. The flame is stable at low HABs ($HAB < 0.4$ cm); however, instabilities develop early on, leading to vortical structures that stretch the flame front and eventually break the jet. Intense turbulent mixing and a wide range of turbulent length scales are evident at downstream locations. Furthermore, the velocity field exhibits a recirculation zone (as can be seen by the negative streamwise velocities in Fig. 3.1a) in the vicinity above the nozzle tips due to the different inflow stream velocities. The inflow velocity of the stream coming through the 2nd annulus is almost seven times larger than the central-jet velocity, leading to the development of the recirculation zone. The flame temperature reaches values up to 2800 K at low HABs (200 K more than the maximum temperatures found in the laminar-flame simulations) but decreases rapidly due to the effect of mixing of the flame with the O_2 inflow jet. As is typical in diffusion flames, the flame front is positioned off the flame centerline at low HABs ($HAB < 0.8$ cm), while the temperatures at the centreline at these HABs are well below the temperatures found in the flame reaction zone where reactants meet.

The instantaneous and time-averaged fields for particle volume concentration (or silica

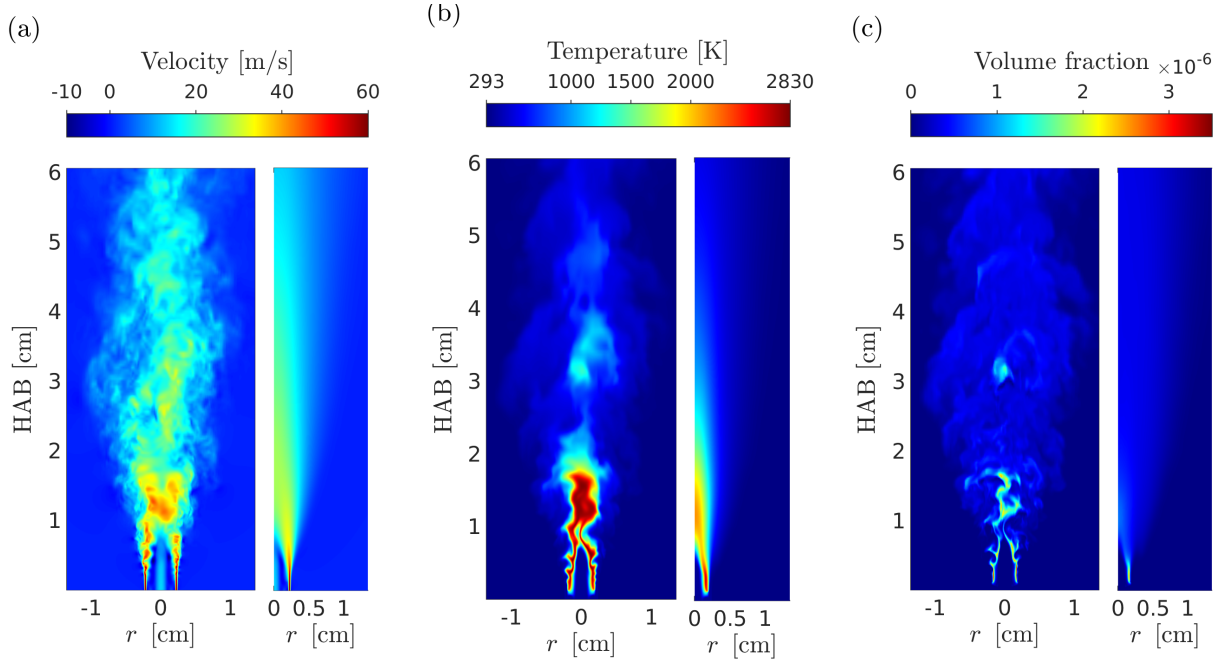


Figure 3.1: Contour plots of the instantaneous (left) and time-averaged (right) fields for (a) streamwise velocity, (b) temperature and (b) silica volume fraction. HAB stands for height above burner.

volume fraction), V , are presented in Fig. 3.1c. Particles are formed by nucleation quite early in the flame. As will be shown later, most of the gas-to-particle conversion occurs in the flame reaction zone at low HABs ($\text{HAB} < 2$ cm). The maximum time-averaged silica volume fraction is found in the flame reaction zone at $\text{HAB} < 0.4$ cm, where the flame is relatively stable. At downstream locations, the jet stream becomes unstable and breaks into smaller vortices. This causes the appearance of fluid patches with large values of V , larger than the time-averaged value, at downstream locations.

A comparison of numerical predictions for temperature with the experimental Fourier transform infrared (FTIR) spectroscopy data of Camenzind et al. (2008) is shown in Fig. 3.2. As discussed earlier (see the discussion in Section 2.6.1), the radial maximum temperatures are more representative of the experimental FTIR data; thus, numerical results for the radial maximum value of time-averaged temperatures are plotted in Fig. 3.2 against heights above the burner. Error bars of ± 60 K (Kammler et al., 2002) have been used in the figure for the experimental FTIR data. Overall, numerical results for flame temperature are in good agreement with the experimental data. Focussing on the SAXS data at low HABs, it is observed that the radial maximum temperature increases suddenly at $\text{HAB} = 0.8$ cm and decreases afterwards; this behaviour is reproduced well by the simulation. The simulation slightly underpredicts the

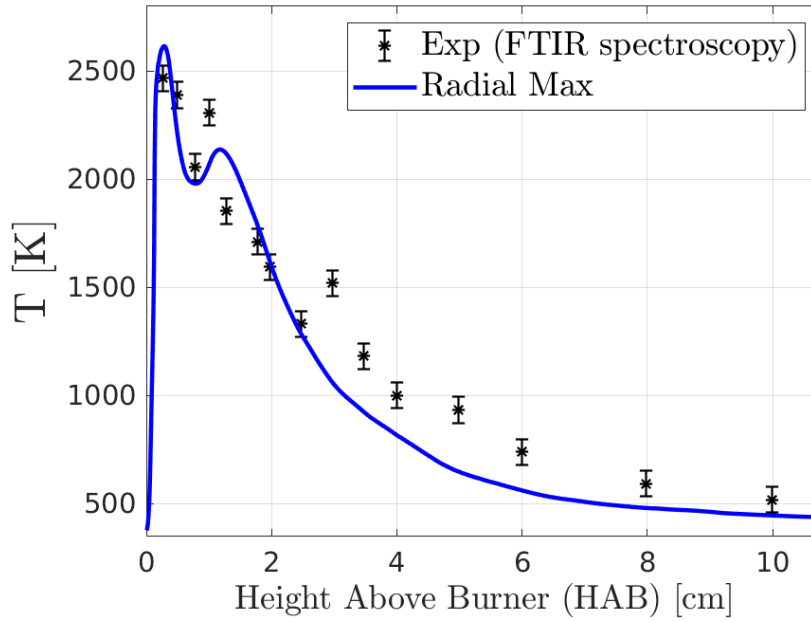


Figure 3.2: Comparison of numerical predictions with the experimental FTIR data of Camenzind et al. (2008) for flame temperature along the centreline. An average experimental error of ± 60 K given by Kammler et al. (2002) was used in the figure for the FTIR data.

experimental data at downstream locations ($3 < \text{HAB} < 8$ cm). This is likely due to uncertainties in the inflow boundary conditions and the micromixing model (Eq. (3.29)). As mentioned earlier, no turbulent fluctuations were superimposed at the inflow velocity profiles. Nevertheless, the flame temperature is predicted accurately at low HABs in the region of interest where nucleation, condensation, sintering and coagulation occur simultaneously. At downstream locations, the effect of all aerosol processes but aggregation is diminished, while SAXS data are not available for these locations. Based on these considerations, it is expected that the underestimation of temperature at downstream locations will not affect the conclusions drawn in the present study.

3.4.2 Comparison with experimental SAXS data

In the present section, numerical predictions for particle quantities are compared with the experimental SAXS data of Camenzind et al. (2008) and the nature of the discrepancies is discussed. For the reasons explained in Section 2.6.2, we present simulation results along the pathline of maximum silica volume fraction, where intense particle growth and high temperatures are found. Although, it should be mentioned that the maximum silica volume fractions are found on the centreline at $\text{HAB} > 1$ cm due to the effect of turbulent mixing; therefore, the

simulation results presented for $HAB > 1$ cm correspond to centerline results.

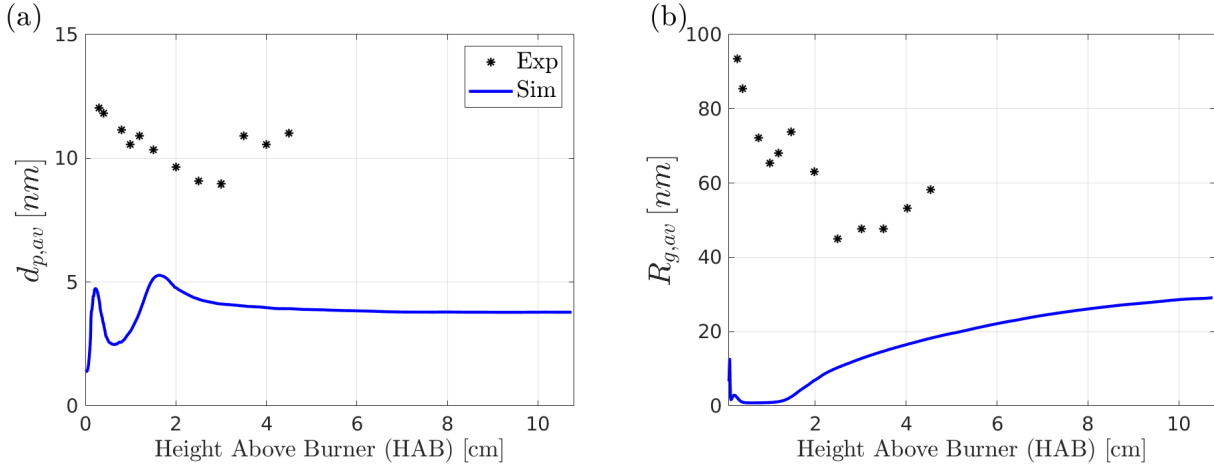


Figure 3.3: Comparison of the experimental SAXS data of Camenzind et al. (2008) with numerical predictions for (a) primary particle diameter and (b) radius of gyration of aggregates along the pathline of maximum silica volume fraction. Results were obtained with the extended one-PBE model described in Section 3.2.1.

Numerical predictions for the primary particle diameters, $d_{p,av}$, along the pathline of maximum silica volume fraction are shown in Fig. 3.3a, while numerical predictions for the average aggregate radius of gyration, $R_{g,av}$, are shown in Fig. 3.3b. The average aggregate radius of gyration is estimated by Eq. (3.9). The simulation predicts fully fused particles (spherical structures) at low HABs, while aggregate structures are predicted at downstream locations ($HAB > 1.4$ cm). This can also be seen from the small values of $R_{g,av}$ at low HABs and it is the aftermath of the high sintering rates predicted by the simulation at low HABs (see also Fig. 3.7 to be discussed later). On the contrary, the SAXS data suggest that fractal aggregates consisting of a large number of primary particles $O(100)$ are formed very early in the flame (Camenzind et al., 2008). While the experimental uncertainty of the SAXS data for $d_{p,av}$ is unknown to the authors at this point, it can be seen from Fig. 3.3a that the LES simulation underpredicted particle sizes by a factor of 2. It is worth mentioning that the relative difference of $d_{p,av}$ with the SAXS data in our laminar-flame simulation with the two-PBE model was about 15 % (see Fig. 2.5a). The underprediction of $R_{g,av}$ observed in Fig. 3.3b is a consequence of the underprediction of $d_{p,av}$; larger $d_{p,av}$ would result in smaller sintering rates, leading to aggregate structures. Primary particles can grow in size by sintering and simultaneous aggregation (coalescence), condensation, and surface reactions. The uncertainty involved in the models employed in the present study (presented in Section 3.2.2) for the description of these aerosol processes will be discussed here.

Focussing firstly on the sintering process, it is anticipated that the selection of a different sintering model for the present study, which would give larger sintering rates, would not result in higher estimates for $d_{p,av}$, since the simulation already predicts fully fused particles at HAB < 1.4 cm. In our laminar-flame simulation, results for primary particles were in good agreement with the SAXS data (see Fig. 2.5a), giving evidence that the sintering process is represented well by the model. Good agreement between simulation and experimental data was also found for the geometric standard deviation (see Fig. 2.6), suggesting that aggregation dynamics is described well by the extended one-PBE model. The condensation model described in Section 3.2.2 is based on the assumption that collisions between particles and product molecules occur in the free molecule regime, an assumption easily satisfied at these elevated flame temperatures found at low HABs. From this discussion, it can be concluded that the models for sintering and condensation are not associated with the main cause of the discrepancies observed in Fig. 3.3.

The evolution of primary particle sizes is also affected by the nucleation model; particles grow due to coagulation and coagulation/aggregation rates qualitatively follow nucleation rates at the early stages of nanoparticle synthesis (see, for example, Fig. 3.7b and Fig. 2.7a). In the present study, nucleation is treated as a collision process of gas molecules (monomers), resulting in the formation of dimers that serve as the first particles. Similar approaches are found in the literature (Shekar et al., 2012b). The dimers-based model described adequately particle-morphology evolution in our laminar-flame simulation in Chapter 2 and was in better agreement with the experimental data compared to the instantaneous-nucleation-assumption and classical-nucleation-theory models (see Section 2.6.4). However, it should be acknowledged that accurate prediction of particle nucleation rates remains an unresolved problem in the field of nanoparticle flame synthesis (Rosner, 2005).

Another source of uncertainty is associated with the precursor decomposition/oxidation reaction mechanism. The two-step chemical reaction mechanism of Feroughi et al. (2017) for HMDSO combustion (presented here in Table 2.2) was developed by optimising model parameters to fit experimental data obtained with low-pressure flames and low HMDSO concentrations. The experiment under investigation in the present study was conducted at atmospheric pressure and with relatively higher precursor concentrations.

Primary particles can grow in size through surface reactions. For example, an accurate description of such processes is of great importance in soot studies (Rigopoulos, 2019) where mass addition to particle phase occurs to a large extent by surface growth (Sun and Rigo-

poulos, 2022). Likewise, Arrhenius-type expressions for surface reactions have been employed by researchers (see (Tsantilis and Pratsinis, 2004) and references therein) to describe flame synthesis of TiO_2 nanoparticles. However, the contribution of surface reactions to particle growth of SiO_2 nanoparticles through flame synthesis is still unclear in the literature (at least from the author's viewpoint). Shekar et al. (2012a) and Shekar et al. (2012b) proposed a model for describing synthesis of silica nanoparticles from tetraethoxysilane (TEOS) and employed a dehydration surface reaction, while condensation was not included in their model. According to this model, a silicic acid $\text{Si}(\text{OH})_4$ molecule in the gas phase reacts with a $-\text{OH}$ site on a particle leading to the removal of a H_2O molecule. The surface reaction rate was estimated by assuming that the collision between a molecule in the gas phase and a particle can be described by the free molecular collision kernel. However, this surface reaction model is not directly applicable in the present study since $\text{Si}(\text{OH})_4$ is absent from the HMDSO reaction mechanics of Feroughi et al. (2017)). Ji et al. (2007) investigated silica flame synthesis via CFD and achieved good agreement between simulation and experimental data by fitting their model parameters, i.e. nucleation and surface growth rate constants. They concluded that particle growth was controlled largely by surface reaction.

There are also uncertainties in the closure models for describing turbulence-chemistry and turbulence-particle dynamics interaction. In the present analysis, the PDF-stochastic field method was employed to describe the influence of the unresolved scales and modelling was required for the micromixing term (Eq. (3.29)). While uncertainty about the micromixing model for nanoparticles remains, here it is argued that the uncertainty involved in the turbulence-particle dynamics interaction modelling is not the main cause for the discrepancies observed in Fig. 3.3. This argument is based on the fact that primary particles are underpredicted even at $\text{HAB} < 0.6$ cm where the flame is still relatively stable and turbulence is not yet developed (see Fig. 3.1a and 3.1b). In support of this argument, two different values of the micromixing constant for number densities were tested and results showed that $d_{p,av}$ is relatively insensitive to the micromixing constant $C_{d,p}$, at least for the present flame configuration (see Fig. 3.5b to be discussed in Section 3.4.3). Finally, the other model parameter in the PDF-stochastic field method is the number of stochastic fields. Results obtained with eight and sixteen stochastic fields (to be discussed in Section 3.4.4) were almost identical, indicating that this model parameter is not associated with the discrepancies observed in Fig. 3.3.

In light of the aforementioned arguments, the discrepancy between the simulation data for

$d_{p,av}$ and the experimental SAXS data (presented in Fig. 3.3) is attributed mainly to uncertainties involved in the nucleation model, the absence of a surface reaction model and the precursor decomposition kinetics.

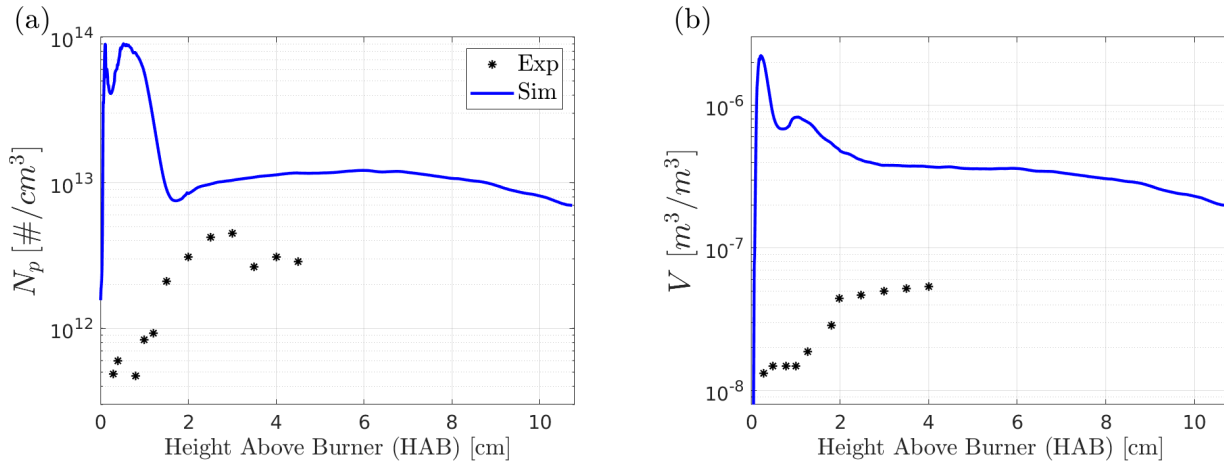


Figure 3.4: Comparison of the experimental data of Camenzind et al. (2008) with numerical predictions for (a) primary particle number concentration and (b) silica volume fraction along the pathline of maximum silica volume fraction. Results were obtained with the extended one-PBE model (described in Section 3.2.1). A logarithmic scale was used for the vertical axes.

Numerical predictions for the number concentration of primary particles, N_p , along the pathline of maximum silica volume fraction are compared with the experimental data of Camenzind et al. (2008) in Fig. 3.4a. The model overpredicts the experimental data, which is consistent with our laminar-flame study (see Fig. 2.5b). This discrepancy is most likely related to uncertainties involved in the nucleation model, the absence of a surface reaction model in the present simulation, and the SAXS measurements. It is anticipated that the incorporation of a surface reaction model would result in lower particle number concentrations at low HABs, since gas species would be consumed by surface reactions; thus, they would contribute less to the formation of new nuclei.

Numerical predictions for the silica volume fraction, V , are displayed in Fig. 3.4b together with experimental data given by Camenzind et al. (2008). It should be emphasised that SAXS data analysis gives only an indication of the total volume fraction of silica species in the aerosol (Kammler et al., 2005); therefore, quantitative comparisons are not sought at this point. It is, however, interesting to examine the data qualitatively. In a series of preliminary simulations for both flames, i.e. the turbulent case and the laminar case, with different nucleation models, it was observed that the total gas-to-particle mass conversion predicted by the model was relatively

insensitive to the nucleation model. It was the contribution of condensation versus nucleation that was altered but not the total gas-to-particle conversion. This implies that the qualitative discrepancy observed in Fig. 3.3b is most likely related to the precursor decomposition/oxidation reaction mechanism (presented in Table 2.2). Specifically, the experimental data suggest that V increases gradually, while the LES model predicts that V reaches a maximum value at $HAB = 0.3$ cm and decreases afterwards. This suggests that the two-step HMDSO reaction mechanism of Feroughi et al. (2017) is rather fast, at least for the flame conditions examined here.

3.4.3 Effect of particle sub-grid mixing

It is of interest at this point to investigate the influence of the sub-grid contribution and examine the effect of the associated model parameters. The model parameter that directly affects the sub-grid contribution is the micromixing constant $C_{d,\alpha}$ (Eq. (3.30)). Jones and Prasad (2010) employed the PDF-stochastic field method to describe a series of particle-free turbulent diffusion flames and examined the effect of the micromixing constant $C_{d,\alpha}$ on the LES results. Specifically, Jones and Prasad (2010) demonstrated that simulations with different values for $C_{d,\alpha}$, i.e two and three, resulted in negligible differences in the predicted flame temperatures. This suggests that the significance of the micromixing model is severely diminished in LES as compared to RANS (Jones and Prasad, 2010). However, the impact of the micromixing model on particulate flames is more questionable due to the very low diffusivity of nanoparticles.

The diffusivity of nanoparticles is much lower than that of gas-phase species. To account for this effect in the present study, the value $C_{d,p} = 0.002$ was assigned to the discretised number densities, while the value $C_{d,s} = 2$ was used for the chemical gas-species and enthalpy (see Section 3.2.4). To further investigate the effect of the micromixing constant, a simulation with $C_{d,p} = 2$ (and $C_{d,s} = 2$) was performed and comparisons of the two simulation cases are presented in Fig. 3.5.

Numerical predictions for the flame temperature obtained with the two different values of the micromixing constant for number densities are presented in Fig. 3.5a. The flame temperature is relatively insensitive to the value of $C_{d,p}$. This can be partly explained from that the fuel-combustion reactions are only weakly coupled to the precursor decomposition chemical reactions (Roth, 2007). Furthermore, the effect of thermal losses due to the radiation from nanoparticles, which could affect the flame temperature profile, seems to be less significant at

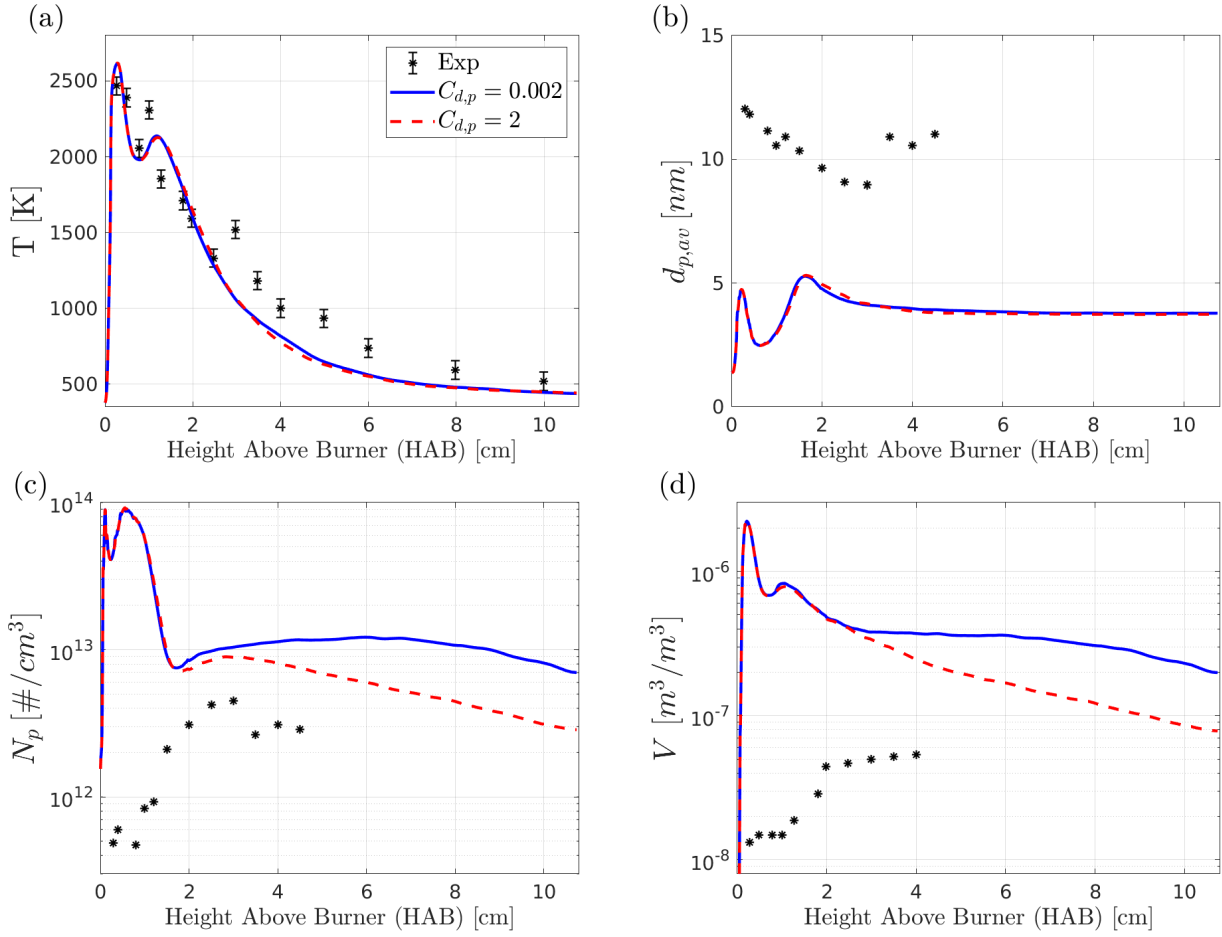


Figure 3.5: Comparison of numerical predictions obtained with two different values of the micromixing constant for number densities, i.e. $C_{d,p} = 0.002$ and $C_{d,p} = 2$: (a) flame temperature; (b) primary particle diameter; (c) primary particle number concentration; (d) particle volume fraction. In both cases, the micromixing constant for the gas-phase species and enthalpy was $C_{d,s} = 2$. Comparison is also made with the experimental data of Camenzind et al. (2008).

downstream locations where lower temperatures are encountered; $q_{rad,p}$ scales with the fifth power of temperature (see Eq. (3.19)). Results for the primary particle diameter, $d_{p,av}$, for the two cases are shown in Fig. 3.5b. The two cases with the different values of $C_{d,p}$ resulted in identical results for $d_{p,av}$. This is to be expected since sintering becomes negligible at roughly $HAB < 2.1$ cm as will be discussed in Section 3.4.5 and shown in Fig. 3.7b.

Numerical predictions for N_p and V obtained with the two different values of the micromixing constant for number densities are presented in Fig. 3.5c and 3.6d, respectively. Small differences are found between the two cases at low HABs in the core region of the flame ($0.8 < HAB < 2$ cm) where nucleation, condensation, sintering and coagulation occur simultaneously. Deviations between the two cases emerge at $HAB > 2$ cm, where intense turbulent mixing occurs. The case with the lower value of the micromixing constant ($C_{d,p} = 0.002$)

resulted in larger values for N_p and V at downstream locations. The micromixing model (see Section 3.2.4) represents sub-grid scale mixing (Jones and Prasad, 2010). A smaller value of the micromixing constant for the discretised number densities means less mixing of nanoparticles at the sub-grid scale level.

3.4.4 Effect of the number of stochastic fields

The results presented so far were obtained by using eight stochastic fields for the solution of Eq. (3.28) through Eq. (3.32). The choice of the number of stochastic fields, N_f , has been investigated by Mustata et al. (2006). Specifically, Mustata et al. (2006) used the PDF-stochastic field method to describe a turbulent diffusion flame. By performing simulations with eight and sixteen stochastic fields they showed that the two cases produced results with negligible differences. Similar findings were reported by Jones and Navarro-Martinez (2007). However, these studies dealt with particle-free flames. A similar analysis is performed in the present study but in the context of the LES-PBE-PDF method. Comparisons of LES results with eight and sixteen stochastic fields (for some representative variables) are presented in Fig. 3.6. Both simulation cases produced almost identical results, suggesting that eight stochastic fields are sufficient to obtain convergence and represent the sub-grid scale effects for both species and number densities.

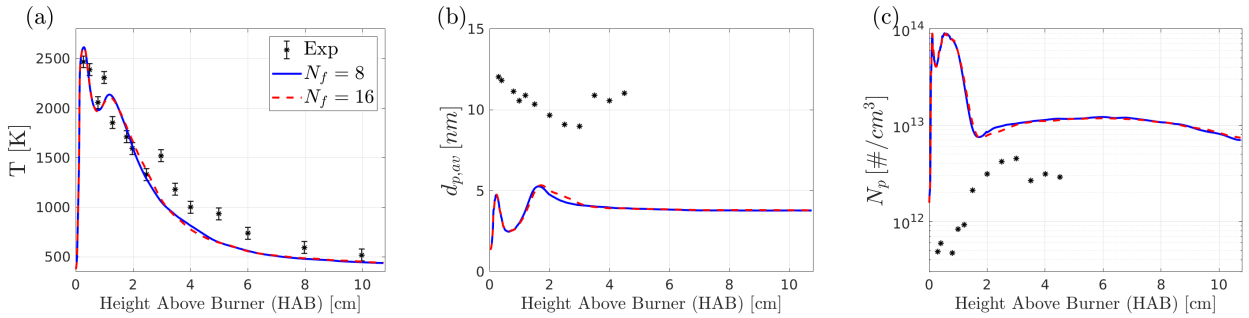


Figure 3.6: Comparison of numerical predictions obtained with eight and sixteen stochastic fields: (a) flame temperature; (b) primary particle diameter; (c) primary particle number concentration. For both cases, the micromixing constants were $C_{d,s} = 2$ and $C_{d,p} = 0.002$. Comparison is also made with the experimental data of Camenzind et al. (2008).

3.4.5 Investigation of gas-to-particle conversion

In the present section, the silica formation processes in the turbulent flame, as predicted by the LES method, are further analysed to provide further insight into the results demonstrated so

far. We start with describing the $\text{SiO}_2(\text{g})$ formation rate as it is driving many of the subsequent processes. The formation rate of $\text{SiO}_2(\text{g})$ species, R_{G2} , (see $G2$ reaction step in Table 2.2) along the pathline of maximum silica volume fraction is shown in Fig. 3.7a. It is observed that the peak values are found at low HABs (HAB < 0.6 cm) where the flame is still relatively stable, while most of the precursor is converted to $\text{SiO}_2(\text{g})$ at HAB < 1.65 cm.

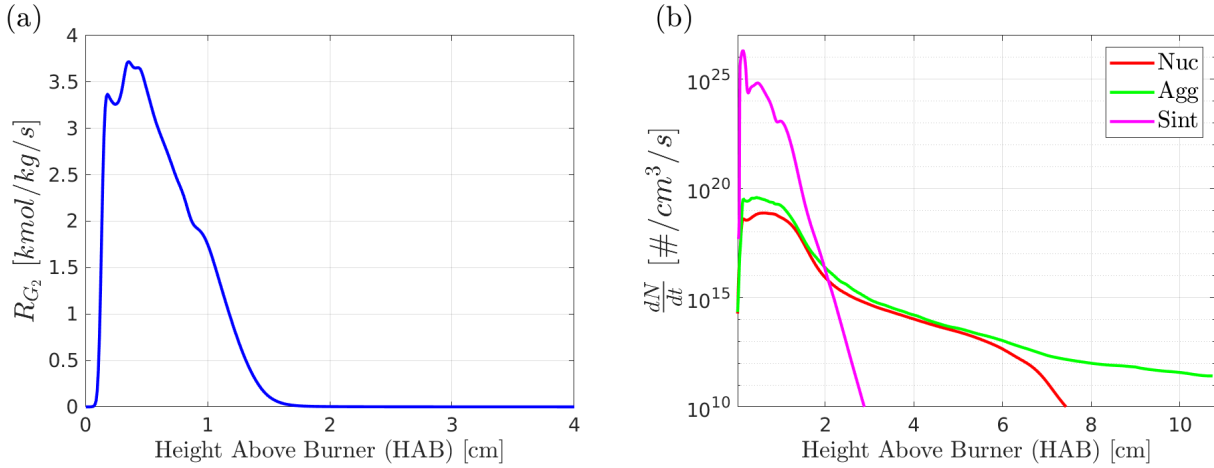


Figure 3.7: (a) Formation rate of $\text{SiO}_2(\text{g})$ species, R_{G2} , along the pathline of maximum silica volume fraction; (b) Rate of change of particle number concentration due to kinetic processes (absolute values) along the pathline of maximum silica volume fraction. Note that, for the sintering process in (b), the rate refers to the number concentration of primary particles, N_p . A logarithmic scale was used for the vertical axis of figure (b).

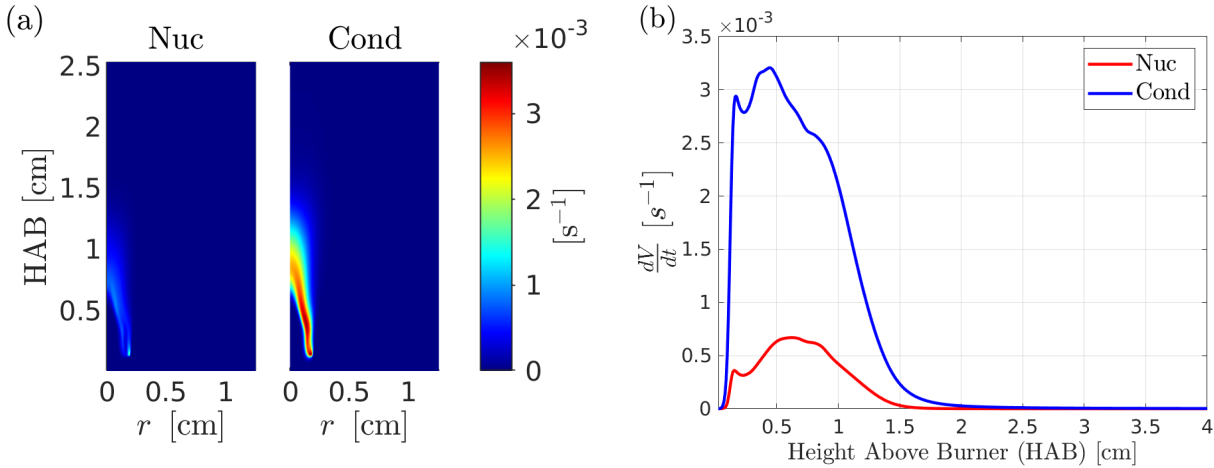


Figure 3.8: Rate of change of silica volume fraction due to nucleation and condensation. (a) Contour plots; (b) results along the pathline of maximum silica volume fraction.

The rate of change of particle number concentration due to aerosol processes along the pathline of maximum silica volume fraction is given in Fig. 3.7b. At HAB < 1.4 cm, it is seen that the sintering rate is many orders of magnitude higher than the rates of the other processes.

At these HABs, the simulation predicts fully fused particles, as already discussed in Section 3.4.2a. Subsequently, the sintering rate decreases rapidly by several orders of magnitude due to the drop in flame temperature, and aggregated particles start to form at $\text{HAB} > 1.4$ cm. The effect of sintering becomes negligible at downstream locations (see intersection of curves at $\text{HAB} = 2.1$ cm), which explains why the primary particle sizes remain constant at these locations (see Fig. 3.3a). The nucleation rate reaches maximum values at $\text{HAB} < 1.2$ cm in the flame reaction zone where new $\text{SiO}_2(\text{g})$ species are constantly formed, while it decreases by several orders of magnitude downstream where precursor conversion is almost complete. The predicted $d_{p,av}$ slightly decreases at $1.8 < \text{HAB} < 3$ cm partly because of the effect of nucleation. Interestingly, nucleation of particles continues to take place until $\text{HAB} \approx 7$ cm; however, its effect on $d_{p,av}$ and other particle quantities at $3 < \text{HAB} < 7$ cm is less profound. The aggregation rate follows the nucleation rate qualitatively, while aggregation becomes the dominant mechanism at $\text{HAB} > 7$ cm. The PSD reaches a self-preserving state (Vemury and Pratsinis, 1995) at $\text{HAB} > 7.3$ cm (not shown here).

The rate of change of the silica volume fraction due to aerosol processes is portrayed in Fig. 3.8a, while results along the pathline of maximum silica volume fraction are given in Fig. 3.8b. There are two features worth noting. The first one is that most of the gas-to-particle conversion occurs at low HABs ($\text{HAB} < 2$ cm). Intense particle formation and growth take place in the flame reaction zone at $\text{HAB} < 0.5$ cm where the flame is relatively stable; the maximum silica volume fraction was found at $\text{HAB} = 0.22$ cm (see Fig. 3.1c and 3.4b). The second one is that the condensation rate is almost five times larger than the nucleation rate. Thus, it can be seen that condensation is responsible for the largest proportion of the mass addition into the particle phase. The same was also observed in our laminar-flame simulation. Interestingly, in the soot study of Sun and Rigopoulos (2022), the contribution of condensation to gas-to-particle conversion was found to be less significant than that of nucleation. This different behaviour observed in the two cases can be partly explained by the highly supersaturated conditions found usually in nanoparticle flame synthesis. Finally, a spatial correlation between nucleation and condensation is also observed in Fig. 3.8a, as expected.

3.5 Summary

Synthesis of silica nanoparticles in a turbulent diffusion flame has been investigated numerically and results were presented in the present Chapter. The main objectives of the present study

were to apply a comprehensive LES methodology, employ the same set of models and parameters for gas-phase chemistry and aerosol dynamics as those employed for simulating silica synthesis in a laminar flame presented in Chapter 2, and finally compare the LES results with the experimental data of Camenzind et al. (2008). Particular emphasis was given to the nature of the discrepancies between predictions and experimental data, while possible sources of uncertainties in the model were discussed in light of our aforementioned laminar-flame simulation results.

The LES-PBE-PDF approach was employed for the simulations. The model components encompass a comprehensive description of gas-phase chemistry and aerosol dynamics. The evolution of particle morphology was described with an extended population balance model proposed in Chapter 2, which is based on the conservative sectional method (Liu and Rigopoulos, 2019; O’Sullivan and Rigopoulos, 2022); thus predicts the particle size distribution of silica. Furthermore, the model predicts the evolution of primary particle sizes by solving the PBE together with a transport equation for the number concentration of primary particles. The extended one-PBE model was incorporated into the filtered probability density function method, while the Eulerian stochastic field solution technique was employed for solving the LES-PBE-PDF equations. This approach accounts for the complex small-scale interaction between turbulence, chemistry and particle dynamics.

The LES results were compared with the experimental SAXS data of Camenzind et al. (2008) for the S-10 turbulent flame. To the best of the author’s knowledge, this was the first simulation of this experiment. Overall, good agreement was found between numerical predictions and experimental data for time-averaged temperature along the centreline. However, the LES model underestimated primary particle sizes by a factor of two. By examining the components of the methodology and leveraging knowledge that has been gained from our laminar-flame simulations and other studies in literature, the discrepancy was attributed to uncertainties associated with the nucleation model, the absence of a surface reaction model, and the precursor decomposition kinetics. Furthermore, the number concentration of primary particle sizes and the silica volume fraction were overestimated by the LES model, indicating that the two-step HMDSO reaction mechanism employed in the present study is rather fast, at least for the flame conditions examined here. It must be noted that the results were obtained without any adjustment of the model parameters, which were also employed in our laminar-flame simulation.

The effect of the particle sub-grid scale mixing was investigated by comparing results ob-

tained with two different values of the micromixing constant for number densities. A lower value of the micromixing constant, which counts for the low diffusivity of the nanoparticles, resulted in larger values for the silica volume fraction at downstream locations. Finally, results obtained with eight stochastic fields were almost identical to those obtained with sixteen stochastic fields suggesting that eight stochastic fields are sufficient to represent the sub-grid scale effects for both species and number densities.

An investigation of the gas-to-particle conversion processes was also conducted. The LES-PBE-PDF simulation predicted that most of the precursor was fully converted to product species in the vicinity above the burner. Furthermore, the results showed that the contribution of condensation to the total gas-to-particle conversion was more significant than that of nucleation. Notably, the opposite behaviour has been observed in soot studies.

Overall, the LES-PBE-PDF method has been shown to be a promising tool for simulating nanoparticle synthesis in turbulent flames. It is, however, clear that further research is required to reach a state where a quantitative agreement between simulations and experiments can be achieved without any adjustments in model parameters.

Chapter 4

Analysis of coagulation in turbulent flow

4.1 Introduction

The objective of the present chapter is to present an investigation of turbulence-coagulation interaction. Particle dynamics are described by the PBE, whose Reynolds decomposition leads to unclosed terms involving correlations of number density fluctuations. In this work, we employ a discretisation (sectional) method for the solution of the PBE, which is free of *a priori* assumptions regarding the particle size distribution (PSD), and couple it with a DNS for the flow field in order to study the behaviour and significance of the unknown correlations. The investigation is conducted on a 3-D planar jet laden with monodisperse nanoparticles, and coagulation in the free-molecule regime is considered.

Coagulation occurs in several contexts, such as atmospheric aerosols, cloud formation, flame synthesis of nanoparticles and combustion aerosols originating from sources such as incinerators and pulverised combustion units (Friedlander, 2000). In particular, coagulation is the dominant mechanism in aerosol synthesis of nanomaterials such as fumed silica (SiO_2), pigmentary titania (TiO_2), and zinc oxide (ZnO) vulcanising catalysts (Buesser and Pratsinis, 2012). In most cases, particle formation and coagulation occur in turbulent flows. The complexity of turbulence and the non-linear interactions involved in the aerosol processes render the resulting problem intractable via simplified methods. The objective of this study is to employ direct numerical simulation (DNS) of turbulence coupled with a discretised form of the PBE as a numerical tool for studying the turbulence-coagulation interaction.

The effect of turbulence on coagulation is manifested in two ways. The first is associated with the collision mechanism, which is substantially different in turbulent flows depending on

the particle size and inertia. This problem was first studied by Saffman and Turner (1956) and Levich (1962), who proposed expressions for the turbulent coagulation kernel. Numerous works, including Delichatsios and Probstein (1975), Wang et al. (1998) and Reade and Collins (2000), investigated experimentally and numerically the collision mechanism in turbulent flows and the assumptions inherent in the expressions for the kernels proposed.

The present study is concerned with the second, and rather less studied, effect of turbulence on coagulation, which is the influence of fluctuations in the particle number density. This is the “closure problem” of turbulence for aerosols, and it arises from the non-linear interactions between number densities of particles of different sizes that appear within the PBE for coagulation. Early discussions of this problem appear in the works of Levin and Sedunov (1966, 1968); Scott (1967) and Warshaw (1967). These studies were concerned with turbulent coagulation in the context of coalescing cloud droplets and were reviewed by Drake (1972). More specifically, Levin and Sedunov (1968) dropped the correlations due to the coagulation source term because of the lack of knowledge at that time regarding the fluctuations in the collision integral, while Warshaw (1967) assumed that the correlations can be neglected in the case of a very large cloud volume. Friedlander (2000) also stated that the importance of these terms has not been carefully studied, while Drossinos and Housiadas (2006) mentioned that more attention must be given to the PBE in turbulent flows.

4.1.1 Literature review

The first study of coagulation with a DNS–PBE approach was done by Settumba and Garrick (2003), where simulations of a two-dimensional (2-D) incompressible temporal mixing layer were performed. A moment method, which requires *a priori* assumptions on the shape of the PSD, was used to describe the coagulating aerosol. A coagulation Damköhler number was also defined, which represents the ratio of the convection to coagulation time scales.

A nodal method that makes no *a priori* assumptions regarding the PSD was used by Miller and Garrick (2004) for their simulations of nanoparticle coagulation in a 2-D turbulent planar jet. They showed that large-scale vortical structures perturb the PSD from the self-preserving distribution and lead to particle distributions with larger geometric standard deviations. However, the computation of turbulent fluctuations which occur when decomposing the particle concentration field into time-averaged and fluctuations (in the context of Reynolds-averaged Navier-Stokes (RANS)) or resolved and subgrid components (in the context of large-eddy sim-

ulation (LES)) was left for future work. Garrick et al. (2006) performed further DNS of nanoparticle coagulation in a 2-D temporal mixing layer, where a nodal representation with 12 bins was used. An increase in the coagulation Damköhler number was found to result in an increase in particle growth and in prediction of PSDs wider than the self-preserving limit. It was concluded that three-dimensional (3-D) simulations, where vortex tilting and stretching can occur, are needed to fully understand the effects of turbulence on the PSD.

The interaction of turbulence with nanoparticle coagulation was studied by Garrick (2011). Coagulation was the sole aerosol mechanism in a 3-D turbulent shear flow. A method of moments, which assumes that the PSD is log-normal, was employed to describe the particle field. The particle growth rate was decomposed into large- and small-scale interactions in order to investigate the effect of the flow dynamics and the coagulation Damköhler number. The DNS results showed that small-scale interactions act to both increase and decrease particle growth. Furthermore, PDFs conditioned on the Q-criterion suggested that in rotation-dominated regions, the effect of the small-scale interactions is primarily to reduce particle growth.

The effect of turbulence on nanoparticle growth in turbulent reacting flows was studied by Das and Garrick (2010). A nodal approach with 22 “bins” was utilised to describe nucleation, condensation and coagulation in a planar turbulent jet via DNS. Instantaneous, filtered and spanwise averaged data of the particle field were computed in order to examine the nature of the unresolved contributions (turbulent fluctuations) on particle growth. The effect of turbulence on particle dynamics was assessed by decomposing the particle growth rate in averaged and fluctuating components (in the context of RANS) and filtered and unresolved components (in the context of LES). The results revealed that unresolved small-scale fluctuations can both augment and inhibit particle growth, but the predominant effect is to reduce particle growth. That research concluded that turbulence or sub-grid scale (SGS) models are needed for accurately simulating particle dynamics in turbulent flows.

One of the few experimental studies of nanoparticle coagulation in turbulent flows was done by Junzong et al. (2013). The authors studied silica SiO_2 nanoparticle dispersion and coagulation in a high-Reynolds-number round jet. It was shown that there is an intermediate region across the centreline with high turbulence intensity where the Sauter mean diameter, which was used to characterise particle size, increases. This was attributed to the turbulence coagulation effect, where turbulent vortices promote coagulation. The experimental configuration of Junzong et al. (2013) was investigated numerically by Pasmazoglou et al. (2017), where a stochastic

aggregation model based on a Lagrangian framework was applied in the context of LES. The results showed good agreement with the experiments. However, the authors concluded that aggregation did not play a big role for this configuration since no significant differences were found by including or excluding the aggregation model.

One of the first attempts to model the effect of turbulent fluctuations on the PBE was made by Rigopoulos (2007) where a PDF approach, which overcomes the closure problem, was developed and tested in a partially stirred reactor. It was concluded that future work should evaluate the error that occurs by neglecting the turbulent fluctuations of the PSD in particle formation/coagulation problems. Later work studied these fluctuations in nucleation-growth problems via the PBE-PDF method in RANS (Rigopoulos, 2010; Di Veroli and Rigopoulos, 2009, 2010, 2011) and LES (Sewerin and Rigopoulos, 2017, 2018, 2019). The PBE in turbulent flow was also studied via coupling with DNS in the context of a nucleation-growth problem by Tang et al. (2020). However, none of these studies included coagulation.

4.1.2 Present investigation

From the preceding review, it can be concluded that the turbulence-coagulation interaction is not yet fully understood. This work aims to study in more detail this interaction, and in particular to shed light on the long-standing problem of the unknown correlations that arise in the Reynolds decomposition of the PBE. The behaviour and significance of these correlations are investigated by performing DNS of a 3-D spatially developing planar jet laden with monodisperse nanoparticles. This flow case is relevant to many engineering and environmental processes involving particle coagulation (gas-phase synthesis of nanoparticles, plumes with particulate emissions). The mathematical methodology used for the characterisation of the nanoparticle dynamics is the PBE coupled with DNS, and thus results in a fully Eulerian description of aerosol dynamics in a turbulent flow. The PBE is solved via a recently proposed discretisation method (Liu and Rigopoulos, 2019), and the whole distribution is retrieved without any assumptions about its shape. By keeping the approach model-free, we aim to focus on the turbulence-coagulation interaction and draw conclusions that will aid the development of new models. The findings of the study are relevant to any problem featuring turbulence and coagulation, such as soot formation and nanoparticle synthesis. However, in such problems, it is difficult to distinguish the result of this interaction from other effects, particularly those associated with chemical kinetic processes such as nucleation and growth. As a result, it is

difficult to determine the contribution of this effect to discrepancies in comparisons between experimental and numerical results, which are usually attributed to different reasons. The present study is effectively a DNS-based computational experiment that isolates the effect of turbulence–coagulation interaction.

The rest of this chapter is structured as follows. Section 4.2 presents the governing equations, the numerical solution method, and details on the flow configuration and the computational setup. Subsequently, in Section 4.3, results for the flow field are validated with experimental and other reference DNS data, while results of the particle field are validated by comparing the PSD with the theoretical self-preserving distribution. The results are presented and discussed in Section 4.4, in the following order. First, the evolution of the moments and the effects of coagulation and turbulent mixing are discussed. Following this, the discussion focuses on the analysis of turbulent fluctuations of the number densities. Particular emphasis is given to the effect of the unknown correlations that occur when applying Reynolds decomposition to the transport equations of the zeroth and second moments. Finally, the conclusions are presented in Section 4.5.

4.2 Methodology

4.2.1 Governing equations

The flow is assumed to be incompressible and isothermal, governed by the Navier-Stokes equations:

$$\frac{\partial u_i^*}{\partial t^*} + u_j^* \frac{\partial u_i^*}{\partial x_j^*} = -\frac{\partial p^*}{\partial x_i^*} + \frac{1}{Re} \frac{\partial^2 u_i^*}{\partial x_j^* \partial x_j^*}, \quad (4.1)$$

$$\frac{\partial u_j^*}{\partial x_j^*} = 0, \quad (4.2)$$

where u_i^* is the Cartesian velocity component in the i th direction, and p^* is the pressure. The asterisk denotes non-dimensional variables, defined as:

$$u_i^* = \frac{u_i}{U_o}, \quad p^* = \frac{p}{\rho U_o^2}, \quad x_i^* = \frac{x_i}{h}, \quad t^* = \frac{t}{h/U_o}, \quad (4.3)$$

where U_o is the jet velocity, h is the jet width at the inlet, and ρ is the fluid density. The Reynolds number is defined as $Re = U_o h / \nu$, where ν is the kinematic viscosity.

The nanoparticle dynamics is described by the PBE, which assumes the form (Friedlander,

2000):

$$\begin{aligned} \frac{\partial n}{\partial t} + u_j \frac{\partial n}{\partial x_j} = & \frac{\partial}{\partial x_j} \left(D_p \frac{\partial n}{\partial x_j} \right) \\ & + \frac{1}{2} \int_0^v \beta(w, v-w) n(w) n(v-w) dw - \int_0^\infty \beta(v, w) n(v) n(w) dw \end{aligned} \quad (4.4)$$

where v and w denote particle volume, $n = n(\mathbf{x}, t, v)$ is the number density function per unit volume of fluid (such that $n dv$ is the concentration of particles with volume between v and $v + dv$), D_p is the diffusion coefficient of particles of volume v yielded by the Stokes-Einstein equation (Friedlander, 2000), and $\beta(v, w)$ is the coagulation kernel, a function that represents the frequency of collisions that lead to coagulation events and will be discussed further below. Coagulation is described by the two integral terms in (4.4), which denote particle birth and death. The birth term accounts for all possible particle pairs whose coalescence results in particles of volume v , while the death term accounts for the disappearance of particles of volume v due to coagulation with particles of any volume. The PBE can include additional mechanisms representing nucleation, growth and breakage, but the focus of the present study is on coagulation.

When the particle diameter is much smaller than the mean free path of the carrier gas, the particles can be assumed to behave like rigid elastic spheres, and an expression for the collision frequency $\beta(v, w)$ can be derived from the kinetic theory of gases. In this case, coagulation takes place in the free-molecule regime and the kernel is:

$$\beta(v, w) = A_1 \left(\frac{1}{v} + \frac{1}{w} \right)^{1/2} (v^{1/3} + w^{1/3})^2, \quad (4.5)$$

with the factor A_1 defined as:

$$A_1 = \left(\frac{3}{4\pi} \right)^{1/6} \left(\frac{6k_b T}{\rho_p} \right)^{1/2} \quad (4.6)$$

where ρ_p is the particle density, T is the temperature, and k_b is the Boltzmann constant.

For future reference, we also present the transport equation for the moments of the distribution $n = n(\mathbf{x}, t, v)$. The k th moment, M_k , is defined as:

$$M_k = \int_0^\infty v^k n(v) dv. \quad (4.7)$$

Some of the low-order moments have a physical interpretation. For example, the zeroth moment, M_0 , is the total number concentration of particles, while the first moment, M_1 , represents the particle volume fraction. Furthermore, when the diameter of the particles is smaller than the

wavelength of the incident light, the second moment, M_2 , is proportional to the total light scattering by particles (Friedlander, 2000). The following transport equation for the evolution of M_k can be derived (Whitby and McMurry, 1997; Williams and Loyalka, 1991):

$$\frac{\partial M_k}{\partial t} + u_j \frac{\partial M_k}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D_p \frac{\partial M_k}{\partial x_j} \right) + \frac{1}{2} \int_0^\infty \int_0^\infty (v+w)^k \beta(v, w) n(v) n(w) dv dw - \frac{1}{2} \int_0^\infty \int_0^\infty (v^k + w^k) \beta(v, w) n(v) n(w) dv dw. \quad (4.8)$$

In the absence of convection and diffusion (i.e. in a perfectly stirred reactor), it can be shown that (4.4) admits self-similar solutions. It must be noted that M_1 is constant under these conditions. If the number density function and particle volume are scaled as:

$$\psi = \frac{M_1}{M_0^2} n, \quad (4.9)$$

$$\eta = \frac{M_0}{M_1} v, \quad (4.10)$$

and substituted in (4.4), then the solution reaches a time-independent distribution $\psi(\eta)$ after a sufficient amount of time. The initial particle distribution affects the time to reach the self-preserving (SP) state but not the distribution itself (Friedlander, 2000). For an initially monodisperse aerosol undergoing coagulation in the free-molecule regime, the time to reach the self-similar distribution is (Landgrebe and Pratsinis, 1990; Vemury et al., 1994):

$$\tau_{SP} = \frac{\tau_f}{A_1 v_o^{1/6} N_0}, \quad (4.11)$$

where $\tau_f \approx 5$ (Vemury et al., 1994), v_o is the initial particle volume, and N_0 is the initial particle concentration.

Using (4.3) and the non-dimensional variables:

$$n^* = \frac{n}{n_o}, \quad v^* = \frac{v}{v_o}, \quad (4.12)$$

where n_o, v_o are the number density and volume of particles at the inlet, respectively, and substituting into (4.4) we obtain:

$$\frac{\partial n^*}{\partial t^*} + u_j^* \frac{\partial n^*}{\partial x_j^*} = \frac{1}{Sc} \frac{1}{Re} \frac{\partial^2 n^*}{\partial x_j^* \partial x_j^*} + Da_{coag} \left(\frac{1}{2} \int_0^{v^*} \beta^*(w^*, v^* - w^*) n^*(w^*) n^*(v^* - w^*) dw^* - \int_0^\infty \beta^*(v^*, w^*) n^*(v^*) n^*(w^*) dw^* \right), \quad (4.13)$$

where $\beta^*(v^*, w^*) = (1/v^* + 1/w^*)^{1/2} (v^{*1/3} + w^{*1/3})^2$ is the normalised collision function, and $Sc = \nu/D_p$ is the particle Schmidt number (defined as the ratio of the kinematic viscosity to the

particle diffusion coefficient). The factor Da_{coag} is the coagulation Damköhler number, which is equal to the ratio of a convection time scale to a coagulation time scale. The time scales are defined here as in Garrick et al. (2006) and for the case of the free-molecule regime Da_{coag} is given by:

$$Da_{coag} = \frac{\tau_{conv}}{\tau_{coag}} = \frac{A_1 h N_0}{U_o} v_o^{1/6}, \quad (4.14)$$

where the convection time scale is $\tau_{conv} = h/U_o$, and the coagulation time scale is $\tau_{coag} = (A_1 N_0 v_o^{1/6})^{-1}$. For the case of an initially monodisperse aerosol, (4.11) shows that the coagulation time scale is one-fifth of the time needed to reach the self-preserving distribution. Based on (4.11) and (4.14), the coagulation Damköhler number can be written as:

$$Da_{coag} = \frac{5\tau_{conv}}{\tau_{SP}}. \quad (4.15)$$

The assumptions of the approach adopted in the present study are listed below.

- Coagulation in the free-molecule regime is considered, which means that particles should be smaller than the mean free path in the carrier fluid. It must be mentioned that our simulations are carried out in terms of dimensionless variables, but if we assume, for example, that the particles at the inlet of the jet have diameter 5 nm, then the maximum particle mean size in the jet would be around 25 nm, which is less than the mean free path in the air at normal temperature and pressure (about 65 nm).
- The particles have no effect on the fluid motion and do not affect the fluid properties (density, viscosity etc.). If we assume that the particles at the inlet have diameter 4–5 nm, the jet nozzle width is roughly 1 cm and the temperature of the jet is close to 50°C, conditions not far from those in the experimental work of Junzong et al. (2013), then the particle volume fraction at the inlet is less than 10^{-6} . This value is small enough to ensure the validity of the assumption (Elghobashi, 2006).
- The particles are spherical due to instantaneous coagulation. While we are not considering a particular physical system, this is usually true for nanoparticle coagulation in the free-molecule regime.
- The flow is assumed to be isothermal.
- Electrostatic effects (Van der Waals forces) are not taken into account.
- The Stokes number St – which is the ratio of a characteristic time scale of the particles, $\tau_p = \rho_p d_p^2 / (18\mu)$ (Friedlander, 2000), to that of the flow τ_f – is much smaller than unity and therefore the particles follow the fluid. This assumption is satisfied easily for nano-

particles, and an example is given here to justify this assertion. If we assume that particles at the inlet have diameter 5 nm, then the largest particles found in the jet (at the right edge of the PSD with very low number density) would have diameter 200 nm (as will be found later in this study). Then τ_p can be calculated by using $\rho_p = 2200 \text{ kg/m}^3$, which is a typical value of density for silica nanoparticles, and $\mu = 1.82 \cdot 10^{-5}$. The smallest time scale in our problem is the Kolmogorov time scale, $\tau_\eta = \sqrt{\nu/\epsilon}$, and this is taken as τ_f in this example. The smallest non-dimensional value of τ_η calculated by the present DNS was 0.38, while the way the variables are non-dimensionalised has been shown in (4.3). If we assume a jet nozzle width $h \approx 1 \text{ cm}$, then the corresponding dimensional value of τ_η would be $7.59 \cdot 10^{-4}$. Based on these assumptions, the estimated Stokes number would be $St \approx 4 \cdot 10^{-4} \ll 1$.

- A Schmidt number $Sc = 1$ is assumed for all particle classes. In reality, Sc takes a range of values because it depends on the particle diffusion coefficient D_p , which in turn is a function of particle size according to the Stokes-Einstein equation (Friedlander, 2000). For temperature 298 K, for example, particles with 20 nm diameter have Schmidt number 1415. The use of $Sc = 1$ implies higher diffusive transport, and studies of flows with high Sc have so far been conducted only in the context of 2-D flows, such as the study of Garrick and Khakpour (2004) on a 2-D mixing layer and the study of Cifuentes et al. (2020a) on a 2-D flame–vortex interaction. However, a high Sc results in Batchelor scales, $\eta_c = \eta/\sqrt{Sc}$, that are much smaller than the Kolmogorov scale, η (Davidson, 2004). For example, for $Sc = 1415$, η_c would be roughly 37 times smaller than η ; hence in a 3-D flow, it would require a grid with 37^3 more cells. For the present simulation, which currently uses 52 million cells, this would amount to 2.6 trillion cells. Therefore, the study of the effect of high Sc in a 3-D flow simulation has to be left for future work.

4.2.2 Numerical methods

The simulations were performed with our computational fluid dynamics (CFD) code, PANTARHEI, which is coupled with the in-house code for population balance modelling, CPMOD. PANTARHEI has been used to simulate a number of transitional and turbulent flows (Alves Portela et al., 2020; Xiao and Papadakis, 2019). The incompressible Navier-Stokes equations are discretised by applying the finite volume method in unstructured grids, and all unknown variables are stored at the cell centroids (collocated variable arrangement). A second-order central

discretisation scheme is employed for the convection and viscous terms, while a third-order backward differentiation formula (BDF) is used for the transient term. The orthogonal viscous terms are treated implicitly, while the convection term and the non-orthogonal diffusion terms are extrapolated from the previous three time steps. The pressure-velocity coupling is dealt with by the fractional step method. The code is parallelised with the aid of the PETSc and HYPRE libraries (Balay et al., 2021).

A method developed recently by Liu and Rigopoulos (2019) is employed for the discretisation of the PBE. The method a) provides an accurate prediction of the distribution with a small number of sections, b) conserves the first moment (or any other single moment) in coagulation, c) is applicable to any non-uniform grid (even an adaptive one), and d) is efficient and robust when coupled with CFD. It is based on the framework of finite-volume methods applied to the particle volume domain, v truncated to (v_o, v_{max}) . The latter is discretised in $(v_o, \dots, v_k)$, the intervals $\Delta v_i = v_i - v_{i-1}, i = 1, \dots, k$ are defined, and each interval corresponds to a number density n_i . One of the main challenges in the numerical solution of the PBE is the conservation of the first moment in coagulation, due to the presence of the integral terms. In our method, a transformation is employed to decompose the birth term into fluxes of coagulating particles, and a map is constructed to record them. An algorithm for constructing this map in an arbitrary non-uniform grid has been developed, and the aggregation birth and death terms are then calculated via these fluxes, resulting in mass conservation without introducing correction terms. The map is constructed once at the start of the simulation and accessed throughout the run, making the method computationally efficient and easy to couple with CFD. Test cases, including analytical solutions and a co-flow laminar flame (Liu and Rigopoulos, 2019), have shown that the method produces very accurate solutions that conserve the first moment, even on coarse grids.

After discretisation in the volume domain, the PBE is converted into a coupled system of partial differential equations that govern the temporal and spatial evolution of the PSD in terms of discretised number densities, n_i . The transport equation for n_i is:

$$\frac{\partial n_i}{\partial t} + \frac{\partial(u_j n_i)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D_p \frac{\partial n_i}{\partial x_j} \right) + S_i(n_1, \dots, n_k), \quad (4.16)$$

where the source term, $S_i(n_1, \dots, n_k)$, represents the effect of coagulation for particles in the interval i . The numerical scheme used for the solution of these transport equations is slightly different from that described previously for the flow field. More specifically, the convection and viscous terms are treated explicitly using third-order extrapolation from the previous three

time steps. The values of $n_1, \dots, n_k$ are also extrapolated similarly and used to calculate S_i . In order to ensure boundedness for n_i , the Gamma differencing scheme (Jasak et al., 1999) was employed for the discretisation of the convection term, and the value 0.1 was used for the scheme parameter β_m .

4.2.3 Flow configuration and computational setup

Direct numerical simulations of a 3-D spatially developing planar turbulent jet were performed. The jet is laden with monodisperse nanoparticles and flows into a particle-free co-flow stream. There is a wealth of data for validating the flow field (Stanley et al., 2002; Le Ribault et al., 1999; Klein et al., 2003a,b; Suresh et al., 2008; Watanabe et al., 2014; Pope, 2000; Rajaratnam, 1976).

The flow configuration is similar to that of Stanley et al. (2002). The Reynolds number is $Re = U_o h / \nu = 3000$, and the ratio of co-flow velocity, U_∞ , to the jet velocity, U_o , is $U_\infty / U_o = 0.2$. The x, y and z coordinates (corresponding to indices $i = 1, 2, 3$ in the notation of (4.1)) are defined in the streamwise, cross-stream and spanwise directions, respectively. Turbulent properties are statistically homogeneous in the z -direction. The size of the computational domain $L_x \times L_y \times L_z$ is $25h \times 26h \times 5h$, similar to that of Stanley et al. (2002) and Das and Garrick (2010). The computational domain is long enough in the streamwise direction for the flow to reach fully developed turbulence. In addition, the domain is extended in the cross-stream direction in order to minimise the effect of the top and bottom boundaries.

A convective boundary condition was applied at the outlet boundary in the streamwise direction; this boundary condition allows vortices to propagate through the exit plane with minimal reflection. Periodic boundary conditions were used in the spanwise direction. Finally, a symmetry boundary condition was applied to the top and bottom boundaries. This condition does not allow for mass entrainment, and this causes a small reduction in the local co-flow velocity in the streamwise direction. To mitigate this effect, the computational domain was significantly extended in the cross-stream direction. Good agreement between the DNS and reference data from the literature, to be presented later, in Section 4.3.1, suggests that the effect of the boundaries is very small.

At inflow, a top-hat profile with smooth edges is prescribed for the mean (i.e. time-averaged) velocity. The profile is given by (Klein et al., 2003b; Stanley et al., 2002):

$$\overline{U}(y) = \frac{U_o + U_\infty}{2} + \frac{U_o - U_\infty}{2} \tanh \frac{-|y| + h/2}{2\theta_o}, \quad (4.17)$$

where $\theta_o = h/20$ (Le Ribault et al., 1999) is the shear layer momentum thickness. The mean cross-stream and spanwise velocities were set to zero. The mean profile of the number density for the first interval n_1 is given by the tangential profile:

$$\overline{n_1}(y) = n_{1o} + n_{1o} \tanh \frac{-|y| + h/2}{2\theta_o}, \quad (4.18)$$

where n_{1o} is the time-averaged value of n_1 at the centreline.

The method of Klein et al. (2003a) was employed to generate artificial turbulent fluctuations at the inlet. The method requires a mean velocity profile, a profile for the Reynolds stresses, turbulence length and time scales, a filter width, and the number of slices (snapshots) of data to be generated. The output of the algorithm is a 3-D matrix that represents the velocity components at the inlet plane for different time snapshots. In the present study, the mean velocity profile is given by (4.17). Strictly speaking, the rms profile in the x direction, u_{rms} , should be zero at $y = \pm h/2$. However, it grows quickly due to high shear, and for this reason, u_{rms}/U_o is set to 1.25% at the jet centreline and increases parabolically to 5% at $y = \pm h/2$. The turbulence intensity of the co-flow is set to 1%. This u_{rms} profile is similar to that employed by Stanley et al. (2002). The velocity rms in the y and z directions were set equal to u_{rms} . The turbulence length scale was $l_{Turb} = 0.3h$, and the turbulence time scale was $t_{Turb} = 10h/U_o$, where it was assumed that $t_{Turb} = l_{Turb}/U_{rms}$, with $U_{rms} = 3\%U_o$. A discussion on the value and the effect of the turbulence length scale can be found in Klein et al. (2003a). The number of snapshots was equal to 100, which is large enough to generate data for one flow-through time (defined using the length of the computational domain and the co-flow velocity, $T = L_x/U_\infty$). The number of snapshots was calculated based on the prescribed turbulence length and time scales mentioned above.

The simulations were performed on a non-uniform computational grid with approximately 52 million cells, distributed as $900 \times 452 \times 128$ in the x, y, z directions, respectively. The grid spacing was uniform in the x and z directions, and equal to $\Delta x = 0.028h$ and $\Delta z = 0.039h$. In the y direction, it was very fine close to the centreline, where $\Delta y = 0.018h$, and increased exponentially towards the boundaries, where $\Delta y = 0.124h$. The time step was $\Delta t = 0.005h/U_o$, resulting in a maximum Courant–Friedrichs–Levy (CFL) number of 0.24. Convergence studies with a perfectly stirred reactor showed that this time step is adequate for the coagulation dynamics for the conditions considered.

Each simulation was run first for one flow-through time T to reach a state that is independent of the initial conditions (recall that T is defined using the co-flow velocity U_∞ , which is five times

	Da_{coag}	Re	PSD becomes self-preserving	# of intervals	v_{max}/v_o
Case 1	1	3000	before jet break-up	35	11250
Case 2	$\frac{1}{3}$	3000	after jet break-up	35	2800

Table 4.1: Computational parameters of the simulations.

smaller than U_o). Following this, the simulations were run for 80000 time steps (corresponding to $3.2T$), and statistics were computed by averaging in time and in the homogeneous spanwise direction. Finally, where possible, exploitation of the jet symmetry with respect to the centreline was used to double the sample size. The number of cores was 1008, and 84672 Cray XC30 CPU hours were required for each case.

The maximum value of the ratio of cell size, defined as $\Delta_{cell} = (\Delta x \Delta y \Delta z)^{1/3}$, to the Kolmogorov length scale $\eta = (\nu^3/\epsilon)^{1/4}$ in the domain was 2.8, while the mean value in the region of fully developed turbulence was 1.95. The grid resolution was assessed by checking the balance of the turbulent kinetic energy equation; results are shown in Section 4.3.1, Fig. 4.5. The terms of the equation balance well, and the maximum error was less than 5.5% of the peak absolute value of convection due to mean flow, indicating that the grid resolution is fine enough. The one-dimensional spectra of the velocity fluctuations for a selected point in the fully turbulent region are also presented in Section 4.3.1, Fig. 4.6. The spectra exhibit a $-5/3$ power-law slope over about a decade. There is also a dissipative range with a faster decay rate at high frequencies, indicating that the turbulent motions are well resolved. The maximum Reynolds number $Re_\lambda = \sqrt{|\mathbf{u}'|^2} \lambda / \nu$, based on the Taylor micro-scale $\lambda = \sqrt{\nu |\mathbf{u}'|^2 / \epsilon}$, was found to be 160.

Simulations for two different coagulation Damköhler numbers, $Da_{coag} = 1$ and $Da_{coag} = 1/3$, were performed. The values of Da_{coag} are close to those examined in previous studies of nanoparticle coagulation (Garrick, 2011; Garrick et al., 2006). The two cases correspond to different times for the PSD to reach the self-preserving distribution. According to (4.15), in a perfectly stirred reactor, these times would be $\tau_{SP} = 5$ and $\tau_{SP} = 15$, respectively. As will be shown later, the jet breaks up at $x/h \approx 7.5$. For the chosen values of Da_{coag} , the PSD becomes self-similar upstream and downstream of the break-up location for the first and second cases, respectively.

The PBE was discretised with 35 intervals in the particle volume domain. An exponential grid was employed for all cases; this is well-suited for fast-growing particles. The range $(v_o, \dots, v_{max})$ covered was different for each Da_{coag} case; v_o remained the same but the max-

imum value was $v_{max} = 11250v_o$ for $Da_{coag} = 1$, and $v_{max} = 2800v_o$ for $Da_{coag} = 1/3$ case. Convergence studies with a perfectly stirred reactor showed that this grid is sufficiently accurate and ensures that the size distribution does not grow beyond the maximum value during the simulation time. The computational parameters of the simulations are also summarised in Table 4.1.

The simulations were carried out in terms of dimensionless variables. The non-dimensionalisation of the equations is described in Section 4.2.1, where an asterisk was introduced to denote dimensionless variables; refer to (4.3) and (4.12). In the sections that follow, only dimensionless variables are presented, and for the sake of simplicity, the asterisk has been removed.

4.3 Comparison with reference data

4.3.1 Flow field validation

In this section, the DNS data for the planar jet flow are presented and compared with experimental and other reference simulation data from the literature. Additional data for the balance of the terms in the turbulent kinetic energy equation and the one-dimensional spectra of turbulent fluctuations are given in Section 4.3.1. The turbulent kinetic energy, k , in the (x-y) plane is depicted in Fig. 4.1a (because of symmetry only the top half is shown). The jet breaks up at $x \approx 7.5$, and downstream of this location the turbulent kinetic energy rapidly grows and decays again; the maximum of k is located at $(x, y) = (11, 0.7)$. Contours of instantaneous spanwise vorticity and passive scalar fields, ω_z and ϕ , are shown in Figs 4.1b and 4.1c, respectively. A downstream region with intense turbulent mixing and a wide range of turbulence length scales is evident.

The growth of the jet half-width based on the streamwise velocity, δ_U , is shown in Fig. 4.2a. The jet half-width δ_U is defined as the distance from the symmetry plane (centreline) to the point in the cross-stream direction where the mean streamwise velocity excess with respect to the co-flow velocity, $U_e(x, y) = U(x, y) - U_\infty(x)$, is half that with respect to the centreline, $\Delta U_c(x) = U_c(x) - U_\infty(x)$. The ratio of the velocity excess at the jet nozzle exit, $\Delta U_o = U_o - U_\infty$, to $\Delta U_c(x)$ is shown in Fig. 4.2b.

The growth of the jet half-width based on the passive scalar, δ_ϕ , is shown in Fig. 4.3a. The half-width δ_ϕ is defined (similarly to δ_U) as the distance from the symmetry plane (centreline) to the point where the passive scalar concentration is half of that on the centreline. The mean scalar decay, defined as $(\phi_o/\phi_c)^2$, where $\phi_c(x)$ is the value at the centreline and ϕ_o is the value

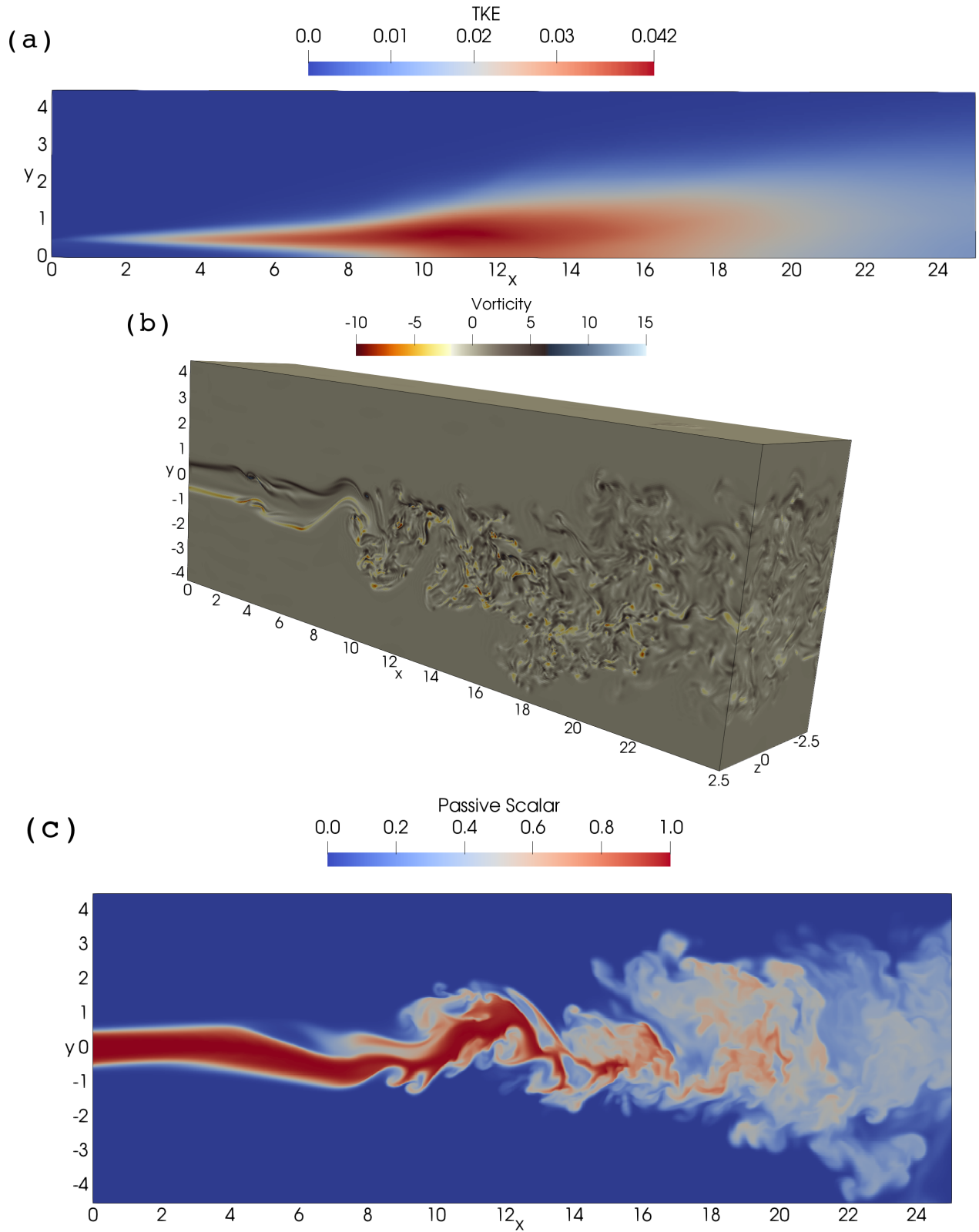


Figure 4.1: Flow field data: (a) turbulent kinetic energy (TKE) k ; (b) 3-D view of the instantaneous spanwise vorticity field ω_z ; (c) instantaneous contours of the passive scalar on (x-y) plane $z = 0$.

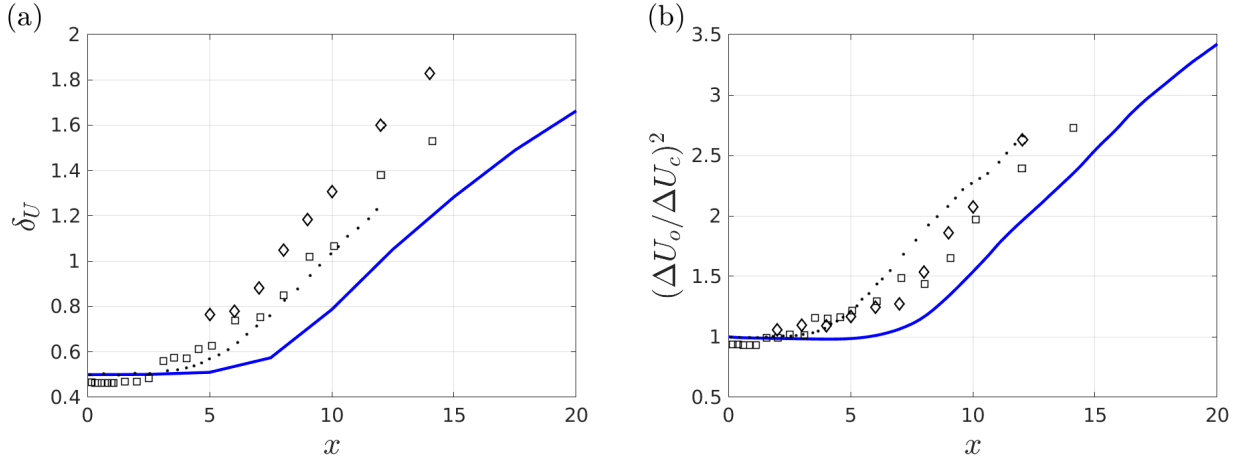


Figure 4.2: Growth of the jet half-width based on the velocity (a) and centreline mean velocity excess decay (b). — Present results; $\square$ (Thomas and Chu, 1989); $\diamond$ (Browne et al., 1983); $\cdots$ DNS (Stanley et al., 2002).

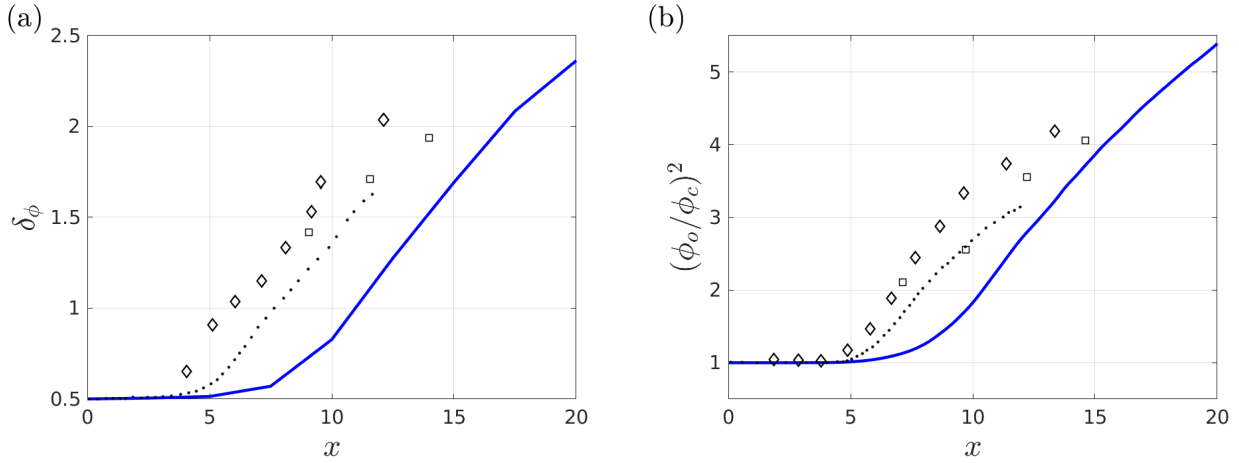


Figure 4.3: Downstream growth of the jet half-width based on the passive scalar (a) and decay of the mean scalar on the jet centreline (b). — Present results; $\diamond$ (Browne et al., 1983); $\square$ (Davies et al., 1975); $\cdots$ DNS (Stanley et al., 2002).

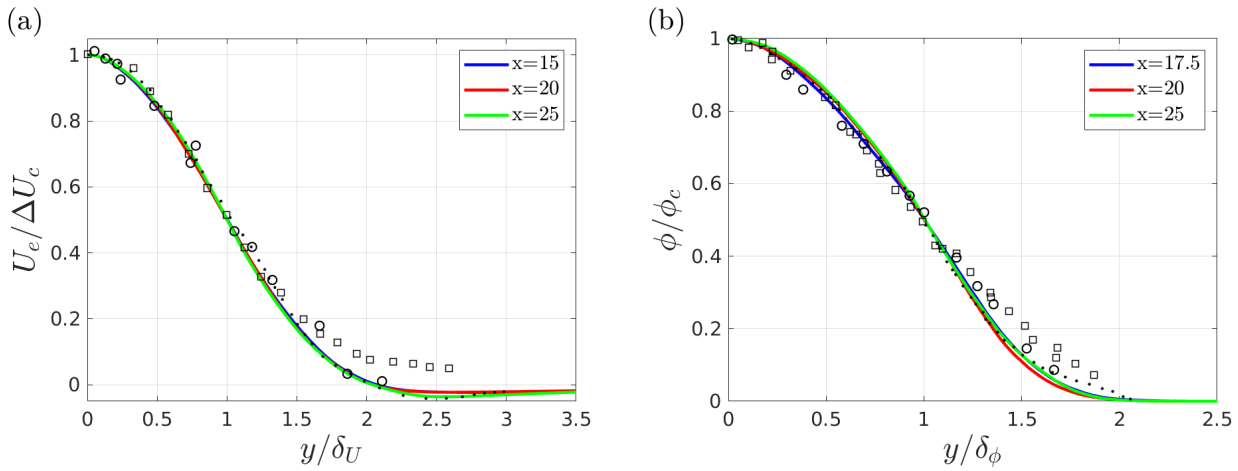


Figure 4.4: Self-similar profiles of mean velocity and mean passive scalar for three axial positions. (a) Mean velocity. — Present results; $\square$ (Gutmark and Wygnanski, 1976); $\circ$ (Ramaprian and Chandrasekhara, 1985); $\cdots$ DNS (Stanley et al., 2002). (b) Mean scalar. — Present results; $\square$ (Davies et al., 1975); $\circ$ (Jenkins and Goldschmidt, 1973); $\cdots$ DNS (Stanley et al., 2002).

at the jet nozzle exit, is shown in Fig. 4.3b.

It can be seen that there is good agreement with the experimental and other reference data. Theoretical analysis (Pope, 2000; Rajaratnam, 1976) suggests that $\delta_U \propto x$ and $U_c \propto 1/\sqrt{x}$ for planar jet flow, and the same scaling is also valid for the scalar concentration. It has been documented (Stanley and Sarkar, 2000; Stanley et al., 2002; Da Silva et al., 2015) that the jet break-up location is highly affected by the inlet conditions at the nozzle. The jet characteristics are also affected by the value of the Reynolds number in cases where $Re < 10000$ (Deo et al., 2008; Klein et al., 2003b). Therefore, independently of the exact location of the jet break-up, the slope of the curves shown in Figs 4.2 and 4.3 for the present DNS exhibits good agreement with that of reference data.

The self-similar cross-stream profiles for velocity and scalar are depicted in Figs 4.4a and 4.4b, respectively. The velocity profiles collapse to a single curve, and there is good agreement with reference (experimental or other DNS) data. The velocity field reaches self-similarity at $x \approx 12$, while the passive scalar is slightly slower to develop and the self-similar region is reached at $x \approx 17$. The same behaviour was also observed by Stanley et al. (2002).

Turbulent kinetic energy budgets

The turbulent kinetic energy (TKE) equation takes the form (Pope, 2000):

$$\underbrace{-\bar{u}_j \frac{\partial}{\partial x_j} \left(\frac{1}{2} \overline{u'_i u'_i} \right)}_{C_k} - \underbrace{\frac{\partial}{\partial x_j} \left(\frac{1}{\rho} \overline{u'_j p'} \right)}_{\pi_k} - \underbrace{\frac{\partial}{\partial x_j} \left(\frac{1}{2} \overline{u'_i u'_i u'_j} \right)}_{T_k} + \underbrace{\frac{\partial}{\partial x_j} (2 \nu \overline{u'_i s_{ij}})}_{D_k} - \underbrace{\overline{u'_i u'_j} S_{ij}}_{P_k} - \underbrace{2 \nu \overline{s_{ij} s_{ij}}}_{\epsilon_k} = 0, \quad (4.19)$$

where S_{ij} and s_{ij} denote the mean and fluctuating strain rates, respectively:

$$S_{ij} = \frac{1}{2} \left(\frac{\partial \bar{u}_i}{\partial x_j} + \frac{\partial \bar{u}_j}{\partial x_i} \right), \quad (4.20)$$

$$s_{ij} = \frac{1}{2} \left(\frac{\partial u'_i}{\partial x_j} + \frac{\partial u'_j}{\partial x_i} \right). \quad (4.21)$$

In equation (4.19), terms C_k , π_k , T_k , D_k , P_k and ϵ_k denote convection due to mean flow, pressure gradient work, transport by velocity fluctuations, viscous diffusion, production by mean flow, and dissipation, respectively. The variation of these terms together with their sum, Σ , along the jet centreline is shown in figure 4.5. Overall, the equation is well balanced, with the maximum error being less than 5.5% of the peak absolute value of convection due to mean flow. This indicates that the resolution of the computational grid is fine enough.

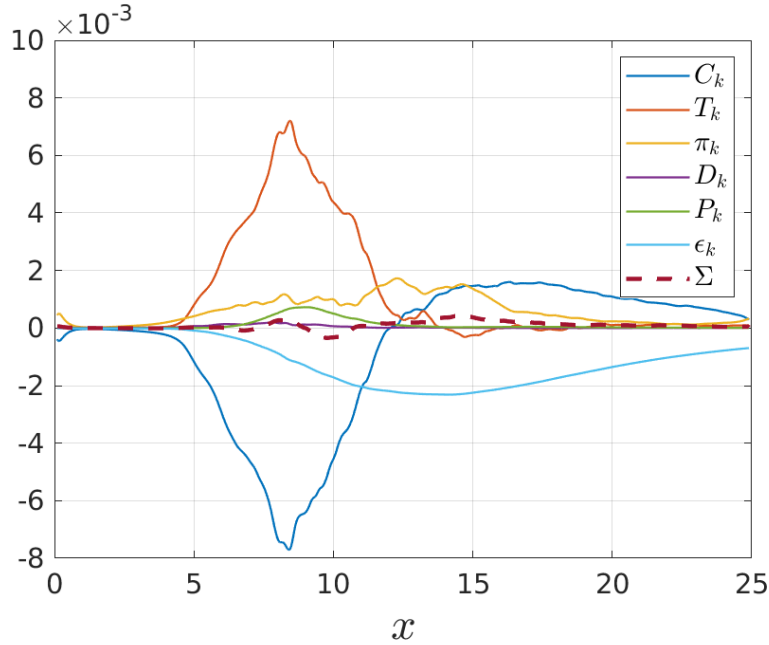


Figure 4.5: Variation of turbulent kinetic energy budgets along the jet centreline (all terms are non-dimensionalised with the variables defined in equation (4.3)).

One-dimensional power spectra

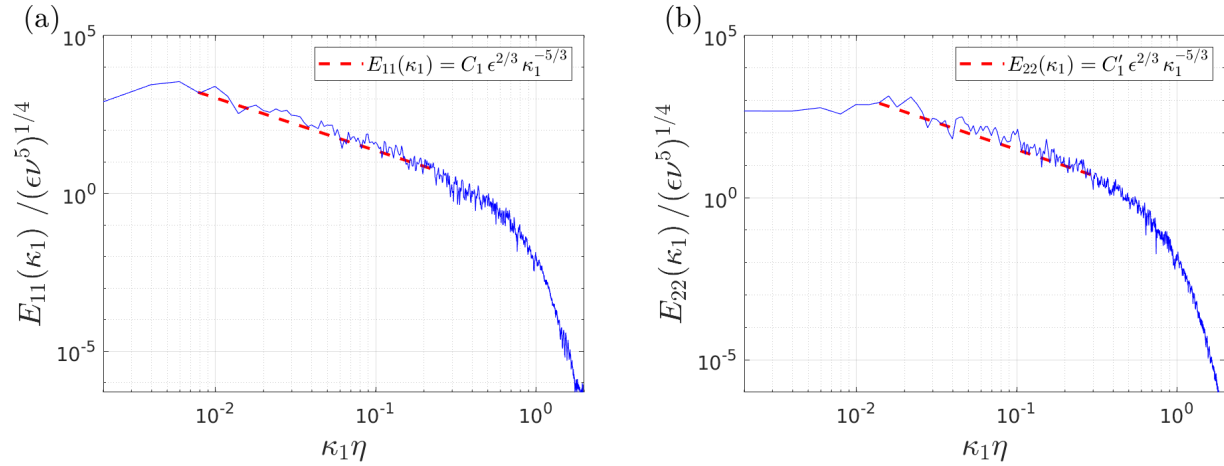


Figure 4.6: One-dimensional power spectra $E_{11}(\kappa_1)$ (a) and $E_{22}(\kappa_1)$ (b) obtained from the frequency spectra of the streamwise and cross-stream velocity fluctuations at the probe point $(x, y, z) = (20, 1.5, 0)$. Kolmogorov’s universal scaling was used. The dashed red lines represent the one-dimensional wavenumber spectra (a) $E_{11}(\kappa_1) = C_1 \epsilon^{2/3} \kappa_1^{-5/3}$ (b) and $E_{22}(\kappa_1) = C'_1 \epsilon^{2/3} \kappa_1^{-5/3}$. Logarithmic scales were used for both axes.

Figure 4.6 shows the one-dimensional $E_{11}(\kappa_1)$ and $E_{22}(\kappa_1)$ spectra of turbulent fluctuations, plotted with Kolmogorov scaling. For the definition of these quantities, we refer to Pope (2000). The spectra are presented as functions of streamwise wavenumber κ_1 , and they were obtained from the frequency spectra of the streamwise and cross-stream velocity fluctuations at the probe point $(x, y, z) = (20, 1.5, 0)$, which is located in the region of fully developed turbulence. The conversion of the frequency to wavenumber spectra is based on Taylor’s “frozen turbulence” hypothesis (Taylor, 1935) and was performed through the variable transformation $\kappa_1 = 2\pi f/U_c$, where f is the frequency and U_c is a convection velocity taken as the time-averaged streamwise velocity at that probe point. The Kolmogorov $-5/3$ power-law one-dimensional spectra $E_{11}(\kappa_1) = C_1 \epsilon^{2/3} \kappa_1^{-5/3}$ and $E_{22}(\kappa_1) = C'_1 \epsilon^{2/3} \kappa_1^{-5/3}$ were also calculated using the value of the turbulent kinetic energy dissipation rate at that probe point and presented in the figures for comparison. The values of the universal constants C_1 and C'_1 are 0.49 and 0.65, respectively (Pope, 2000). Although, for the flow conditions examined, an extended inertial region is not expected, the DNS data do exhibit a power-law close to $-5/3$ over about a decade, and match well the theoretical spectra. Furthermore, at high frequencies, a dissipative range with a faster decay rate is observed, which indicates that the turbulent motions are well resolved.

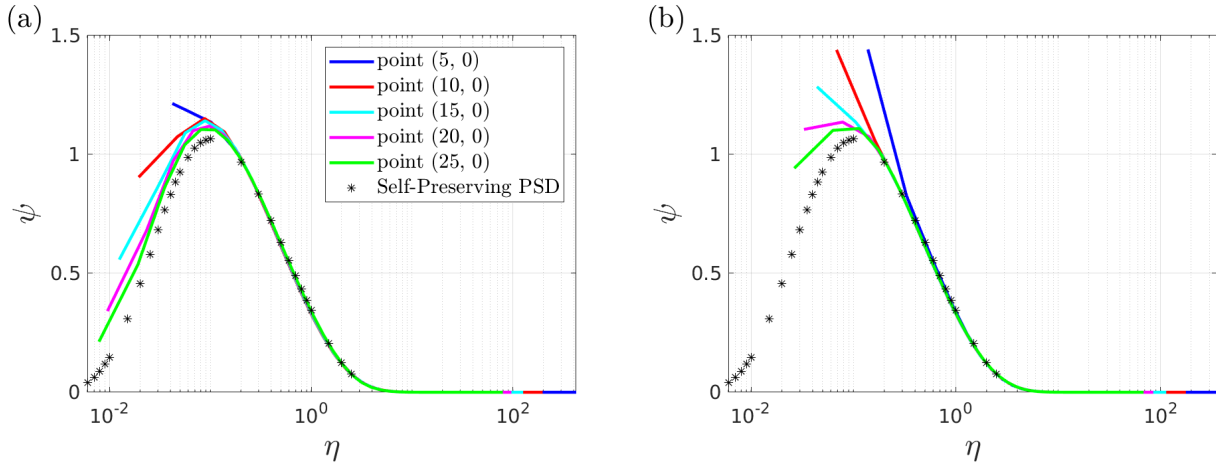


Figure 4.7: Normalised time-averaged PSDs at several probe points along the centreline. The results are compared with reference data for the self-preserving distribution (Vemury and Pratsinis, 1995). A logarithmic scale was used for the horizontal axes. (a) $Da_{coag} = 1$; (b) $Da_{coag} = 1/3$.

4.3.2 Particle size distribution

The DNS-PBE approach allows for the prediction of the PSD at every point in the domain. As mentioned in Section 4.2.1, in a perfectly stirred reactor, the PSD reaches a self-preserving distribution. Fig. 4.7 shows the time-averaged PSDs at five different probe points on the centreline for both Da_{coag} number cases. The computed distributions are scaled according to (4.9) and (4.10), and compared with the self-preserving PSD from Vemury and Pratsinis (1995). It can be seen that as the PSDs develop, they approach the self-preserving distribution and there is good agreement with the reference data, especially close to the exit of the domain. Turbulence may affect the time to reach the self-preserving state (Friedlander, 2000). As mentioned earlier, the values of Da_{coag} were chosen in such a way that the PSD becomes self-preserving before and after the jet break-up location for the two cases. In particular, for the $Da_{coag} = 1/3$ case, the PSD becomes self-preserving slightly downstream of the expected location ($x \approx 15$). However, the difference observed is small. The fact that the PSDs in the turbulent flow field do not deviate a lot from the self-preserving distribution can be attributed to the lack of recirculating flow structures that would bring into contact particles with different distributions and would make the PSD deviate from the self-preserving state. Finally, the good matching with the reference data indicates that the number and distribution of volume intervals are sufficient to resolve the PSD accurately.

4.4 Results and discussion

4.4.1 Effect of coagulation and mixing on the moments

The evolution of the moments is dominated by two physical mechanisms, coagulation and turbulent mixing, and by their interaction. Coagulation reduces the total number of particles, M_0 , with increasing distance from the orifice, but it does not alter the total particle volume, M_1 , which behaves as a passive scalar. It also brings about an increase in the second moment, M_2 , due to the heavier weighting of the large particles on the distribution. Turbulent mixing brings about dilution, which can be quantified using M_1 .

The instantaneous M_0 fields for the two Da_{coag} cases are depicted in Figs 4.8a and 4.8b, while the instantaneous M_2 fields are shown in Figs 4.9a and 4.9b. It is evident that M_0 reduces at downstream locations. The second moment, M_2 , attains small values close to the jet nozzle and increases rapidly due to coagulation until the jet break-up location. The jet becomes unstable and breaks into smaller vortices, while the entrainment of co-flow fluid dilutes the large values of M_2 . However, as can be seen, for example, in Fig. 4.9a, the remnants of the core of the jet (see region $14 < x < 22$) are fluid patches with large values of M_2 . Further downstream, the small-scale motion due to the strong turbulence in the jet has mixed further the fluid patches of the jet core. However, it is evident that M_0 reduces quite fast, while fluid patches with large values of M_2 start to emerge.

The evolution of the zeroth moment, M_0 , is governed by the following equation in non-dimensional form, derived from (4.8) for $k = 0$:

$$\frac{\partial M_0}{\partial t} + u_j \frac{\partial M_0}{\partial x_j} = \frac{1}{Sc} \frac{1}{Re} \frac{\partial^2 M_0}{\partial x_j \partial x_j} - \frac{1}{2} Da_{coag} \int_0^\infty \int_0^\infty \beta(v, w) n(v) n(w) dv dw. \quad (4.22)$$

The source term is negative because coagulation results in a reduction in the total number of particles. Fig. 4.10a shows the centreline variation of the time-averaged $\overline{M_0}$, juxtaposed with $\overline{M_1}$. There is a rapid reduction of the particle number concentration close to the jet nozzle, and the rate is higher for the higher Da_{coag} ; this is expected because higher Da_{coag} represents more intense coagulation. Both curves start to change behaviour at $x \approx 7.5$, where the jet breaks up and turbulent mixing starts to play an important role. From Fig. 4.10a it is evident that the rate of reduction (slope) of $\overline{M_0}$ is larger than that of $\overline{M_1}$ in the region of fully developed turbulence ($x > 15$). Dilutions due to turbulent mixing and coagulation work in unison and result in a reduction of M_0 . The contribution of each mechanism can be quantified as follows. In the case of $Da_{coag} = 1$, $\overline{M_0}$ is reduced by 89% between the jet break-up location and the exit

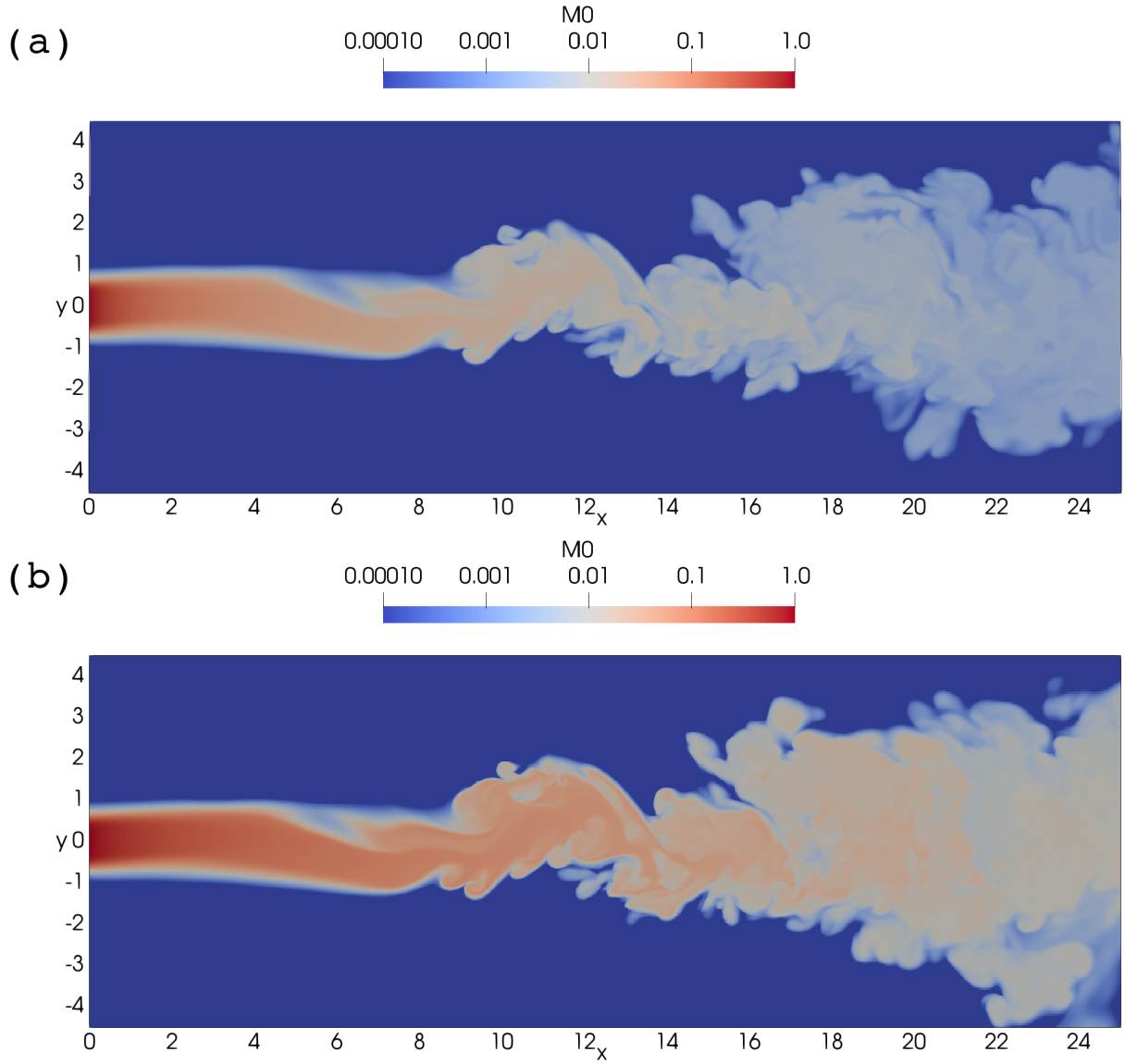


Figure 4.8: Instantaneous contour plots of M_0 on $(x-y)$ plane $z = 0$. (a) $Da_{coag} = 1$; (b) $Da_{coag} = 1/3$. A logarithmic scale colourbar is used.

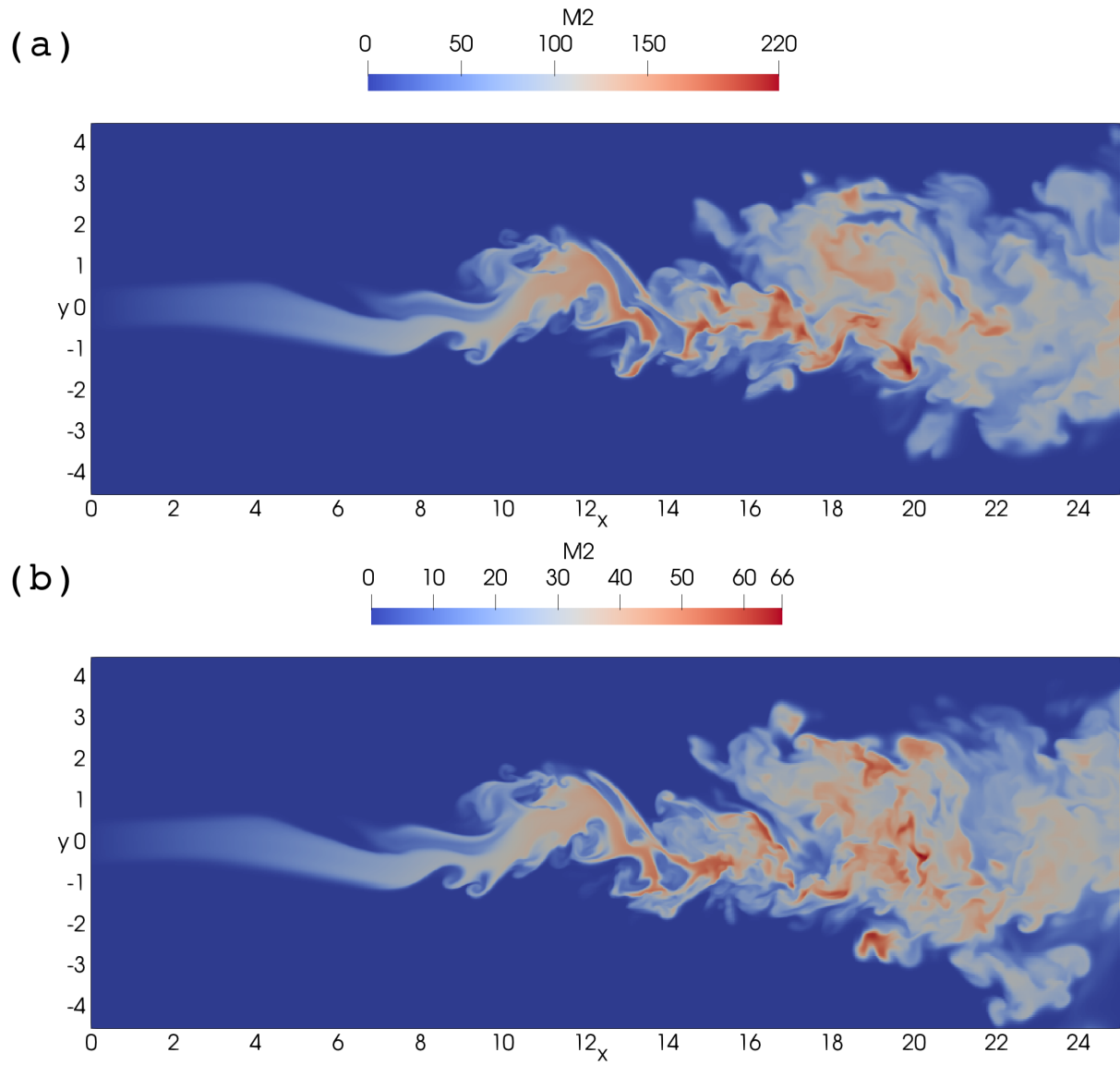


Figure 4.9: Instantaneous contour plots of M_2 on $(x-y)$ plane $z = 0$. (a) $Da_{coag} = 1$; (b) $Da_{coag} = 1/3$.

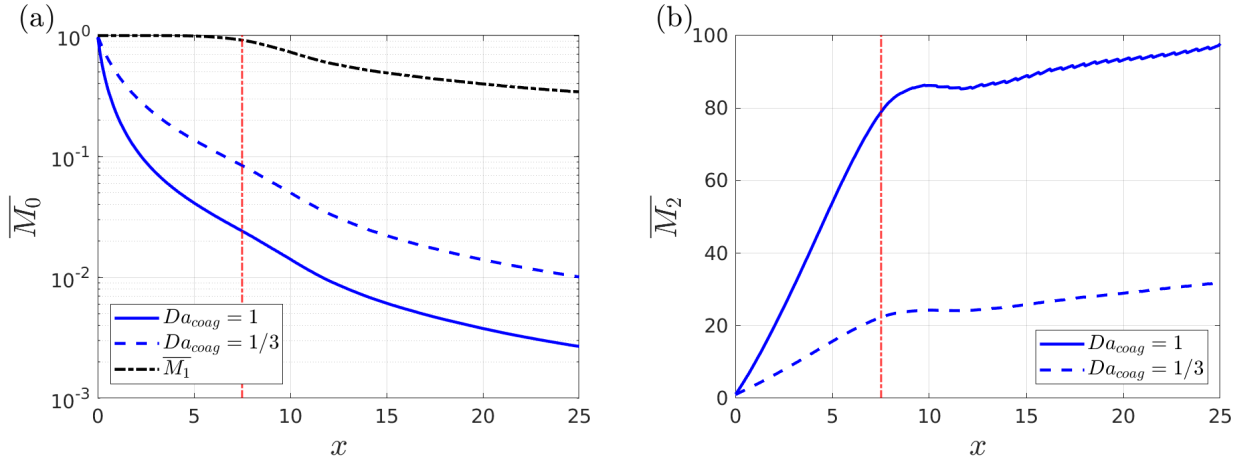


Figure 4.10: Centreline variation of time-averaged M_0 (a) and M_2 (b) for the two Da_{coag} cases. The red dashed-dotted line indicates the jet break-up location. A logarithmic scale was used for the vertical axis in (a). A black dashed-dotted line is used for $\overline{M}_1$ in (a).

of the domain, while a passive scalar, such as $\overline{M}_1$, is reduced by 58%. Similarly, in the case of $Da_{coag} = 1/3$, $\overline{M}_0$ is reduced by 88% between the same locations. This indicates that both effects contribute to the evolution of $\overline{M}_0$, with turbulent dilution (rather than coagulation) having a slightly stronger effect.

The transport equation for the second moment, M_2 , is derived from (4.8) for $k = 2$:

$$\frac{\partial M_2}{\partial t} + u_j \frac{\partial M_2}{\partial x_j} = \frac{1}{Sc} \frac{1}{Re} \frac{\partial^2 M_2}{\partial x_j \partial x_j} + Da_{coag} \int_0^\infty \int_0^\infty vw \beta(v, w) n(v) n(w) dv dw. \quad (4.23)$$

For this moment, the source term is positive. Fig. 4.10b shows the centreline variation of the time-averaged $\overline{M}_2$. Unlike M_0 , in the case of M_2 , there is competition between dilution and coagulation. Turbulent mixing acts towards reducing M_2 , while coagulation acts towards increasing M_2 . As can be seen in Fig. 4.10b, the net result is an increase in M_2 . The effect of turbulence is thus to mitigate the rapid growth of the second moment. The net increase of $\overline{M}_2$ with distance after the jet break-up location indicates that coagulation has a greater effect on the evolution of M_2 compared to dilution.

4.4.2 Reynolds decomposition of the PBE

We now turn our attention to the effect of turbulent fluctuations and consider the Reynolds decomposition of the PBE (Scott, 1967; Friedlander, 2000; Rigopoulos, 2007). Apart from velocities, the number densities are also decomposed into mean and fluctuating parts, and this

decomposition is substituted into (4.4). Time-averaging results in the equation:

$$\begin{aligned} \bar{u}_j \frac{\partial \bar{n}}{\partial x_j} + \frac{\partial \overline{u'_j n'}}{\partial x_j} &= \frac{1}{Sc} \frac{1}{Re} \frac{\partial^2 \bar{n}}{\partial x_j \partial x_j} \\ &+ Da_{coag} \left(\frac{1}{2} \int_0^v \beta(w, v-w) \bar{n}(w) \bar{n}(v-w) dw - \int_0^\infty \beta(v, w) \bar{n}(v) \bar{n}(w) dw \right. \\ &\quad \left. + \frac{1}{2} \int_0^v \beta(w, v-w) \overline{n'(w) n'(v-w)} dw - \int_0^\infty \beta(v, w) \overline{n'(v) n'(w)} dw \right). \end{aligned} \quad (4.24)$$

The time-averaging of the transient term in (4.4) is zero for jet flow cases where statistical stationarity is reached. The last two terms arise due to turbulent coagulation; both involve integrals of correlations between number density fluctuations and are unclosed. Lack of understanding of the behaviour of correlations $\overline{n'(v) n'(w)}$ is a long-standing problem in the literature (Levin and Sedunov, 1966, 1968; Scott, 1967; Warshaw, 1967; Drake, 1972).

The Reynolds decomposition can also be applied to the transport equation of moments (4.8), resulting in:

$$\begin{aligned} \bar{u}_j \frac{\partial \overline{M_k}}{\partial x_j} + \frac{\partial \overline{u'_j M'_k}}{\partial x_j} &= \frac{1}{Sc} \frac{1}{Re} \frac{\partial^2 \overline{M_k}}{\partial x_j \partial x_j} \\ &+ Da_{coag} \left(\frac{1}{2} \int_0^\infty \int_0^\infty (v+w)^k \beta(v, w) \bar{n}(v) \bar{n}(w) dv dw \right. \\ &\quad - \frac{1}{2} \int_0^\infty \int_0^\infty (v^k + w^k) \beta(v, w) \bar{n}(v) \bar{n}(w) dv dw \\ &\quad + \frac{1}{2} \int_0^\infty \int_0^\infty (v+w)^k \beta(v, w) \overline{n'(v) n'(w)} dv dw \\ &\quad \left. - \frac{1}{2} \int_0^\infty \int_0^\infty (v^k + w^k) \beta(v, w) \overline{n'(v) n'(w)} dv dw \right). \end{aligned} \quad (4.25)$$

Similarly to the transport equation for the number density, the last two terms are unclosed. Analysis of these terms is important since the moments are measured frequently in experiments, and also a family of numerical methods for modelling particulate flows is based on the method of moments. Our analysis will focus on the unclosed terms in the transport equations of $\overline{M_0}$ and $\overline{M_2}$ (coagulation does not alter $\overline{M_1}$, as already mentioned). Knowledge of these moments is also required in order to characterise the particle field with the method of moments when a log-normal size distribution is assumed (Brock et al., 1986).

4.4.3 Number density fluctuation correlations

As was mentioned in Section 4.2.3, 35 intervals Δv_i were used to discretise the particle volume space v , thus for each computational cell there are 35×35 correlations $\overline{n'_i n'_j}$. As this is a very

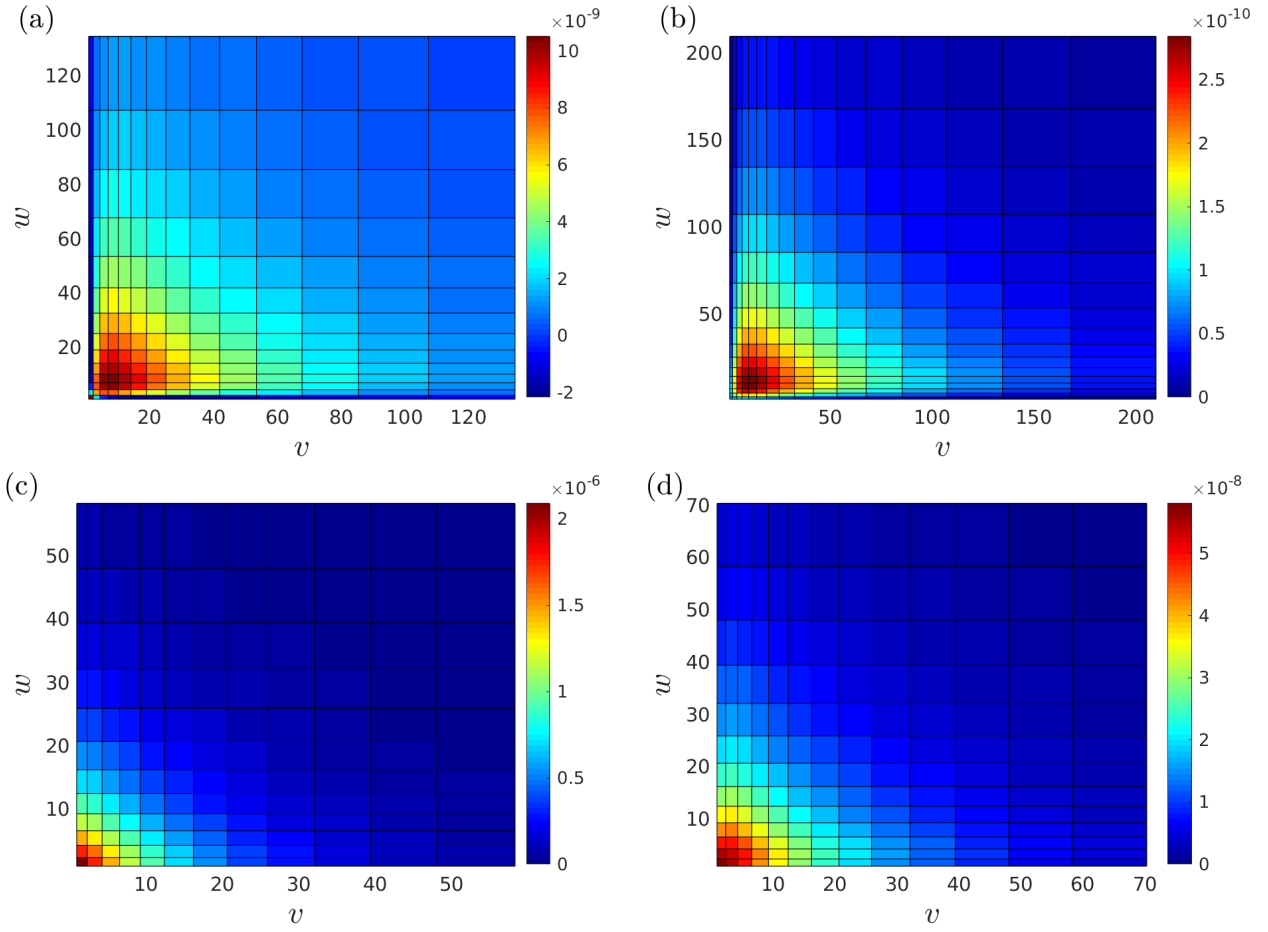


Figure 4.11: Map of number density fluctuation correlations $\overline{n'(v)n'(w)}$: (a) for $Da_{coag} = 1$ at probe point $(10, 0, 0)$; (b) for $Da_{coag} = 1$ at probe point $(17.5, 0.5, 0)$; (c) for $Da_{coag} = 1/3$ at probe point $(10, 0, 0)$; (d) for $Da_{coag} = 1/3$ at probe point $(17.5, 0.5, 0)$.

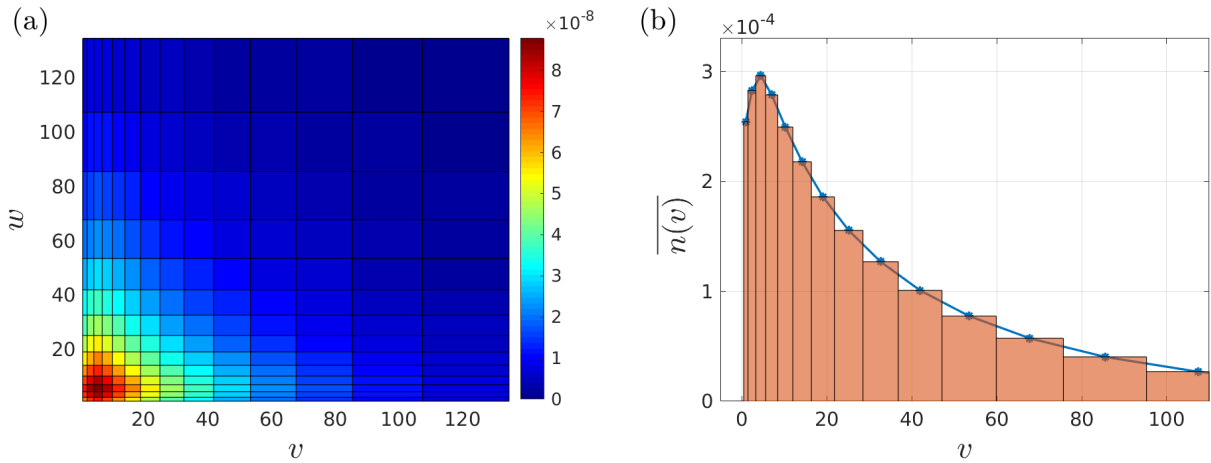


Figure 4.12: (a) Map of time-averaged number density combinations $\overline{n(v)n(w)}$, and (b) time-averaged PSD for $Da_{coag} = 1$ at probe point $(10, 0, 0)$.

large amount of information, maps are presented for only a few points of interest in the domain. Results for the number density fluctuation correlations $\overline{n'(v)n'(w)}$ for the two values of Da_{coag} at points $(x, y, z) = (10, 0, 0)$ and $(17.5, 0.5, 0)$ are shown in Fig. 4.11. The first point is located on the centreline and relatively close to the jet break-up location ($x \approx 7.5$), while the second point is further downstream, in the region of fully developed turbulence and slightly off the centreline. The results are presented in the form of contour maps with nonuniform spacing because of the exponential grid employed for the discretisation of the particle volume space. The map of the time-averaged number density combinations $\overline{n(v)} \overline{n(w)}$ for $Da_{coag} = 1$ at probe point $(10, 0, 0)$ is also shown in Fig. 4.12a. As expected, the maps are symmetric with respect to the diagonal $v = w$. For most of the points examined, it is found that the magnitude of $\overline{n'(v)n'(w)}$ follows that of $\overline{n(v)} \overline{n(w)}$, as can be seen in Figs 4.11a and 4.12a. More specifically, the maximum value of the correlation is found along the diagonal $v = w$ and close to the interval where $\overline{n(v)}$ has a local maximum, which is at the same interval where $\overline{n(v)} \overline{n(w)}$ receives the maximum value. For instance, the PSD at probe point $(10, 0, 0)$ for $Da_{coag} = 1$, shown in Fig. 4.12b, has a local maximum for $v \approx 5$ (in terms of discretised PBE, this corresponds to the third interval, $\overline{n_3}$), while the maximum value of the correlations at the same probe point were found for $(v, w) \approx (7.1, 7.1)$ (see Fig. 4.12a). Furthermore, for large values of v and w , $\overline{n'(v)n'(w)}$ tends to zero. These values correspond to the right tail of the PSD, where the mean number density $\overline{n(v)}$ is small (there are few particles of large size, as seen in Fig. 4.12b).

The correlations $\overline{n'(v)n'(w)}$ are found to be mostly positive for most v, w combinations, as shown in Fig. 4.11. Since we are not considering differential diffusion of particles of different sizes, the distribution is affected as a whole by turbulence, and coagulation is not rapid enough to redistribute fluctuations in a way that generates negative correlations, with the exception discussed below.

Negative values of the correlations $\overline{n'(v)n'(w)}$ can also appear. This can be seen, for example, in Fig. 4.11a for $Da_{coag} = 1$ at probe point $(10, 0, 0)$. These negative values involve mainly the fluctuation of the number density of the first interval, n'_1 , and that of intervals that are on and to the right of the local maximum of $\overline{n(v)}$ (see Fig. 4.12b), e.g. the correlations $\overline{n'_1 n'_3}$ and $\overline{n'_1 n'_4}$ etc. A possible explanation for this effect is that at the inlet, only n_1 is non-zero, and coagulation acts towards reducing the instantaneous values of n_1 and increasing those of n_2, n_3 , etc. A general trend is that the effect of coagulation is to move the distribution to the right in particle volume space towards higher particle volumes. For example, at probe

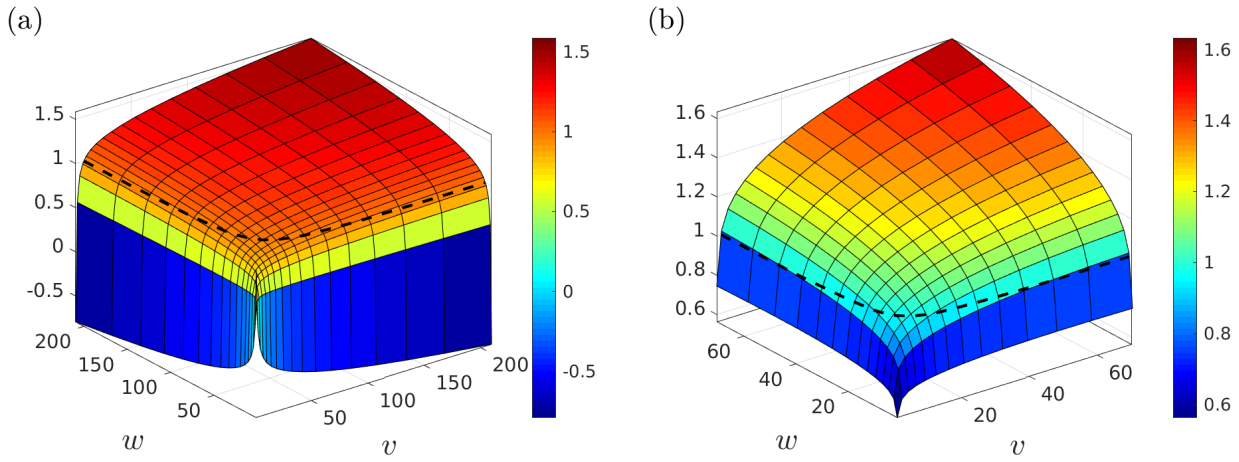


Figure 4.13: Intensity of correlations of number density fluctuations I_n at probe point $(10, 0, 0)$: (a) $Da_{coag} = 1$; (b) $Da_{coag} = 1/3$. Results are normalised by $I_\phi = 0.156$. The black dashed line indicates the location where the fluctuation intensities are equal, i.e. $I_n = I_\phi$.

point $(10, 0, 0)$, on average, coagulation acts towards reducing the instantaneous values of n_1 and increasing those of intervals at the right of the local maximum of $\bar{n}(v)$, such as n_4 (see Fig. 4.12b). Therefore, negative fluctuations of n'_1 , in that case, are correlated with positive fluctuations of n'_4 and vice versa (when n_1 is consumed, n_4 is created). Once coagulation has progressed and the consumption of n_1 is not so intense, the correlations become positive. This also partly explains why negative correlations are found only for the case of intense coagulation ($Da_{coag} = 1$) and for points close to the jet break-up location ($x < 12.5$). Data for the downstream location $(17.5, 0.5, 0)$ are presented in Fig. 4.11b and it is observed that $\overline{n'(v)n'(w)} > 0$ for all combinations of (v, w) . Negative correlations are not found for the case $Da_{coag} = 1/3$ (see also Figs 4.11c, and 4.11d). This means that n'_1 and n'_i have the same sign, probably because of the increased effect of turbulent mixing compared to the effect of coagulation.

It is of interest to examine the value of $\overline{n'(v)n'(w)}$ in relation to the value of $\overline{n(v)n(w)}$. The intensity of the correlations of the number density fluctuations, the square of the passive scalar fluctuation intensity and the turbulence intensity are defined, respectively, as:

$$I_n = \frac{\overline{n'(v)n'(w)}}{\overline{n(v)n(w)}}, \quad I_\phi = \frac{\overline{\phi'^2}}{\overline{\phi^2}}, \quad I_u = \frac{\overline{u_i'^2}}{\overline{U_i^2}}, \quad (4.26)$$

where I_u is defined here for future reference. Fig. 4.13 shows a surface plot of I_n at the probe point $(10, 0, 0)$ for the two Da_{coag} cases. Here, I_n is normalised with the value of I_ϕ at that specific location, while the location where the fluctuation intensities are equal ($I_n = I_\phi$) is also shown. First, note that the negative correlations referred to above can be seen very clearly in this plot. The differences with I_ϕ are small for the combinations (v, w) of interest, i.e. the ones

that make a large contribution to the integral. The value of I_n increases as we move towards diagonal points with increasing v and w , due to the fact that both the numerator and the denominator approach zero at these points. However, these points make a small contribution to the coagulation source term.

4.4.4 Effect of fluctuations on the zeroth moment

The transport equation for the time-averaged zeroth moment, $\overline{M_0}$, is obtained from (4.25) for $k = 0$ as:

$$\begin{aligned} \overline{u_j} \frac{\partial \overline{M_0}}{\partial x_j} + \frac{\partial \overline{u_j' M_0'}}{\partial x_j} &= \frac{1}{Sc} \frac{1}{Re} \frac{\partial^2 \overline{M_0}}{\partial x_j \partial x_j} \\ &+ Da_{coag} \left(-\frac{1}{2} \int_0^\infty \int_0^\infty \beta(v, w) \overline{n(v) n(w)} dv dw - \frac{1}{2} \int_0^\infty \int_0^\infty \beta(v, w) \overline{n'(v) n'(w)} dv dw \right). \end{aligned} \quad (4.27)$$

In this section, we focus on the correlations arising from the Reynolds decomposition of the coagulation source term. This decomposition is shown below, with the terms labelled as A_0 , B_0 and C_0 to facilitate the subsequent discussion:

$$\begin{aligned} \underbrace{-\frac{1}{2} \int_0^\infty \int_0^\infty \beta(v, w) \overline{n(v) n(w)} dv dw}_{A_0} &= \underbrace{-\frac{1}{2} \int_0^\infty \int_0^\infty \beta(v, w) \overline{\bar{n}(v) \bar{n}(w)} dv dw}_{B_0} \\ &\quad \underbrace{-\frac{1}{2} \int_0^\infty \int_0^\infty \beta(v, w) \overline{n'(v) n'(w)} dv dw}_{C_0} \end{aligned} \quad (4.28)$$

A contour plot of the absolute values of A_0 and a contour plot of C_0 for $Da_{coag} = 1/3$ are depicted in Figs 4.14a and 4.14b, respectively (because of symmetry, only the top half is shown). The term C_0 is unclosed and is usually neglected in studies of turbulent coagulation; C_0 attains the maximum value close to the orifice and in particular at the shear layer between the jet stream with the co-flow stream. In this region, Kelvin-Helmholtz instabilities develop, leading to vortical structures, and also the magnitude of the coagulation source term of the M_0 equation is very large close to the inlet. An important observation is that C_0 is negative everywhere in the domain, because for most v, w combinations, the correlations $\overline{n'(v) n'(w)}$ were found to be positive, as discussed in Section 4.4.3 and shown in Fig. 4.11. The fact that $C_0 < 0$ means that, by neglecting it, one would overestimate $\overline{M_0}$. Qualitatively, this is also in agreement with the results of Garrick (2011), where it was found that the predominant effect of the SGS contribution is to reduce particle growth.

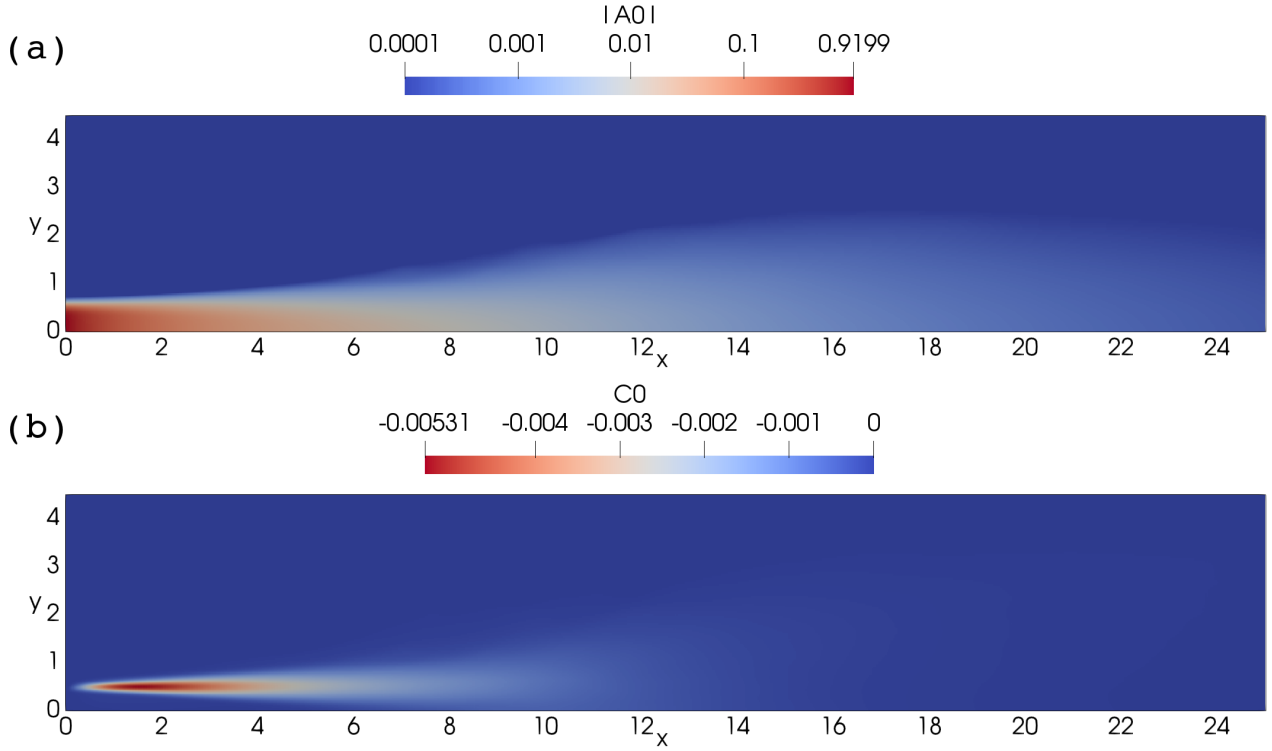


Figure 4.14: Contour plots of $|A_0|$ (a) and C_0 (b) for $Da_{coag} = 1/3$. A logarithmic scale colourbar was used in (a).

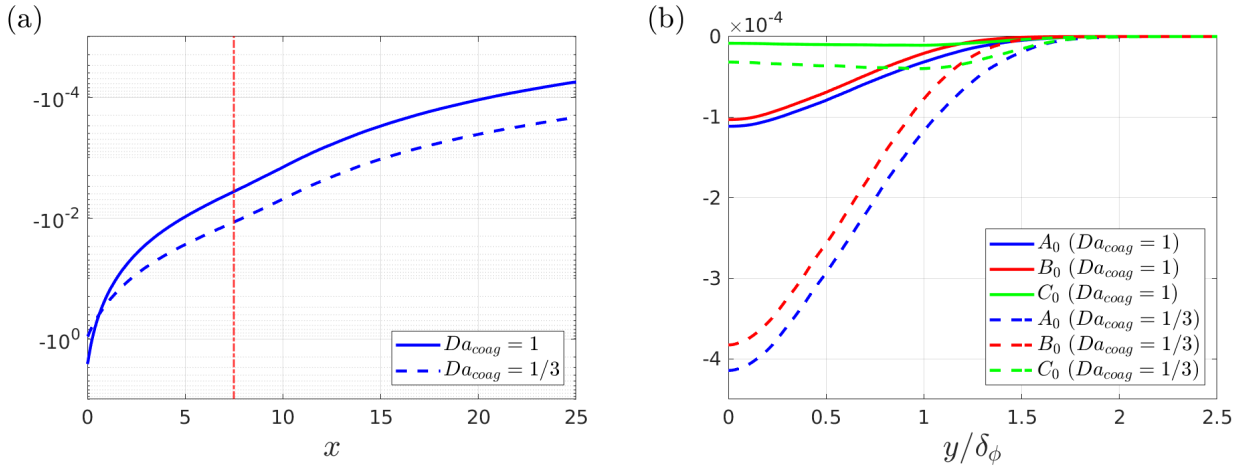


Figure 4.15: Coagulation source terms for the zeroth moment (see (4.28)). (a) Centreline values of A_0 ; the red dashed-dotted line indicates the jet break-up location. (b) Cross-stream profiles of A_0 , B_0 and C_0 at the axial position $x = 20$. A logarithmic scale was used for the vertical axis in (a). The horizontal axis in (b) was normalised by $\delta_\phi = 2.362$. Note the different horizontal axes in (a) and (b).

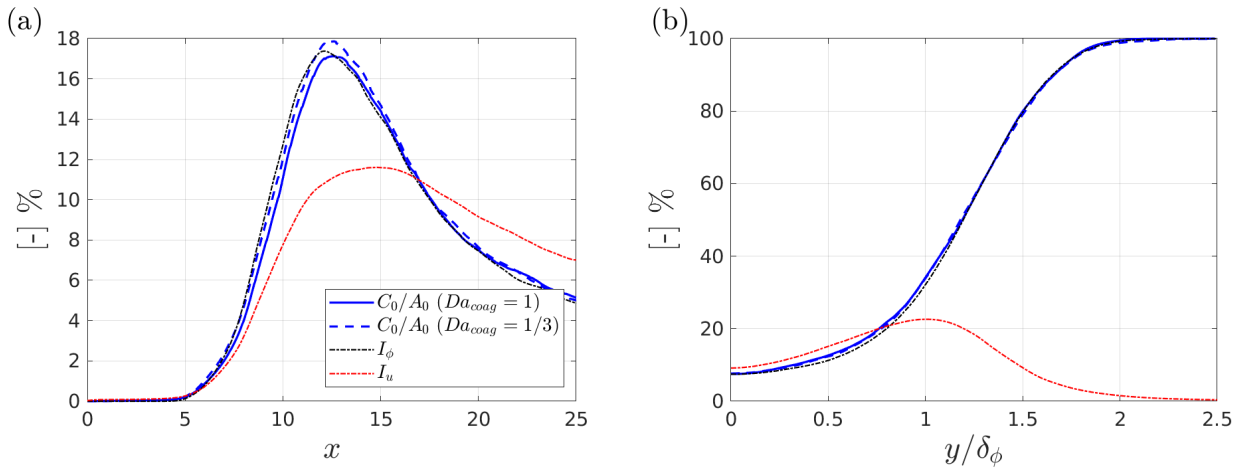


Figure 4.16: C_0/A_0 ratio (see (4.28)). (a) Centreline values of C_0/A_0 . (b) Cross-stream profiles of C_0/A_0 at the axial position $x = 20$. The horizontal axis in (b) was normalised by $\delta_\phi = 2.362$. Note the different horizontal axes in (a) and (b).

The evolution of A_0 for both Da_{coag} numbers is depicted in Fig. 4.15. Solid lines were used for the case of $Da_{coag} = 1$, and dashed lines for $Da_{coag} = 1/3$. The values of A_0 along the centreline are shown in Fig. 4.15a, where a logarithmic scale was used for the y-axis. It is observed that A_0 is larger in magnitude for the low Da_{coag} case, and its values cover a range of four orders of magnitude. Close to the inlet, similarly to $\overline{M_0}$, A_0 attains the highest magnitude, which is $O(1)$. This is a region of rapid coagulation due to the high particle concentration. The value of A_0 drops rapidly with the distance from the orifice and eventually takes values that are $O(10^{-5})$ close to the outlet.

The cross-stream profiles at the axial position $x = 20$ – where self-similarity is verified by both the simulations – of each term in (4.28) are shown in Fig. 4.15b. It is observed that the maximum magnitude of C_0 is not found on the centreline. Specifically, C_0 increases as we move from the centreline to the jet edges, reaches its maximum value, and then decreases. This picture is consistent with the contour plot shown in Fig. 4.14. This behaviour is similar to that found for the TKE and the passive scalar fluctuations $\sqrt{\phi'^2}$ profiles. The horizontal axes in Figs 4.15b and 4.16b are non-dimensionalised with $\delta_\phi = 2.362$ (the jet half-width based on the passive scalar for the axial position $x = 20$).

To elucidate further the effect of turbulent fluctuations on coagulation, the relative contribution of each term on the right-hand side of (4.28) is examined. Here, C_0 is normalised by A_0 , and the results along the centreline for both Da_{coag} values are shown in Fig. 4.16a. The ratio C_0/A_0 represents the contribution of the number density fluctuations to the total coagulation source term. It can also be seen that C_0/A_0 seems to have a weak dependence on Da_{coag}

(Fig.s 4.16a,b). The centreline values of C_0/A_0 are zero close to the inlet. The ratio starts to increase after the jet break-up and reaches the value 18% at $x = 12.4$. After this point, the ratio gradually decreases and reaches the value 5% at the exit of the computational domain. It can be seen that at the centreline, C_0 makes a significant contribution (about 20%) to the mean source term A_0 .

This contribution increases close to the jet edges, as shown by the cross-stream profiles of C_0/A_0 plotted in Fig. 4.16b for $x = 20$ for both Da_{coag} cases. For example, at $y/\delta_\phi = 1$, the ratio C_0/A_0 has values between 30% and 40%. In other words, as the jet spreads, the difference between B_0 and A_0 increases, and at the point where the value of the first moment ($M_1 \equiv \phi$) has dropped to half of the value on the centreline, the difference has reached a value between 30% and 40%. Further away from the centreline, both A_0 and C_0 assume very small values and therefore no significance can be ascribed to their ratio, which approaches 1 as $C_0/A_0 = 1 - B_0/A_0$ and B_0 approaches zero. The same behaviour was also found for I_ϕ . Nevertheless, the region far away from the centreline is not of interest, since the number concentration of particles is also very small. From this discussion, it can be concluded that C_0 should not be neglected in the modelling of turbulent coagulation.

For comparison purposes, the squares of the passive scalar fluctuations intensity, I_ϕ , and the velocity fluctuations intensity, I_u , are also shown in Fig.s 4.16a and 4.16b. An interesting observation is that C_0/A_0 has qualitatively and quantitatively the same behaviour as I_ϕ . Dilution due to turbulent mixing (rather than coagulation) was found to have a slightly greater effect on the evolution of M_0 , as discussed in Section 4.4.1. This partly explains why C_0/A_0 behaves like I_ϕ .

4.4.5 Effect of fluctuations on the second moment

The analysis of the previous section is now performed for the second moment. The transport equation of $\overline{M_2}$ can be derived by setting $k = 2$ into (4.25), which results in:

$$\begin{aligned} \overline{u_j} \frac{\partial \overline{M_2}}{\partial x_j} + \frac{\partial \overline{u'_j M'_2}}{\partial x_j} &= \frac{1}{Sc} \frac{1}{Re} \frac{\partial^2 \overline{M_2}}{\partial x_j \partial x_j} \\ + Da_{coag} &\left(\int_0^\infty \int_0^\infty vw \beta(v, w) \overline{n(v)} \overline{n(w)} dv dw + \int_0^\infty \int_0^\infty vw \beta(v, w) \overline{n'(v)} \overline{n'(w)} dv dw \right). \end{aligned} \quad (4.29)$$

The correlations arising from the Reynolds decomposition of the coagulation source term are labelled as follows:

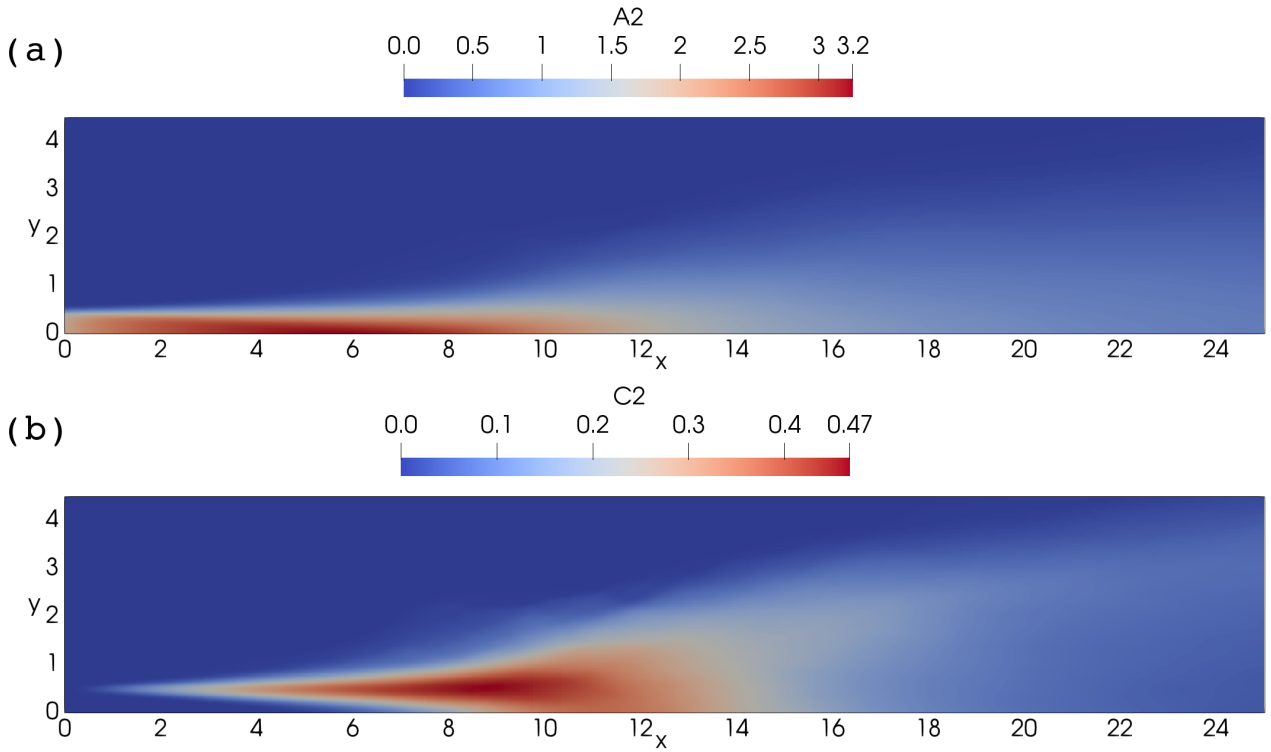


Figure 4.17: Contour plots of A_2 (a) and C_2 (b) for $Da_{coag} = 1/3$.

$$\underbrace{\int_0^\infty \int_0^\infty vw \beta(v, w) \overline{n(v)n(w)} dv dw}_{A_2} = \underbrace{\int_0^\infty \int_0^\infty vw \beta(v, w) \overline{n(v)n(w)} dv dw}_{B_2} + \underbrace{\int_0^\infty \int_0^\infty vw \beta(v, w) \overline{n'(v)n'(w)} dv dw}_{C_2} \quad (4.30)$$

The evolution of A_2 and C_2 for $Da_{coag} = 1/3$ is shown in Fig. 4.17. The value of the term C_2 is positive everywhere in the domain, again because $\overline{n'(v)n'(w)}$ is mostly positive, as discussed in Section 4.4.3. This implies that neglecting C_2 would lead to an underestimation of $\overline{M_2}$. Fig. 4.17b shows that away from the centreline towards the jet edges, C_2 increases until reaching a local maximum, at roughly $(x, y) = (9, 0.55)$ for both runs, and then drops to zero. The maximum is located slightly downstream of the jet break-up and coincides with the location where the rms value of the passive scalar fluctuations $\sqrt{\overline{\phi'^2}}$ is maximised. For reference, the location of the maximum TKE is $(x, y) = (11, 0.7)$.

The variation of A_2 in the centreline is shown in Fig. 4.18a for both Da_{coag} numbers. In the absence of flow, A_2 would increase monotonically with time. Indeed, this is exactly what happens close to the jet nozzle; A_2 increases with distance away from the orifice (time can be

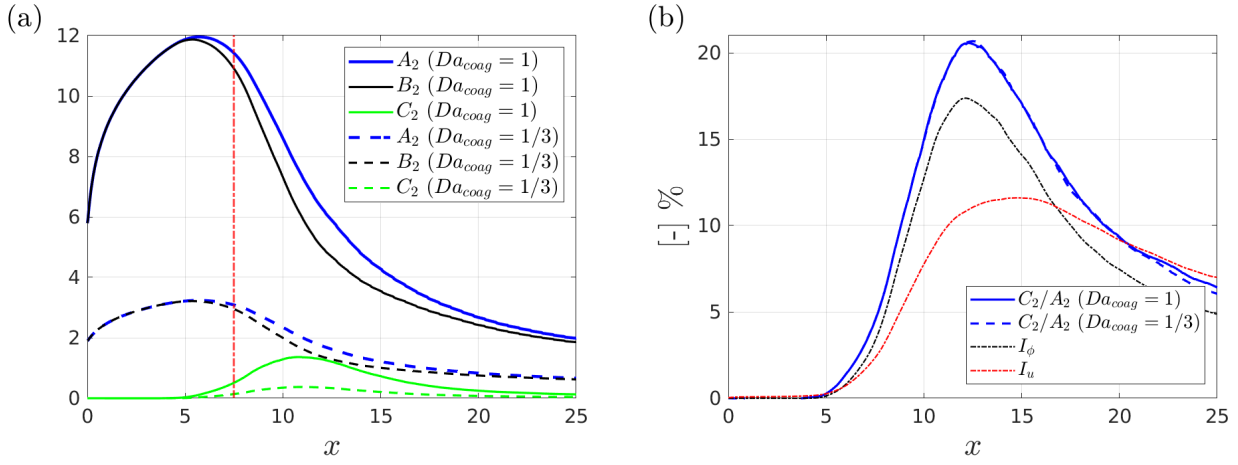


Figure 4.18: Coagulation source terms of the second moment equation (see (4.30)). (a) Centreline values of A_2 , B_2 and C_2 ; the red dashed-dotted line jet break-up location. (b) Centreline values of ratio C_2/A_2 .

converted easily to distance). Shortly upstream of the jet break-up location (red dashed-dotted line in Fig. 4.18a), A_2 starts to decrease and eventually reaches values smaller even than those at the inlet. The maximum of C_2 along the centreline is found at around $x = 11$. The highest deviation between A_2 and B_2 is found in the region between $x = 7.5$ and 18, and this is true for both Da_{coag} numbers. It is also noted that even though A_2 is reduced, the effect of coagulation can compensate for the effect of turbulent dilution on mean M_2 ; this can be concluded from the fact that the latter increases in the streamwise direction, as shown in Fig. 4.10b.

The variation of the ratio C_2/A_2 along the centreline is depicted in Fig. 4.18b. This ratio represents the relative contribution of the number density fluctuations to the total source term. Note that C_2/A_2 was found to have a weak dependence on Da_{coag} for the cases examined, similar to C_0/A_0 . The maximum along the centreline is 20.6% and is found at $x = 12.5$, while the peak value of C_0/A_0 was around 17.5% found at the same location x . It can be seen that C_2 makes a large contribution to A_2 and therefore should not be neglected for accurate modelling of turbulent coagulation.

For comparison purposes, the squares of the passive scalar fluctuations intensity $I_\phi = \overline{\phi'^2}/\overline{\phi^2}$ and the velocity fluctuations intensity $I_u = \overline{u_i'^2}/\overline{U_i^2}$ are also shown in Fig. 4.18b. An interesting observation is that C_2/A_2 reaches higher values than the ratio C_0/A_0 . It was shown in Section 4.4.4 that C_0/A_0 reaches values close to I_ϕ (see Fig. 4.16a). On the contrary, it is observed from Fig. 4.18b that the relative difference between the peak value of C_2/A_2 and that of I_ϕ is 18%. Coagulation was found to have greater effect on the evolution of M_2 in this region, as discussed in Section 4.4.1. This has to do with the heavier weighting of the large particles of

the distribution, which are formed due to coagulation at downstream positions, on the second moment. On the other hand, turbulent dilution (rather than coagulation) was found to have a slightly stronger effect on the evolution of M_0 . This partly explains why C_2/A_2 reaches higher values than the ratio C_0/A_0 .

4.5 Summary

The objective of the present chapter was to present a DNS study of turbulence–coagulation interaction. In particular, the study focused on the behaviour and significance of the unknown correlations of fluctuations that arise from the Reynolds decomposition of the PBE and moment transport equations. These correlations appear in any problem featuring turbulence and coagulation, such as soot formation and nanoparticle synthesis, but usually in conjunction with other physical and chemical effects, such as those associated with chemical kinetics. Hence the numerical experiments in the present study are intended to isolate the effect of turbulence–coagulation interaction. The numerical experiments were conducted in the Eulerian DNS–PBE framework, where the DNS resolves the flow down to the Kolmogorov scale, while the PBE is solved via a discretisation method that is free of *a priori* assumptions regarding the shape of the PSD. A unity Schmidt number was employed, as it is not feasible at present to resolve the Batchelor scales that result from diffusion at high Schmidt numbers. Direct numerical simulations of a 3-D turbulent planar jet flow at $Re = 3000$ were performed, for which it was feasible to obtain a fully resolved turbulent flow as well as an accurate numerical solution of the PBE in the whole domain, and the flow field was validated by comparison with reference experimental and DNS data. The jet was laden with monodispersed nanoparticles issued into a particle-free co-flow stream. The phenomena under investigation were turbulent mixing and particle coagulation in the free-molecule regime. Simulations for two different coagulation Damköhler numbers, $Da_{coag} = 1$ and $1/3$, were carried out, where Da_{coag} is defined as the ratio of a convection time scale to a coagulation time scale, the latter related to the time needed to reach the self-preserving distribution.

The correlations of the fluctuating number densities were calculated at specific probe points in the domain. It was found that the correlations were mostly positive for all combinations of particle volumes. However, negative correlations were also present for the case of more intense coagulation, i.e. $Da_{coag} = 1$, close to the jet break-up location. Furthermore, the intensity of the correlations was examined by normalising them with the mean of the product of the

number densities. Results showed that the intensity maps have rather uniform values with a magnitude close to the square of the passive scalar fluctuations intensity.

Unclosed terms also arise during the Reynolds decomposition of the transport equations for the zeroth and second moments. The unclosed terms make a large contribution to the time-averaged coagulation source terms and therefore should not be neglected. More specifically, for the transport equation of $\overline{M_0}$, the ratio of the term with the unknown correlations (denoted as C_0) to the time-averaged coagulation source term (denoted as A_0) reaches values as high as 18% on the jet centreline and increases up to 40% close to the jet edges. Furthermore, the value of C_0 was negative everywhere in the domain because, for most particle size combinations, the correlations of the fluctuating number densities were found to be positive. The negative value of C_0 indicates that neglect of C_0 could lead to an overestimation of $\overline{M_0}$. For the transport equation of $\overline{M_2}$, the ratio of the term with the unknown correlations (denoted as C_2) to the time-averaged coagulation source term (denoted as A_2) reached values as high as 20% on the jet centreline, and the value of C_2 was positive everywhere in the domain.

In the present flow configuration, the ratio C_0/A_0 showed the same behaviour as that of the square of the passive scalar fluctuations intensity. This indicates that dilution due to turbulent mixing (rather than coagulation) had a slightly greater effect on the evolution of M_0 in the region downstream of the jet break-up location. On the contrary, C_2/A_2 was found to reach higher values than C_0/A_0 , with a relative difference of the peak values close to 18%, indicating that coagulation (rather than turbulent dilution) had a greater effect on the evolution of M_2 . Finally, both ratios were found to have a weak dependence on the Da_{coag} number, at least for the cases examined.

To summarise, the present study aimed to refine our understanding of the effect of turbulent fluctuations on the coagulation process. Coagulation is a key process in several engineering and environmental problems – including soot formation, flame synthesis of nanoparticles such as silica and titania, and atmospheric aerosols – and understanding its interaction with turbulence is important for developing judicious assumptions and developing accurate models for predicting particle-laden flows. Future work should examine these interactions within more complex flows and in situations where other particulate phenomena, such as nucleation and growth, are present.

Chapter 5

Conclusions and future work

5.1 Conclusions

Nanoparticle formation in reacting flows involves many complex phenomena such as turbulence, chemical kinetics, aerosol processes, PSD evolution, etc. Simulations of such processes should incorporate several models and solution methods, while the quality of such simulations is subject to the uncertainties and assumptions involved in all of these elements. The main objective of the present work was to develop and employ comprehensive methodologies for simulating particle formation and flame synthesis in laminar and turbulent flows. The applications that served as validation study cases in the previous chapters included a study of silica formation in a laminar flame, a study of silica formation in a turbulent flame via LES, and an analysis of turbulence-coagulation interaction via DNS. While some of these cases were primarily concerned with silica nanoparticles, it should be emphasised that the proposed methodologies can be easily extended for the study of other nanomaterials.

In the first part of the thesis, the synthesis of silica nanoparticles in a laminar diffusion flame was studied via population balance modelling coupled with CFD. The population balance models that were employed for this purpose were: a) a monodisperse model, b) a comprehensive two-PBE model, and c) an extended one-PBE model. The last of these models constitutes a new development and, unlike conventional one-PBE models, the extended one-PBE model accounts for finite-rate sintering. More specifically, a discretised/sectional method is employed for the numerical solution of the PBE, while the PBE is solved together with a transport equation for the number concentration of primary particles. In this manner, the extended one-PBE model can predict the evolution of primary particle sizes, thus particle morphology, while the computational cost is substantially reduced as compared with the two-PBE model. The three models were coupled with an in-house CFD code in order to conduct 2-D simulations of silica

synthesis via oxidation of HMDSO in a laminar diffusion jet flame. The methodology was validated against the experimental *in-situ* SAXS data of Camenzind et al. (2008) for the S-2 flame. The main results of this investigation are summarised below:

- Good agreement was found between numerical predictions and experimental data for temperature along the centreline with all PBE models. Thermal losses due to radiation from particles were found to have a non-trivial effect on the evolution of the temperature field.
- The predictions by the two-PBE and extended one-PBE model for primary particle sizes were in good agreement with the SAXS data (by about 15 % for the two-PBE model) indicating that aggregation and sintering were described relatively well. The two models slightly overestimated the aggregate sizes. On the other hand, the monodisperse model did not capture particle morphology at the early stages of the synthesis.
- The particle formation rate was overpredicted by all models, leading to an overestimation of the number concentration of primary particles. This discrepancy was attributed to uncertainties in the experimental data, precursor decomposition kinetics and the nucleation model.
- To further investigate the sensitivity of the predictions on the individual sub-models employed in the present work, simulations with alternative nucleation and sintering models were also conducted. These models were selected from the literature. The outcome of this analysis showed that the dimers-based nucleation model and the sintering characteristic time of Tsantilis et al. (2001) resulted in predictions that were in better agreement with the experimental data compared to those obtained with the other models.
- Good agreement was found between the extended one-PBE and the more comprehensive two-PBE model for most of the variables of interest, while both of them provide a substantial improvement over the monodisperse model.
- The extended one-PBE model substantially reduces the computational cost as compared with the two-PBE model, indicating that the extended one-PBE model provides a good balance of physical detail and computational speed. Furthermore, the CFD-PBE simulation with the one-PBE model required less than twice the time needed for the CFD-monodisperse model. The superior speed of the one-PBE model is largely owing to the tabulation of the aggregation kernel.

The computational advantage offered by the extended one-PBE model paved the way for its

coupling with LES and the comprehensive simulation of aerosol synthesis in turbulent flames, which was the objective of the second part of the present thesis. Specifically, the extended one-PBE model was introduced into the filtered probability density function/stochastic field modelling framework (denoted as LES-PBE-PDF) and was employed to investigate flame synthesis of silica nanoparticles in a turbulent diffusion flame. This Eulerian approach accounts for the complex small-scale interaction between turbulence, chemistry and particle dynamics, while a different sub-grid mixing time scale was introduced into the model to account for the low diffusivity of nanoparticles. Furthermore, gas-phase chemistry and aerosol dynamics were described by the same models (without any adjustments in parameters) as those employed for the laminar-flame simulation discussed earlier. Therefore, by maintaining the same kinetics, we attempted to investigate the modelling issues arising in silica synthesis in turbulent flames. The LES-PBE-PDF results were compared with the experimental SAXS data of Camenzind et al. (2008) for the S-10 flame. Particular emphasis was given to the nature of the discrepancies between predictions and experimental data, while possible sources of uncertainties in the model were discussed by leveraging knowledge acquired from our laminar-flame simulation results. Overall, the LES-PBE-PDF method was demonstrated to be a promising tool for simulating nanoparticle synthesis in turbulent flames. The main results of the turbulent-flame investigation are summarised below:

- Good agreement was found between numerical predictions and experimental data for time-averaged temperature along the centreline.
- The LES-PBE-PDF model underestimated the experimental SAXS data for primary particle sizes by a factor of two. The underestimation of primary particle sizes led to an underestimation of aggregate sizes. The nature of this discrepancy was thoroughly discussed by examining the components of the methodology and leveraging knowledge that has been gained from our laminar-flame simulations and other studies in the literature. Based on that, the discrepancy was attributed to uncertainties involved in the nucleation model, the precursor decomposition kinetics, and the absence of a surface reaction model.
- The number concentration of primary particle sizes and the silica volume fraction were overestimated by the LES-PBE-PDF model. Comparisons with the SAXS data suggested that the two-step HMDSO reaction mechanism of Feroughi et al. (2017) is rather fast, at least for the flame conditions examined here.

- The effect of the particle sub-grid scale mixing was investigated. The impact of the micromixing constant for particle number densities is more questionable due to the very low diffusivity of nanoparticles. Therefore, simulations with two different values of the micromixing constant for number densities were performed. In the first case, the value of the micromixing constant for number densities was set equal to that used for the gas-phase species. In the second case, in order to reflect the low diffusivity of nanoparticles, the value of the micromixing constant for number densities was selected to be two orders of magnitude smaller than that of the gas-phase species. The lower value of the micromixing constant resulted in larger values for the silica volume fraction at downstream locations.
- Simulations using eight and sixteen stochastic fields were performed. Results obtained with eight stochastic fields were almost indistinguishable from those obtained with sixteen stochastic fields. This strongly suggests that eight stochastic fields are sufficient to represent the sub-grid scale effects for both species and number densities.
- Gas-to-particle conversion processes as predicted by the LES-PBE-PDF model were also analysed. Results showed that the contribution of condensation to the total gas-to-particle conversion was more significant than that of nucleation.

In the last part of the thesis, a DNS study of turbulence-coagulation interaction was presented. DNS simulations of a 3-D turbulent planar jet flow ($Re = 3000$) laden with coagulating nanoparticles were performed. A discretisation (sectional) model for the solution of the PBE was employed; thus, the employed DNS-PBE methodology is free of *a priori* assumptions regarding the turbulent motions and the shape of the PSD. This allowed us to investigate in detail the behaviour and significance of the unknown correlations of fluctuations that arise from the Reynolds decomposition of the PBE and moment transport equations. A unity Schmidt number was employed for the number densities, as it is not feasible at present to resolve the Batchelor scales that result from diffusion at high Schmidt numbers. Simulations for two different coagulation Damköhler numbers, $Da_{coag} = 1$ and $1/3$, were conducted, where Da_{coag} is defined as the ratio of a convection time scale to a coagulation time scale. The main findings of the analysis are summarised below:

- The correlations of the fluctuating number densities arising from the Reynolds decomposition of the PBE were calculated at several locations in the domain. Results showed that the correlations were mostly positive for all combinations of particle volumes. Unexpectedly, negative correlations were also found. Specifically, negative correlations were

encountered in the case of more intense coagulation, i.e. $Da_{coag} = 1$, and located primarily close to the jet break-up point. A proposed explanation of this behaviour was thoroughly discussed.

- Unclosed terms arising from the Reynolds decomposition of the transport equations for the zeroth and second moments were also investigated. The analysis showed that the unclosed terms make a large contribution to the time-averaged coagulation source terms and therefore should not be neglected in turbulent coagulation studies (as is common practice in literature). In more detail, taking as an example the analysis for the zeroth moment transport equation, the ratio of the term involving the unknown correlations (denoted as C_0) to the time-averaged coagulation source term (denoted as A_0) reached values as high as 18% on the jet centreline and increased up to 40% close to the jet edges.
- The value of C_0 was found to be negative everywhere in the domain. The negative value of C_0 indicates that neglecting C_0 (as is common practice in literature) could lead to an overestimation of the zeroth moment.

To summarise, the objective of the present thesis was to develop and employ comprehensive methodologies for simulating particle formation and flame synthesis in laminar and turbulent flows. In line with this objective, an extended one-PBE model for sintering and aggregation was proposed and applied to study synthesis of nanoparticles in a laminar flame. Then, the extended one-PBE model was introduced into the LES-PBE-PDF framework and applied to study synthesis of nanoparticles in a turbulent flame. Finally, turbulence-coagulation interaction was investigated via DNS coupled with population balance equation. The presented investigations aimed to improve our understanding of the predictive capabilities and limitations of state-of-the-art modelling strategies for simulating particle formation and flame synthesis in laminar and turbulent flows.

5.2 Future work

This section provides some thoughts for extending the work presented in the previous chapters. Suggestions for further research in the field of nanoparticle flame synthesis are also given.

- The proposed methodologies and models in the present work were applied to simulate flame synthesis of silica nanoparticles. Silica was chosen mainly because there are more experimental data available in the literature for this nanomaterial. Experimental and

CFD-based studies associated with silica have been presented in Tables 2.1 and 3.1. In future work, the proposed methodologies should also be applied to study other nanomaterials. Titania is a possible choice for future applications on the basis that the chemistry of titanium tetrachloride (a precursor frequently used for the flame synthesis of titania) has been studied to a greater extent than other systems (Raman and Fox, 2016).

- Synthesis of silica nanoparticles in a turbulent flame was investigated in the present work via an LES-PBE-PDF approach (presented in Chapter 3) and numerical predictions were compared with experimental *in-situ* data. While results for the flame temperature were in good agreement with the experimental data, the LES-PBE-PDF model underestimated primary particle sizes. Further research and more comparisons with experiments are required in order to reach a state where a quantitative agreement between simulations and experiments can be achieved without any adjustments in model parameters. Furthermore, the S-10 flame of Camenzind et al. (2008), which was studied in the present work, is a turbulent diffusion (non-premixed) flame. Future work should apply the LES-PBE-PDF approach to simulate nanoparticle synthesis in premixed flames. The turbulent premixed flames of Kammler et al. (2005) are potential options for this purpose. Kammler et al. (2005) studied flame synthesis of silica nanoparticles via *in-situ* USAXS measurements and provided experimental data for many variables.
- In both the laminar and turbulent cases investigated in the present work, the simulation overestimated the number concentration of primary particles by roughly an order of magnitude. The discrepancy with the experimental data was attributed to uncertainties in the precursor decomposition kinetics and the nucleation model. The reliable prediction of particle nucleation rates remains an unresolved issue in the field of flame synthesis of nanomaterials (Rosner, 2005). Further research is needed to improve the models describing nucleation as well as the reaction mechanisms describing precursor chemistry.
- Uncertainty quantification and sensitivity-analysis methods are promising tools for assessing the reliability of simulation predictions and interpreting discrepancies between simulations and experiments. Future work in flame synthesis of nanoparticles should employ these tools for a systematic evaluation of uncertainties (Raman and Fox, 2016).

Appendix A

The Camenzind et al. experiment

A.1 On the selection of the Camenzind et al. experiment

The choice of the flame to be simulated is crucial for the validation strategy, and simulation-friendly experiments are sought. Experimental investigations of flame synthesis via non-intrusive *in-situ* measurements are ideal test cases for model validation. A literature review focusing on *in-situ* measurements of silica nanoparticle synthesis in flames has been conducted, and the studies are presented in table format in table 2.1, along with the experimental technique followed each time. For more comprehensive lists of references focusing on the investigation of particle morphology of titania, silica and alumina nanoparticles, we refer to the review paper of Park and Park (2015).

The simulations presented in Chapter 2 and Chapter 3 were validated against the detailed experimental data of Camenzind et al. (2008). Camenzind et al. (2008) investigated flame synthesis of silica nanoparticles by oxidation of hexamethyldisiloxane (HMDSO) in oxygen/methane diffusion flames, and they provided a plethora of particle data for several heights above the burner (HAB) obtained via *in-situ* small-angle X-ray scattering (SAXS). Furthermore, thermophoretic sampling (TS) of the particles and analysis by transmission electron microscopy (TEM) and *ex-situ* ultra-small-angle X-ray scattering (USAXS) were employed to study particle morphology and support the SAXS data. The flame temperature for several HABs was measured by *in-situ* Fourier transform infrared (FTIR) spectroscopy. In summary, the particle data provided for several HAB along with their symbols were:

- Flame temperature - T
- primary particle diameter - $d_{v/s}$
- Aggregate size / Radius of gyration - R_g

- Number of primary particles per aggregate - n_p
- Number concentration of primary particles - N_p
- Silica volume fraction - ϕ_v
- Geometric standard deviation of primary particles - σ_g
- Mass fractal dimension - D_f

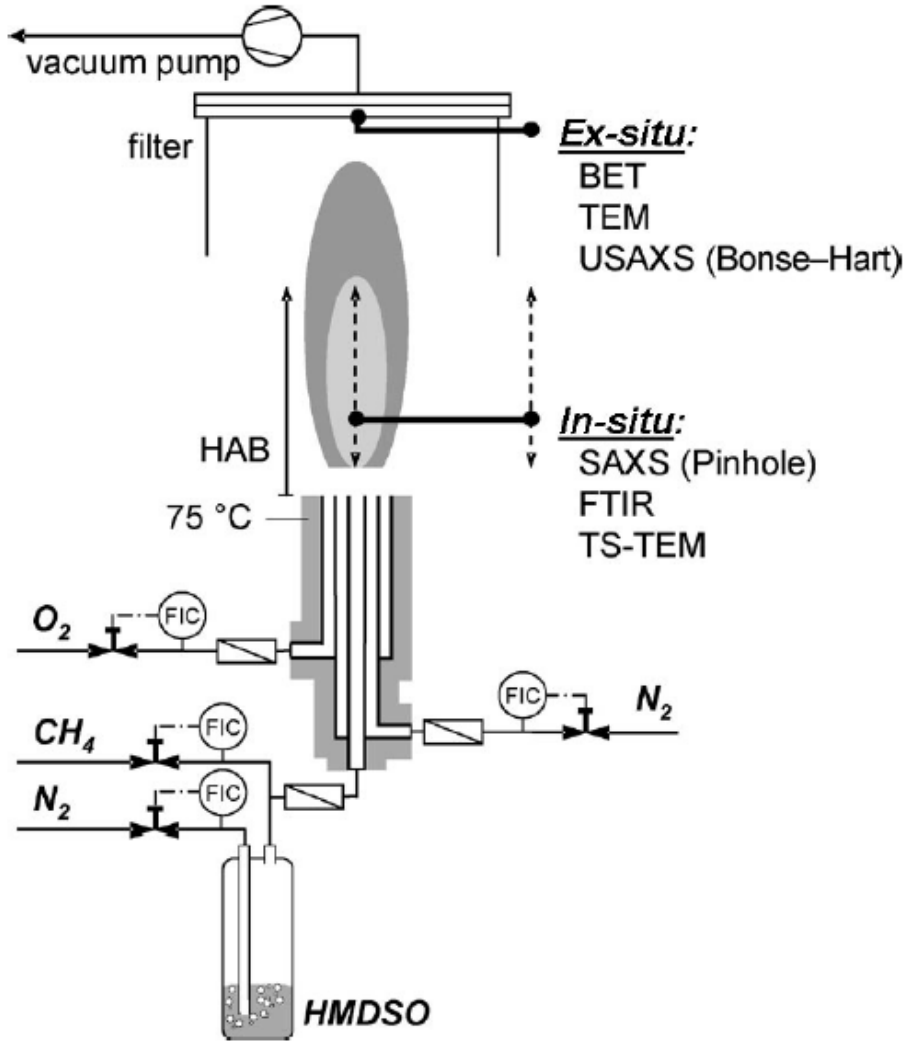


Figure A.1: Experimental setup for the synthesis of the SiO_2 nanoparticles with a co-flow diffusion flame burner. Reprinted from Camenzind et al. (2008).

Camenzind et al. (2008) used the notation “S-y” to refer to a series of SiO_2 -producing flames with different O_2 flow rates “y” [L/min]. The experimental setup for the S-y flames is presented in Fig. A.1. The flame under numerical investigation in Chapter 2 corresponds to the “S-2” laminar case of Camenzind et al. (2008). The flame under numerical investigation in Chapter 3 corresponds to the “S-10” turbulent case of Camenzind et al. (2008). To the best of the authors’ knowledge, the present work is the first simulation of these experiments. The S-2

laminar flame was selected as it is one of the few laminar flames for which *in-situ* experimental data for the particle field are available in the literature (see table 2.1). Laminar flames are sought since they are free of the impediments found in turbulent flames, and this allows for the validation of specific components of our methodology. At the same time, Camenzind et al. (2008) presented data also for a turbulent flame (S-10 case) on the same burner.

The co-flow diffusion flame reactor shown in Fig. A.1 was employed for both the laminar (S-2) and turbulent (S-10) cases. The burner comprised three concentric stainless-steel tubes of inner tube diameters of $D = 1.8$ mm, $D_1 = 3.5$ mm and $D_2 = 4.8$ mm, while the tube wall thickness was 0.3 mm (Wegner and Pratsinis, 2003a). HMDSO vapour was made by passing 0.3 l/min of N_2 through a reservoir filled with liquid HMDSO. Then, the HMDSO-laden N_2 gas flow was mixed with 0.5 l/min of methane CH_4 and introduced into the reactor through the centre tube. The consumption rate of HMDSO was 6.5 g/h, which corresponds to a production rate of silica SiO_2 of 4.8 g/h (oxidation of one mole of HMDSO produces two moles of SiO_2). The 1st annulus was fed with 0.5 l/min of N_2 to slightly lift the flame and prevent particle deposition on the nozzle tips. The 2nd annulus was fed with 2 l/min of O_2 for the S-2 case and 10 l/min of O_2 for the S-10 case. All gas flow rates have been given at standard temperature and pressure (STP) conditions. The temperature of the tubes was maintained at 75°C to prevent precursor condensation on the tube walls. The Reynolds number, based on the bulk velocity and the outer diameter of the burner, was $Re_{S-2} \approx 1414$ and $Re_{S-10} \approx 4280$ for the S-2 and S-10 cases, respectively. The experiment was conducted under atmospheric pressure. Here, it should be stressed that the only difference between the S-2 and S-10 flames is the O_2 flow rate through the 2nd annulus. In the S-2 case, the O_2 flow rate was 2 l/min leading to a laminar flame, while in the S-10 case, the O_2 flow rate was five times larger, resulting in a turbulent flame.

Appendix B

Supplementary information of the laminar-flame simulation

B.1 Validation of the monodisperse model

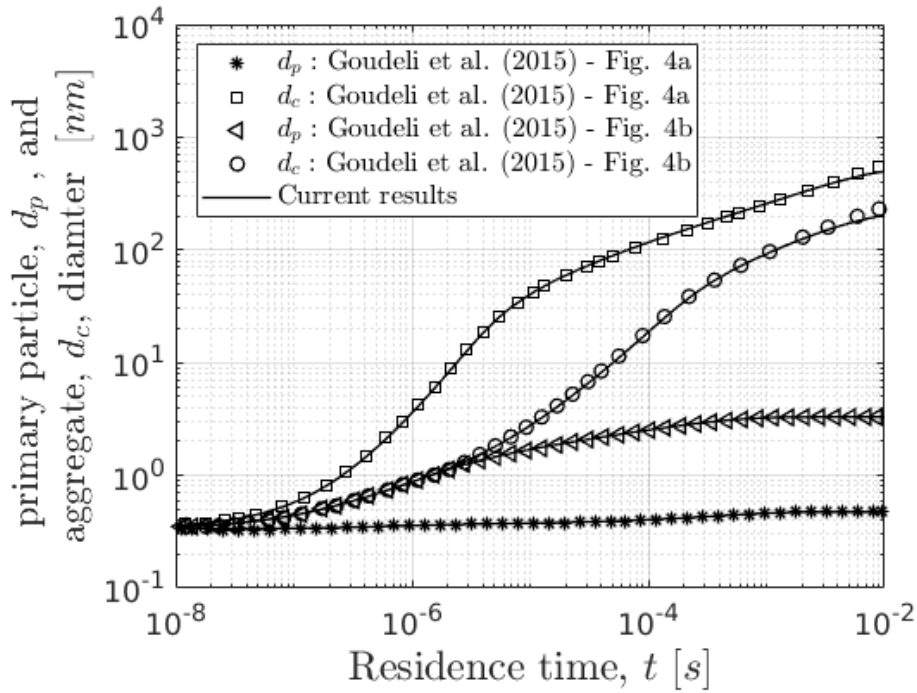


Figure B.1: Validation of the monodisperse model presented in Section 2.2.3. Aggregation and sintering of nanoparticles at conditions described in Goudeli et al. (2015) were simulated with the monodisperse model “Mono” (see Section 2.2.3). Results were in excellent agreement with the data of Goudeli et al. (2015).

B.2 Inlet velocity profile

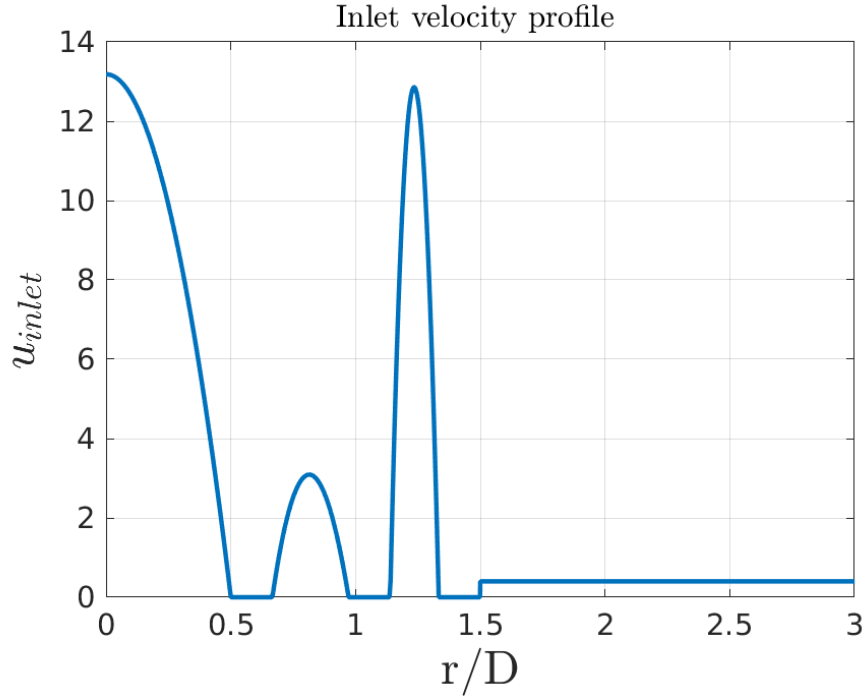


Figure B.2: Inlet velocity profiles in the streamwise direction. The stream bulk velocities u_{inlet} of the jets coming from the inner tube, the first and second annulus were $U = 6.715$ m/s, $U_1 = 2.057$ m/s and $U_2 = 8.57$ m/s, respectively. The inlet velocities were estimated based on the given mass flow rates (Camenzind et al., 2008) and by assuming that the temperature of the streams was 75°C . A parabolic laminar flow velocity profile was employed for the inner jet and Poiseuille laminar profiles through annulus sections were employed for the other two jet streams. A uniform velocity $U_{air} = 0.4$ m/s was used for the air co-flow stream at the inlet. See also Table 2.4 in Section 2.5.2.

B.3 Effect of air co-flow velocity

A uniform velocity $U_{air} = 0.4$ m/s was used for the air co-flow stream at the inlet and the ambient temperature was set to $T_{amb} = 20^\circ\text{C}$. It is expected that the effect of air entrainment is diminished in the flame configuration that we studied. We base this argument on two critical factors. First, the flame under investigation is laminar with relatively small inlet flow rates. This means that the induced air entrainment should be small. Secondly, the flame under investigation is a co-flow diffusion flame Camenzind et al. (2008). The fuel is delivered in the reactor through the centre tube and the O_2 co-flow stream is introduced in the reactor through the second annulus. The O_2 flow rate is larger than that from the centre tube. The excess O_2 introduced in the reactor serves as the primary oxidiser of the fuel and therefore the effect of the entrained air is negligible. This is also supported by the fact that test cases with different values for U_{air} , i.g. $U_{air} = 0.2$ m/s and $U_{air} = 0.6$ m/s, resulted in similar temperature fields (see Fig. B.3). The value of U_{air} had a negligible effect on the results.

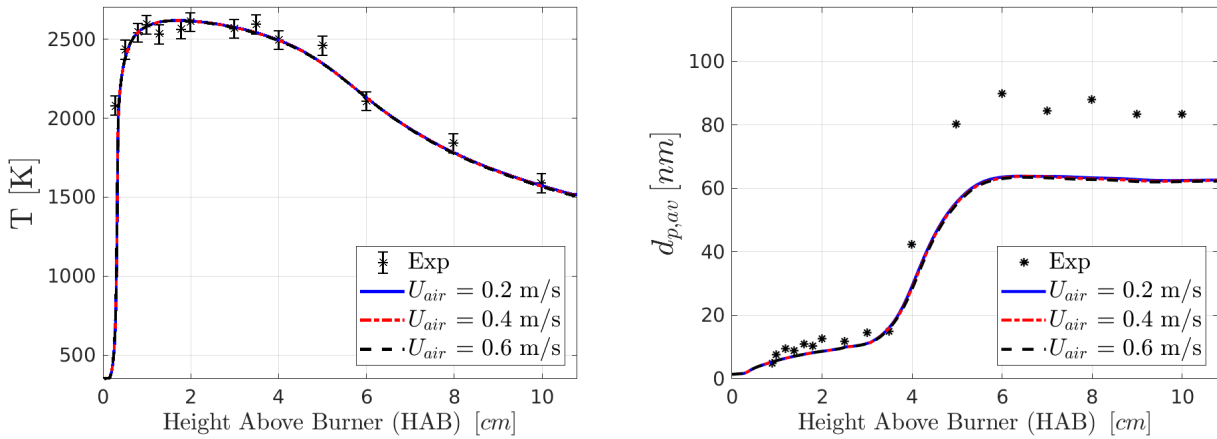


Figure B.3: Numerical predictions for flame temperature and primary particle diameter for different values of air co-flow velocity U_{air} . Results were obtained with the monodisperse model. Comparison is also made with the experimental data of Camenzind et al. (2008).

B.4 Computational domain and grid

The burner configuration is axisymmetric, making it possible to solve the governing equations onto a 2-D rectangular plane. Following standard methods (Sun et al., 2021; Liu and Rigopoulos, 2019; Smooke et al., 2005), the burner tubes were excluded from the solution domain. The inflow boundary corresponds to the region immediately above the burner nozzle. Therefore, the computational domain comprises a rectangle and a boundary condition is applied on each of the four sides of the rectangle. In particular, 2-D axisymmetric simulations were performed, with an axisymmetric boundary condition being applied along the centreline (bottom side in Fig. B.4 (top)) and a symmetry boundary condition being applied at the opposite side (top side in Fig. B.4 (top)). A zero-gradient boundary condition was applied at the outlet boundary in the streamwise direction. In the plots, the x and r coordinates are defined to denote the streamwise and cross-stream directions, respectively.

The size of the computational domain is $60D \times 15D$, where $D = 1.8$ mm is the inner tube diameter. A computational grid with 264×162 cells with spacing increasing exponentially by factors 1.0132 and 1.03 in the axial and radial directions, respectively, was employed. Grid refinement was employed at the height of the second annulus to ensure that at least ten cells were used to capture the inlet velocity profile (see Fig. B.4 (bottom)).

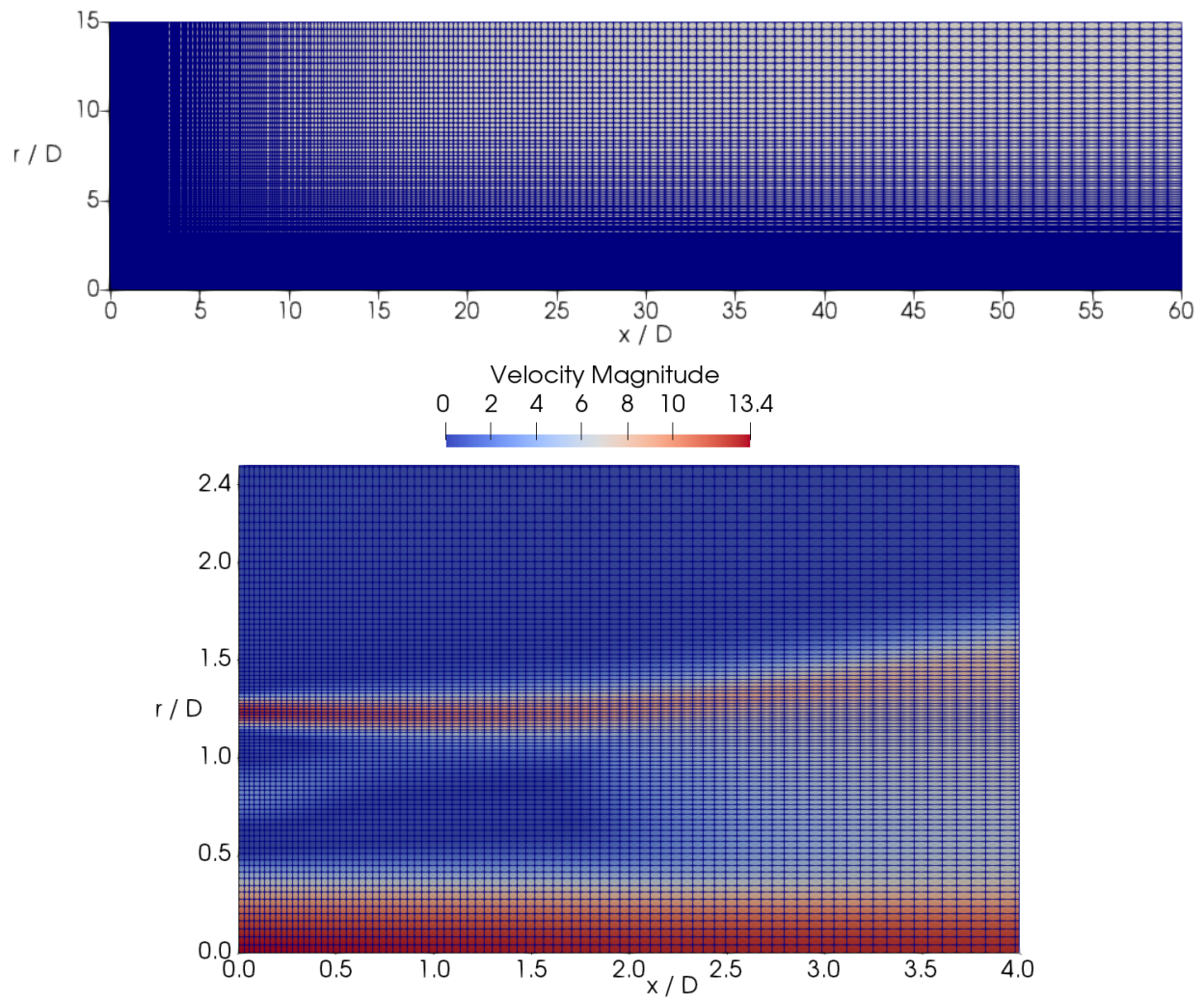


Figure B.4: Computational domain/grid (top) and computational grid focussing in the region above the burner (bottom).

B.5 Grid independence

Further checks for CFD grid independence are presented here. Simulations were performed on two different grids with the PBE model (see Section 2.2.5). In the first case, named "Coarse grid", the size of the computational domain was $60D \times 15D$, where $D = 1.8 \text{ mm}$ is the inner tube diameter. A computational grid with $264 \times 162 = 42768$ cells in x and r directions was employed. The grid spacing increased exponentially in the axial and radial directions by factors 1.0132 and 1.03, respectively. Grid refinement was employed at the height of the second annulus to ensure that at least ten cells were used to capture the inlet velocity profile. In the second case, named "Fine grid", the size of the computational domain was $60D \times 30D$ while a computational grid with $792 \times 246 = 194832$ cells in x and r directions was employed. The fine grid has roughly 4.5 times more cells than the coarse grid. The time step was $\Delta t = 10^{-7} \text{ s}$ for the coarse grid and $\Delta t = 0.4 \cdot 10^{-7} \text{ s}$ for the fine grid, resulting in a maximum Courant–Friedrichs–Levy (CFL) number of 0.03.

Numerical predictions for temperature are presented in Fig. B.5 while the main analysis results that led to the comparison of the numerical predictions with the experimental SAXS data of Camenzind et al. (2008) are demonstrated in Fig. B.6. Overall, it is observed from all figures that the differences between the two cases are negligible.

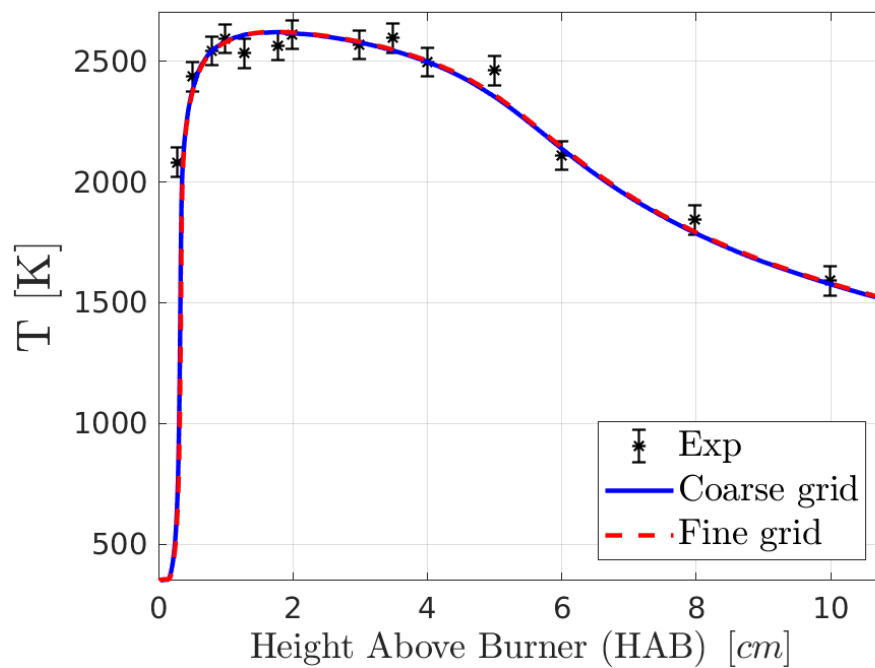


Figure B.5: Effect of the computational grid on the flame temperature. Results were obtained with the one-PBE model. Comparison is also made with the experimental data of Camenzind et al. (2008).

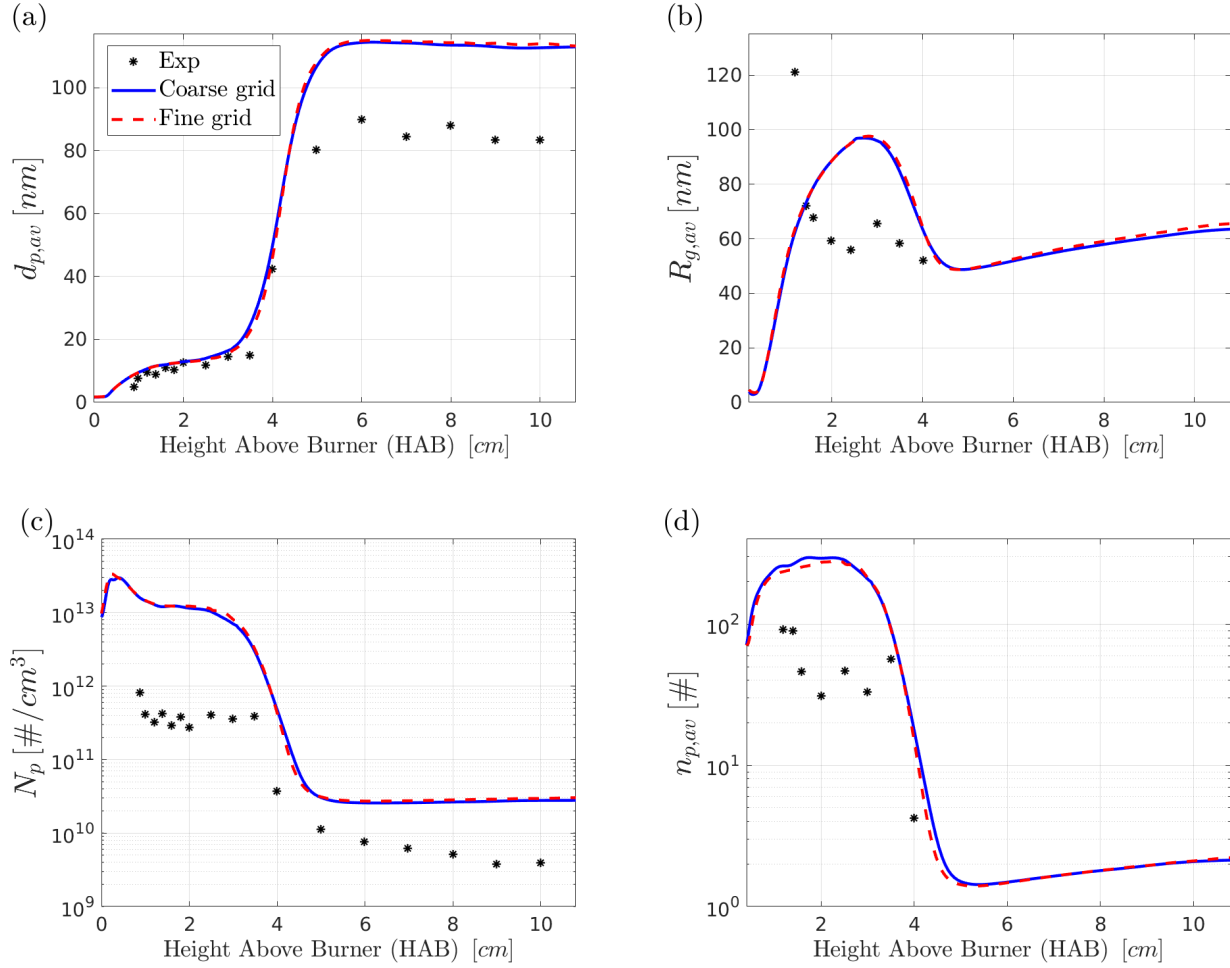


Figure B.6: Effect of computational grid on (a) primary particle diameter, (b) radius of gyration of aggregates, (c) primary particle number concentration and (d) average number of primary particles per aggregate. Data are plotted along the pathline of maximum silica volume fraction. Results were obtained with the one-PBE model. Comparison is also made with the experimental data of Camenzind et al. (2008).

Appendix C

Scalability analysis of code PANTARHEI

C.1 Introduction

In the present section, a scalability analysis of the DNS code PANTARHEI is presented. The strong scaling analysis was conducted by the author during July and August 2021. All the simulations were performed on ARCHER2, the UK National high-performance computing service.

C.1.1 Flow-solver description

PANTARHEI is a Fortran-90 in-house CFD solver. The incompressible Navier-Stokes equations are discretised using the finite volume method in unstructured grids and all unknown variables are stored at the cell centroids (collocated variable arrangement). At the moment, all our simulations are performed with hexahedral meshes that are created using external packages, like ICEM-CFD. The code however can handle arbitrary cell topologies and cell shapes.

A second-order central discretisation scheme is employed for the convection and viscous terms, while a third-order backward differentiation formula (BDF) is used for the transient term. The orthogonal viscous terms are treated implicitly, while the convection term and the non-orthogonal diffusion terms are extrapolated from the previous three timesteps. The pressure-velocity coupling is dealt with by the fractional step method.

The matrices for the velocity and pressure that result from the discretisation of the Navier-Stokes and the pressure correction equations respectively, are constructed only once at the beginning and reused throughout the simulation. Whenever possible, we loop over cell faces and add the contribution of each face to the cells on either side. This is, for example, how we compute the conservative terms of the turbulent kinetic energy equation when doing budget

analysis. On the other hand, the source term is computed by looping over cells.

Parallelisation programming

The code is parallelised with the aid of the PETSc library. The domain is partitioned using a separate partition code based on ParMetis. The grid information for every core (vertex coordinates, cell definitions, inter-processor boundaries etc) is stored in a single file. This file is then accessed in parallel by all cores and each core starts reading from a specific location in the file.

The code does not handle overlapping cells. Instead, cells on either side of a partition share a common face, which is treated as a boundary, in exactly the same way as in a single-domain case. This makes the coding much easier and minimises chances for error. A short documentation for the code is available, which is used to introduce new users to the code and explain how the discretisation works and how it is implemented into the code.

A Krylov subspace iterative method (GMRES) and an algebraic multigrid preconditioner (from the Hybre library) are used for the numerical solution of the linear systems. Usually, 2-3 iterations for the velocity matrix and 5-6 for the pressure matrix are sufficient for the residuals to drop 5 or 6 orders of magnitude.

Input/Output requirements

Collective I/O operations are employed in the code. This means that all processes read or write a single file simultaneously. The advantage of this method is that only one restart file is produced, instead of producing many files (i.e. one for each core). It also provides flexibility in terms of restarting. Specifically, this method allows the user to restart a simulation from an existing restart file, even when one may change the number of grid partitions, and/or the way the grid is partitioned. The same approach is used for writing output files for post-processing. For example, for the collection of statistics, one could perform time-averaging on the fly (as the simulation runs), and then mean and rms velocities are stored in a single file for the whole domain. After that, a separate code is employed to convert the output file to a format suitable for visualisation in Paraview. All produced files are in binary format. As an example, the size of the restart file (just velocities) for the $N384$ case (see details below) is 2.32 GB. When variables for the post-processing are also stored in an output file, the size of the restart file is roughly 12 GB.

C.2 Test case: Kolmogorov flow

The three-dimensional Kolmogorov flow was selected as a test case in order to assess the performance of the DNS code PANTARHEI. The Kolmogorov flow comprises a flow in a triply periodic domain which is forced with an external sinusoidal study force (in one direction only). This flow is perhaps the simplest system for studying sustained turbulence and testing numerical schemes. The flow in the periodic domain is presented in Fig. C.1. More details on the Kolmogorov flow can be found in the references (Goto and Vassilicos, 2016; Borue and Orszag, 1996; van Veen and Goto, 2016; Armbruster et al., 1992; Shebalin and Woodruff, 1997).

The 3-D Kolmogorov flow is governed by the incompressible Navier-Stokes equations presented below in non-dimensional form:

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \frac{1}{Re} \nabla^2 \mathbf{u} + \mathbf{f}, \quad (\text{C.1})$$

$$\nabla \cdot \mathbf{u} = 0 \quad (\text{C.2})$$

where $\mathbf{u}(\mathbf{x}, t)$ is the velocity vector field, and p is the pressure. The same set-up as that of Goto and Vassilicos (2016) is employed in the present study. The external force is as simple as possible; it is independent of time and is expressed in terms of a single sinusoidal function:

$$\mathbf{f} = f_0 \sin\left(\frac{2\pi}{L_b} y\right) \mathbf{e}_x \quad (\text{C.3})$$

where $f_0 = \frac{1}{2\pi}$ is a forcing constant, $\mathbf{e}_x$ is the unit vector in the x direction, and $L_b = 2\pi$ is the length of the side of the periodic cube. The forcing constant f_0 was selected in such a way that the Reynolds number (resented in the next paragraph) is the inverse of the kinematic viscosity ($Re = 1/\nu$). The density ρ was set to unity in the simulation in order to non-dimensionalise the equations.

Following van Veen and Goto (2016) and Borue and Orszag (1996), the Reynolds number based on the forcing parameters can be defined as:

$$Re = \frac{\sqrt{L_b f_0}}{2\pi/L_b \nu} \quad (\text{C.4})$$

where ν is the kinematic viscosity. The Kolmogorov flow is laminar for Re number smaller than 100, while the turbulence transition regime appears for $Re \in (100, 170)$ (van Veen and Goto, 2016). This flow is homogeneous in two directions ($x - z$ plane based on the current notation) (Borue and Orszag, 1996).

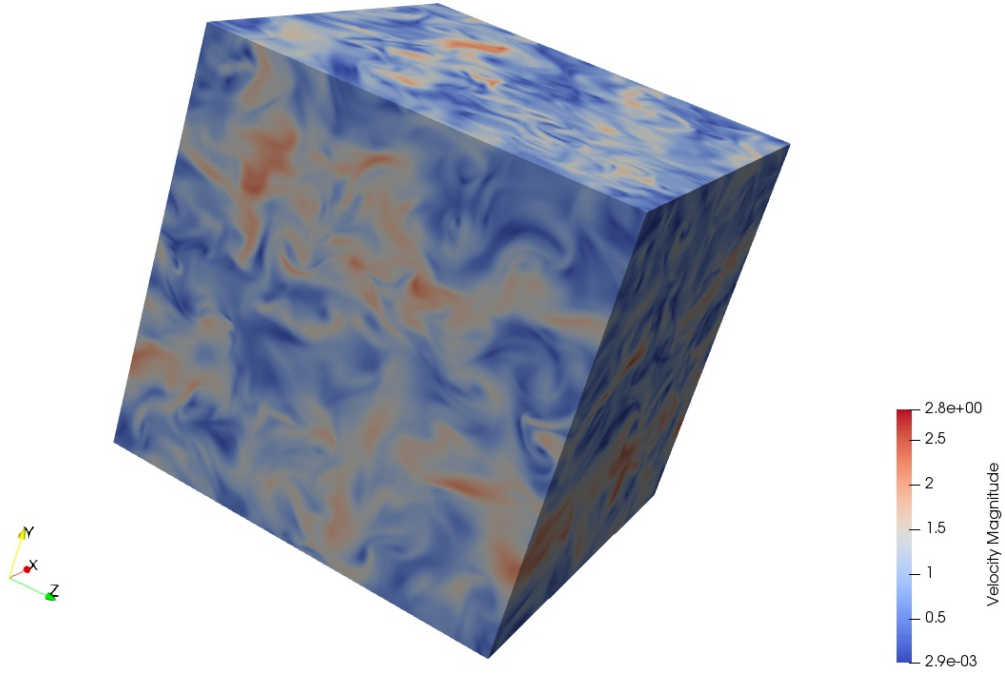


Figure C.1: Three-dimensional Kolmogorov flow in a triply periodic domain driven by a large-scale steady sinusoidal force. The size of the computational domain is $-\pi \geq x, y, z, \geq \pi$. Sustainable turbulence is reached by forcing the Navier-Stokes equations with Eq. (C.3). The Reynolds number based on Eq. (C.4) is 490.

DNS simulations of the 3-D Kolmogorov flow were performed. The Reynolds number based on Eq. (C.4) is 490. The size of the computational domain presented in Fig. C.1 is $-\pi \geq x, y, z, \geq \pi$. The x, y and z coordinates are defined in the streamwise (forced), cross-stream and spanwise directions, respectively. Turbulent properties are statistically homogeneous in the z -direction. Periodic boundary conditions are implemented at all boundaries. The simulations were performed on a uniform computational grid with $N = 384^3 \approx 56$ million cells, distributed evenly in all directions. The time step was $\Delta t = 0.00245$, resulting in Courant–Friedrichs–Levy (CFL) numbers smaller than 0.5 ($\text{CFL} \leq 0.5$). The simulation was run first for several flow-through times to reach a state where the flow is fully turbulent and independent of the initial conditions (a flow-through is evaluated based on the maximum streamwise time-averaged velocity $U_{x,max} \approx 1$ (according to Borue and Orszag (1996)) and the size of the computational domain $L_b = 2\pi$). To collect the statistics, the simulations were run for more than four flow-through times. Statistics were computed by averaging in time and in the homogeneous spanwise direction.

The present DNS simulation is validated against the reference data of Borue and Orszag

(1996) and results are presented in Fig. C.2. Very good agreement was found between the present and the reference data for streamwise time-averaged velocities, U_x , shown in Fig. C.2a. Specifically, the velocity profile is within the lower and upper limits given by Borue and Orszag (1996) for all locations. A qualitative agreement was found between the present and the reference data for turbulent rms velocity fluctuations, u_{rms} , shown in Fig. C.2b; however, lower values of u_{rms} are predicted in the present case. This is to be expected since Borue and Orszag (1996) solved the hyperviscosity-modified Navier-Stokes equations, while here we solve the Navier-Stokes directly. In these equations, the viscous term was replaced by a higher power of the Laplacian in order to extend the inertial range of turbulence. Hyperviscosity was a standard tool of that era (the computational power was much lower than today's standards) for studying turbulent flows.

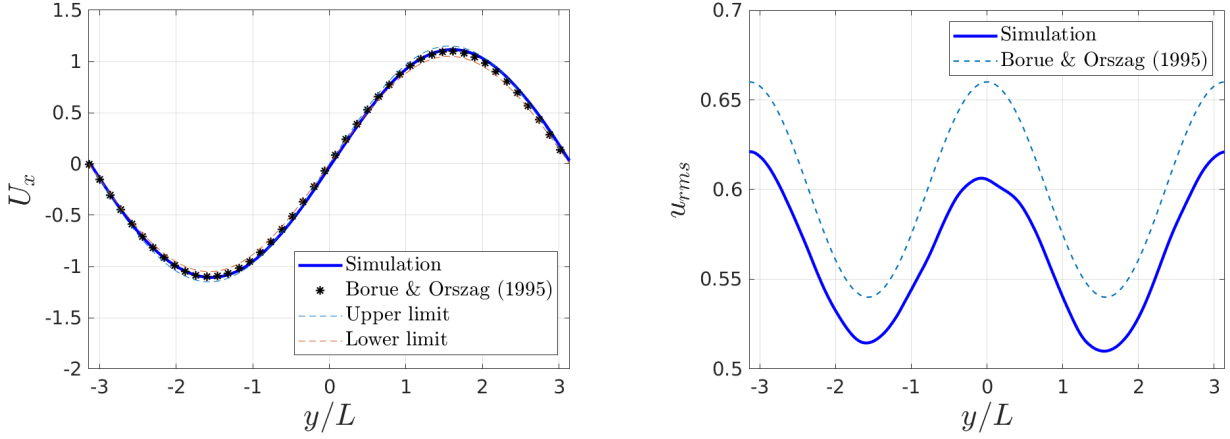


Figure C.2: (a) Time-averaged velocity profile in the forced direction. (b) Turbulent rms velocity fluctuations in the forced direction. The reference data were found in (Borue and Orszag, 1996). The discrepancy in (b) is expected since Borue and Orszag (1996) solved the hyperviscosity-modified Navier-Stokes equations.

The ratio of cell size to Δ_{cell} to the Kolmogorov length scale η is presented in Fig. C.3a. The cell size is evaluated as $\Delta_{cell} = (\Delta x \Delta y \Delta z)^{1/3}$, while the Kolmogorov length scale as $\eta = (\nu^3/\epsilon)^{1/4}$, where ϵ is the dissipation of the turbulent kinetic energy evaluated as $\epsilon = 2\nu \overline{s_{ij}s_{ij}}$ and $s_{ij} = \frac{1}{2} \left(\frac{\partial u'_i}{\partial x_j} + \frac{\partial u'_j}{\partial x_i} \right)$ is the fluctuating rate of strain. The maximum value of cell size to the Kolmogorov length scale was found to be less than unity ($\frac{\Delta_{cell}}{\eta} < 0.95$). Values smaller than 2.1 (Pope, 2000) imply that the grid resolution suffices and turbulent flow structures are well-resolved. The maximum Reynolds number $Re_\lambda = \sqrt{|\mathbf{u}'|^2} \lambda / \nu$, based on the Taylor micro-scale $\lambda = \sqrt{\nu |\mathbf{u}'|^2 / \epsilon}$, was found to be 72 as shown in Fig. C.3b.

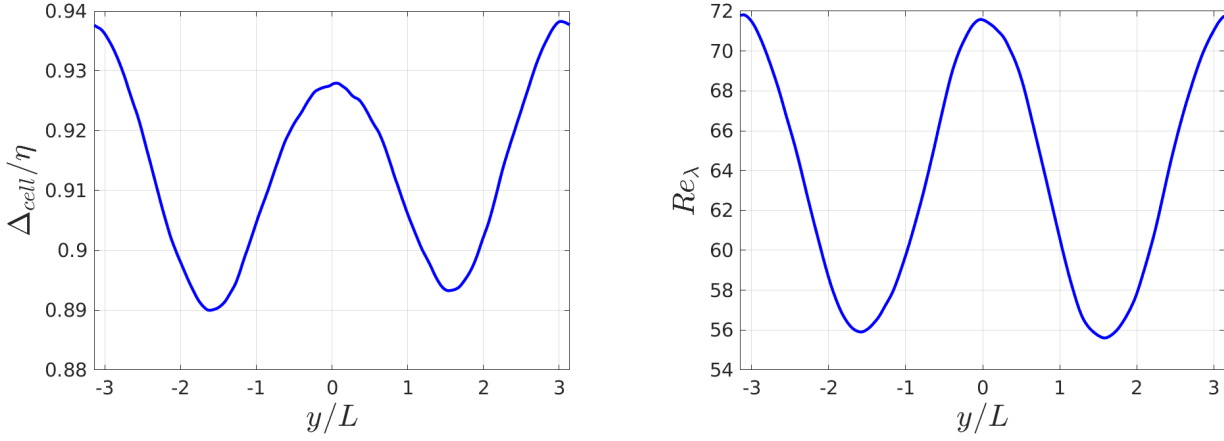


Figure C.3: (a) Ratio of cell size, defined as $\Delta_{cell} = (\Delta x \Delta y \Delta z)^{1/3}$, to the Kolmogorov length scale $\eta = (\nu^3/\epsilon)^{1/4}$. (b) Reynolds number $Re_\lambda = \sqrt{|\mathbf{u}'|^2} \lambda / \nu$, based on the Taylor micro-scale $\lambda = \sqrt{\nu |\mathbf{u}'|^2 / \epsilon}$.

C.3 Performance analysis

The strong-scaling analysis examines how the computational time required to solve a specific problem decreases as the number of partitions (subdomains) of the problem increases. In particular, in CFD codes, it is of interest to examine how the computational time decreases as one increases the number of compute nodes (number of processors), given that the computational grid and the number of grid cells remain the same. On the theoretical limit, the computational speedup gained by increasing the number of processors relative to a reference case (for a given grid) is expected to increase linearly with the number of processors.

We have performed a strong-scaling analysis by examining three grid cases for the 3-D Kolmogorov flow case. The 3-D Kolmogorov flow was presented in Section C.2. The computational domain is a periodic cube with size $-\pi \leq x, y, z \leq \pi$. Periodic boundary conditions are employed for all sides of the cube. This flow case is very similar to the Taylor-Green Vortex (TGV) (Brachet et al., 1983; Van Rees et al., 2011; Drikakis et al., 2007; Yang and Pullin, 2011) case with the difference being that in the Kolmogorov flow the momentum equations are forced by a sinusoidal source term, resulting in sustained turbulence.

The grid cases employed in the present analysis are labelled as “N256”, “N320”, and “N384”. In all cases, the grids were uniform. For the first case, we have 256 cells in each direction, so in total, we have $256^3 \approx 16 \cdot 10^6$ cells in the domain. For the second and third grid case, we have roughly $320^3 \approx 33 \cdot 10^6$ and $384^3 \approx 56.5 \cdot 10^6$ cells, respectively. These grids were chosen because their size is representative of general and potential future cases.

The domain is split in cuboids in such a way so that to distribute the load evenly in all processes (or as evenly as possible) and to minimize the cells / inter-processor boundaries ratio. In ARCHER2, each node has 128 CPUs thus, the one-node case was chosen as the reference case to calculate the speed-up and the efficiency. Each simulation was run for 100 timesteps and then the wall time per timestep was estimated. The simulations were restarted from a “stable” (fully developed turbulence had been reached) solution. Each case was submitted on ARCHER2 five times and then the average value was calculated.

The indices that are used to evaluate the parallel performance of the code are defined in the present paragraph. The relative speedup is defined as:

$$\text{Speedup} = \frac{T_{ref}}{T_n} \quad (\text{C.5})$$

where T_{ref} is the wall time per time step (in seconds) of the reference case. The one-node (128 CPUS) case was set as the reference case. The wall time per timestep (in seconds) for the case with n nodes is denoted with T_n . The parallel efficiency is defined as:

$$\text{Efficiency} = \frac{T_{ref}}{n \cdot T_n} \quad (\text{C.6})$$

The CPU hours per time step is the product of the wall time per timestep (in seconds) with the number of CPUs used for that case divided by 3600. This index is proportional to the ARCHER CUs (Compute Units) and a measure of the computational cost:

$$\text{CPU hours / timestep} = \frac{T_{ref} \cdot n \cdot 128}{3600}. \quad (\text{C.7})$$

Fig. C.4 shows the relative speedup versus the number of compute nodes. The linear scaling is depicted with a solid black line. It is evident that the flow-solver PANTARHEI scales linearly as one increases the number of compute nodes. The parallel efficiency versus the number of compute nodes is shown in Fig. C.5. Interestingly, values greater than 1 are observed in this figure. This behaviour is typical of unstructured codes and it is related to cache effects and to how the memory is managed by the HPC facility. Fig. C.6a shows the wall time per timestep versus the number of compute nodes, while Fig. C.6b contains the same information as in Fig. C.6a but a logarithmic scale was used for the vertical and horizontal axes in that latter figure. In Fig. C.7, we present the CPU hours per time step versus the number of computational cells per process (CPUs). This index is a measure of the computational cost and can serve as an indication of the point where the best “performance” is achieved. For example, the best performance of the code for the $N384$ case is reached when there are roughly 56000 cells per

process. This information is useful for future cases. More information is given in table format (i.e. cells per processor, number of inter-processor boundaries, etc.) in Table C.8.

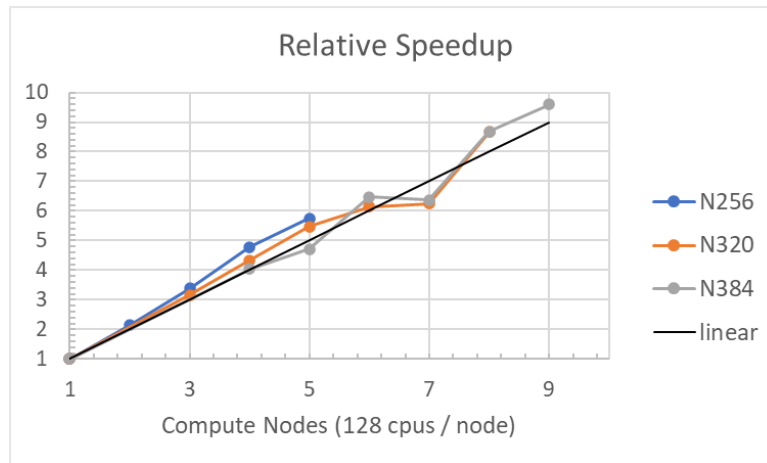


Figure C.4: Relative speedup for the three cases. The solid black line indicates the theoretical linear scaling. The speedup is evaluated with Eq. (C.5).

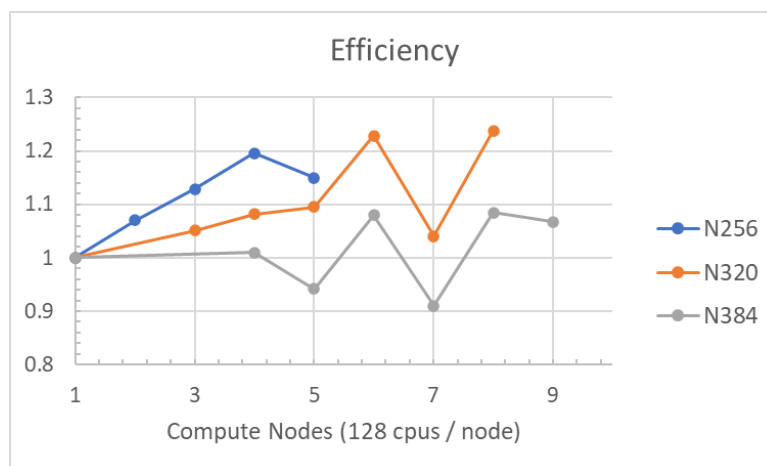


Figure C.5: Parallel efficiency for the three cases. The efficiency is evaluated with Eq. (C.6).

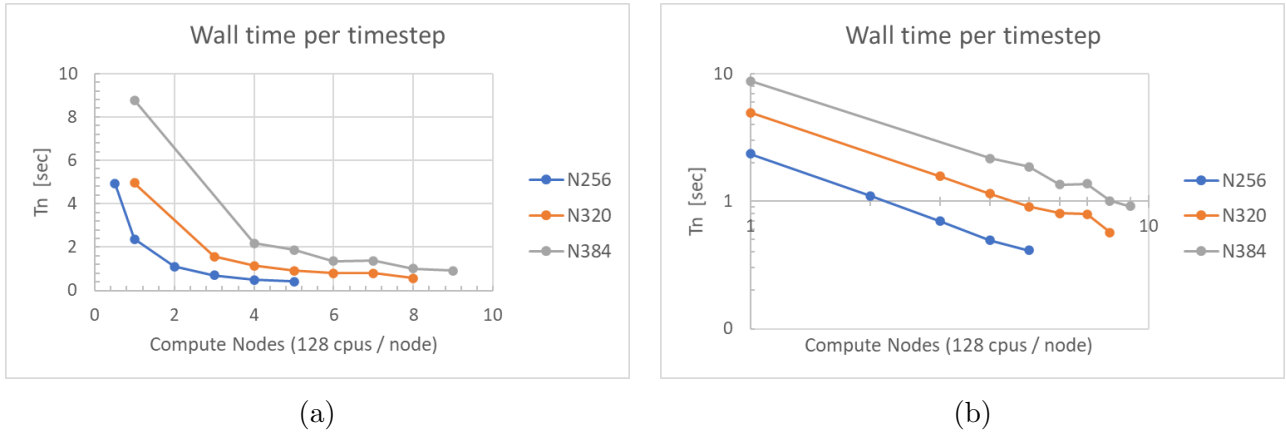


Figure C.6: Wall time per timestep T_n (in seconds) for the three cases. A logarithmic scale was used for both axes in (b).

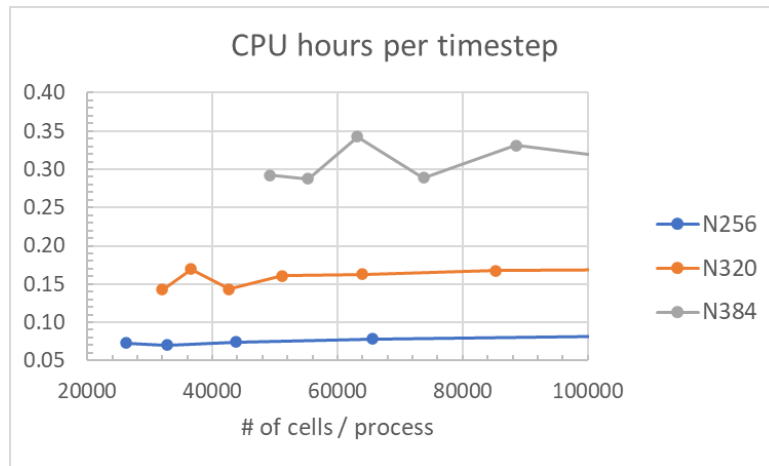


Figure C.7: CPU hours per timestep (in hours) for the three cases. The CPU hours per timestep are evaluated with Eq. (C.7).

Case N256					
Number of Processors	128	256	384	512	640
Uniformity	yes	yes	no	yes	no
Cells per proc - Mean	131072.0	65536.0	43690.7	32768.0	26214.4
Inter-proc boundaries per proc - Mean	16384.0	10240.0	7509.3	6144.0	5324.8
Cells / Inter-proc bnds - Mean	8.0	6.4	5.8	5.3	4.9
Wall time per timestep	2.363567	1.104664	0.697946	0.494241	0.411298
CPU hours per timestep	0.0840379	0.0785539	0.0744476	0.0702920	0.0731197
Speed-up	1	2.140	3.386	4.782	5.747
Efficiency	1	1.070	1.129	1.196	1.149
NPROC/NPROCref	1	2	3	4	5

(a)

Case N320							
Number of Processors	128	384	512	640	768	896	1024
Uniformity	yes	no	yes	yes	no	no	yes
Cells per proc - Mean	256000.00	85333.33	64000.00	51200.00	42666.67	36571.43	32000.00
Inter-proc boundaries per proc - Mean	25600.00	11733.33	9600.00	8320.00	7466.67	6857.14	6400.00
Cells / Inter-proc bnds - Mean	10.00	7.27	6.67	6.15	5.71	5.33	5.00
Wall time per timestep	4.954921	1.571013	1.144759	0.904757	0.806698	0.793749	0.571870
CPU hours per timestep	0.1761750	0.1675748	0.1628102	0.1608457	0.1434130	0.1693332	0.1423320
Speed-up	1	3.153965101	4.3283537	5.4765198	6.1422269	6.2424254	8.6644257
Efficiency	1	1.0513217	1.0820884	1.095304	1.2284454	1.0404042	1.2377751
NPROC/NPROCref	1	3	4	5	6	7	8

(b)

Case N384							
Number of Processors	128	512	640	768	896	1024	1152
Uniformity	yes	yes	no	yes	no	yes	yes
Cells per proc - Mean	442368.00	110592.00	88473.60	73728.00	63195.43	55296.00	49152.00
Inter-proc boundaries per proc - Mean	36864.00	13824.00	11980.80	10752.00	9874.29	9216.00	8192.00
Cells / Inter-proc bnds - Mean	12.00	8.00	7.38	6.86	6.40	6.00	6.00
Wall time per timestep	8.770505	2.170838	1.862858	1.353758	1.376955	1.010912	0.913274
CPU hours per timestep	0.3118402	0.3087415	0.3311748	0.2888016	0.3427087	0.2875482	0.2922476
Speed-up	1	4.040146194	4.7080897	6.4786371	6.3694938	8.6758376	9.6033674
Efficiency	1	1.010036549	0.9416179	1.0797729	0.9099277	1.0844797	1.0670408
NPROC/NPROCref	1	4	5	6	7	8	9

(c)

Figure C.8: Strong-scaling analysis of code PANTARHEI on ARCHER2. Each node on ARCHER2 has 128 CPUs (processors). The one-node case was selected as the reference case. Results are presented in table format. “Uniformity” refers to whether the cells are distributed evenly amongst processors.

Bibliography

- A. Abdelsamie, F. E. Kruis, H. Wiggers, and D. Thévenin. Nanoparticle formation and behavior in turbulent spray flames investigated by dns. *Flow, Turbulence and Combustion*, 105(2): 497–516, 2020.
- J. Akroyd, A. J. Smith, R. Shirley, L. R. McGlashan, and M. Kraft. A coupled CFD-population balance approach for nanoparticle synthesis in turbulent reacting flows. *Chemical Engineering Science*, 66(17):3792–3805, 2011.
- F. Alves Portela, G. Papadakis, and J. C. Vassilicos. The role of coherent structures and inhomogeneity in near-field interscale turbulent energy transfers. *Journal of Fluid Mechanics*, 896:A16, 2020. doi: 10.1017/jfm.2020.341.
- D. Armbruster, R. Heiland, E. J. Kostelich, and B. Nicolaenko. Phase-space analysis of bursting behavior in kolmogorov flow. *Physica D: Nonlinear Phenomena*, 58(1-4):392–401, 1992.
- S. Balay, S. Abhyankar, M. F. Adams, S. Benson, and J. Brown. PETSc users manual. Technical Report ANL-95/11 - Revision 3.15, Argonne National Laboratory, 2021. URL <https://www.mcs.anl.gov/petsc>.
- R. C. Ball and R. Jullien. Finite size effects in cluster-cluster aggregation. *Journal de Physique Lettres*, 45(21):1031–1035, 1984.
- R. S. Barlow, A. N. Karpetis, J. H. Frank, and J. Y. Chen. Scalar profiles and NO formation in laminar opposed-flow partially premixed methane/air flames. *Combustion and Flame*, 127(3):2102–2118, 2001.
- G. Beaucage. Approximations leading to a unified exponential/power-law approach to small-angle scattering. *Journal of Applied Crystallography*, 28(6):717–728, 1995.

- G. Beaucage. Determination of branch fraction and minimum dimension of mass-fractal aggregates. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, 70(3 1):031401–1–031401–10, 2004.
- V. Borue and S. A. Orszag. Numerical study of three-dimensional kolmogorov flow at high reynolds numbers. *Journal of Fluid Mechanics*, 306:293–323, 1996.
- M. E. Brachet, D. I. Meiron, S. A. Orszag, B. G. Nickel, R. H. Morf, and U. Frisch. Small-scale structure of the taylor–green vortex. *Journal of Fluid Mechanics*, 130:411–452, 1983.
- J. R. Brock, P. J. Kuhn, and D. Zehavi. Condensation aerosol formation and growth in a laminar coaxial jet: experimental. *Journal of Aerosol Science*, 17(1):11–22, 1986.
- L. W. B. Browne, R. A. Antonia, S. Rajagopalan, and A. J. Chambers. Interaction region of a two-dimensional turbulent plane jet in still air. In *Structure of complex turbulent shear flow*, pages 411–419. Springer, 1983.
- V. S. Buddhiraju and V. Runkana. Simulation of nanoparticle synthesis in an aerosol flame reactor using a coupled flame dynamics–monodisperse population balance model. *Journal of Aerosol Science*, 43(1):1–13, 2012.
- B. Buesser and A. J. Gröhn. Multiscale aspects of modeling gas-phase nanoparticle synthesis. *Chemical Engineering & Technology*, 35(7):1133–1143, 2012.
- B. Buesser and S. E. Pratsinis. Design of nanomaterial synthesis by aerosol processes. *Annual Review of Chemical and Biomolecular Engineering*, 3:103–127, 2012.
- A. Camenzind, H. Schulz, A. Teleki, G. Beaucage, T. Narayanan, and S. E. Pratsinis. Nanostructure evolution: from aggregated to spherical SiO₂ particles made in diffusion flames. *European Journal of Inorganic Chemistry*, (6):911–918, 2008.
- R. S. Cant and E. Mastorakos. *An introduction to turbulent reacting flows*. Imperial College Press, 2007.
- H. Chang and P. Biswas. In situ light scattering dissymmetry measurements of the evolution of the aerosol size distribution in flames. *Journal of Colloid and Interface Science*, 153(1):157–166, 1992.

- J. Cho and M. Choi. Determination of number density, size and morphology of aggregates in coflow diffusion flames using light scattering and local sampling. *Journal of Aerosol Science*, 31(9):1077–1095, 2000.
- M. Choi, J. Cho, J. Lee, and H. W. Kim. Measurements of silica aggregate particle growth using light scattering and thermophoretic sampling in a coflow diffusion flame. *Journal of Nanoparticle Research*, 1(2):169–183, 1999.
- S.-L. Chung, Y.-C. Sheu, and M.-S. Tsai. Formation of SiO_2 , Al_2O_3 , and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ particles in a counterflow diffusion flame. *Journal of the American Ceramic Society*, 75(1):117–123, 1992.
- L. Cifuentes, J. Sellmann, I. Wlokas, and A. Kempf. Direct numerical simulations of nanoparticle formation in premixed and non-premixed flame-vortex interactions. *Physics of Fluids*, 32(9):093605, 2020a.
- L. Cifuentes, J. Sellmann, I. Wlokas, and A. Kempf. Direct numerical simulations of nanoparticle formation in premixed and non-premixed flame-vortex interactions. *Physics of Fluids*, 32(9):093605, 2020b.
- P. J. Colucci, F. A. Jaber, P. Givi, and S. B. Pope. Filtered density function for large eddy simulation of turbulent reacting flows. *Physics of Fluids*, 10(2):499–515, 1998.
- C. B. Da Silva, D. C. Lopes, and V. Raman. The effect of subgrid-scale models on the entrainment of a passive scalar in a turbulent planar jet. *Journal of Turbulence*, 16(4):342–366, 2015.
- S. Das and S. C. Garrick. The effects of turbulence on nanoparticle growth in turbulent reacting jets. *Physics of Fluids*, 22(10):103303, 2010.
- D. Dasgupta, P. Pal, R. Torelli, S. Som, N. Paulson, J. Libera, and M. Stan. Computational fluid dynamics modeling and analysis of silica nanoparticle synthesis in a flame spray pyrolysis reactor. *Combustion and Flame*, 236:111789, 2022.
- P. A. Davidson. *Turbulence An Introduction for Scientists and Engineers*. Oxford University Press, 2004.

- A. E. Davies, J. F. Keffer, and W. D. Baines. Spread of a heated plane turbulent jet. *The Physics of Fluids*, 18(7):770–775, 1975.
- M. A. Delichatsios and R. F. Probstein. Coagulation in turbulent flow: theory and experiment. *Journal of Colloid and Interface Science*, 51(3):394–405, 1975.
- R. C. Deo, J. Mi, and G. J. Nathan. The influence of reynolds number on a plane jet. *Physics of Fluids*, 20(7):075108, 2008.
- G. Di Veroli and S. Rigopoulos. A study of turbulence-chemistry interaction in reactive precipitation via a population balance-transported PDF method. In K. Hanjalić, Y. Nagano, and S. Jakirlić, editors, *Turbulence, Heat and Mass Transfer 6. Proceedings of the Sixth International Symposium on Turbulence, Heat and Mass Transfer, Rome, Italy*. Begell House, Inc., 2009.
- G. Di Veroli and S. Rigopoulos. Modeling of turbulent precipitation: A transported population balance-PDF method. *AIChE Journal*, 56(4):878–892, 2010.
- G. Y. Di Veroli and S. Rigopoulos. Modeling of aerosol formation in a turbulent jet with the transported population balance equation-probability density function approach. *Physics of Fluids*, 23(4):043305, 2011.
- C. Dopazo. Probability density function approach for a turbulent axisymmetric heated jet. centerline evolution. *The Physics of Fluids*, 18(4):397–404, 1975.
- C. Dopazo. Relaxation of initial probability density functions in the turbulent convection of scalar fields. *The Physics of Fluids*, 22(1):20–30, 1979.
- C. Dopazo and E. E. O’Brien. Functional formulation of nonisothermal turbulent reactive flows. *The Physics of Fluids*, 17(11):1968–1975, 1974.
- H.-S. Dou, B. C. Khoo, and H. M. Tsai. Determining the critical condition for turbulent transition in a full-developed annulus flow. *Journal of Petroleum Science and Engineering*, 73(1-2):41–47, 2010.
- R. Drake. A general mathematical survey of the coagulation equation. In G. M. Hidy and J. R. Brock, editors, *Topics in Current Aerosol Research (Part 2)*, pages 204–376. Pergamon Press, 1972.

- D. Drikakis, C. Fureby, F. F. Grinstein, and D. Youngs. Simulation of transition and turbulence decay in the Taylor–Green vortex. *Journal of Turbulence*, (8):1–12, 2007.
- Y. Drossinos and C. Housiadas. *Aerosol flows*. In *Multiphase flow handbook* (ed. C. T. Crowe), pp. 6-1–6-58. Boca Raton, FL: CRC Press, 2006.
- S. H. Ehrman. Effect of particle size on rate of coalescence of silica nanoparticles. *Journal of Colloid and Interface Science*, 213(1):258–261, 1999.
- S. H. Ehrman, S. K. Friedlander, and M. R. Zachariah. Characteristics of $\text{SiO}_2/\text{TiO}_2$ nanocomposite particles formed in a premixed flat flame. *Journal of Aerosol Science*, 29(5-6): 687–706, 1998.
- S. Elghobashi. An updated classification map of particle-laden turbulent flows. *Fluid Mechanics and its Applications*, 81:3–10, 2006.
- O. M. Feroughi, L. Deng, S. Kluge, T. Dreier, H. Wiggers, I. Wloka, and C. Schulz. Experimental and numerical study of a hmdso-seeded premixed laminar low-pressure flame for SiO_2 nanoparticle synthesis. *Proceedings of the Combustion Institute*, 36(1):1045–1053, 2017.
- K. A. Fichtorn and W. H. Weinberg. Theoretical foundations of dynamical monte carlo simulations. *The Journal of Chemical Physics*, 95(2):1090–1096, 1991.
- I. J. Ford. Statistical mechanics of nucleation: a review. *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science*, 218(8):883–899, 2004.
- R. O. Fox. *Computational models for turbulent reacting flows*. Cambridge University Press, 2003.
- J. Frenkel. Viscous flow of crystalline bodies under the action of surface tension. *J. phys.*, 9: 385, 1945.
- M. Frenklach. Method of moments with interpolative closure. *Chemical Engineering Science*, 57(12):2229–2239, 2002.
- M. Frenklach and S. J. Harris. Aerosol dynamics modeling using the method of moments. *Journal of Colloid and Interface Science*, 118(1):252–261, 1987.

- M. Frenklach, T. Bowman, G. Smith, and B. Gardiner. Mechanism of elementary chemical reaction developed by the gas research institute (GRI), adresse internet: [http://www. me.berkeley. edu/gri_mech](http://www.me.berkeley.edu/gri_mech). *GRI-Mech-2.11*, 1995a.
- M. Frenklach, H. Wang, M. Goldenberg, G. P. Smith, and D. M. Golden. GRI-MECH: An optimized detailed chemical reaction mechanism for methane combustion. topical report, september 1992-august 1995. Technical report, SRI International, Menlo Park, CA (United States), 1995b.
- S. K. Friedlander. *Smoke, Dust, and Haze: Fundamentals of Aerosol Dynamics*. Oxford University Press, 2nd edition, 2000.
- F. Gao and E. E. O'Brien. A large-eddy simulation scheme for turbulent reacting flows. *Physics of Fluids A*, 5(6):1282–1284, 1992.
- F. Gao and E. E. O'Brien. Erratum: “a large eddy simulation scheme for turbulent reacting flows” [phys. fluids a 5, 1282 (1993)]. *Physics of Fluids*, 6(4):1651, 1994.
- S. C. Garrick. Effects of turbulent fluctuations on nanoparticle coagulation in shear flows. *Aerosol Science & Technology*, 45(10):1272–1285, 2011.
- S. C. Garrick and M. Khakpour. The effects of differential diffusion on nanoparticle coagulation in temporal mixing layers. *Aerosol science and technology*, 38(8):851–860, 2004.
- S. C. Garrick, K. E. J. Lehtinen, and M. R. Zachariah. Nanoparticle coagulation via a navier–stokes/nodal methodology: Evolution of the particle field. *Journal of Aerosol Science*, 37(5): 555–576, 2006.
- F. Gelbard, Y. Tambour, and J. H. Seinfeld. Sectional representations for simulating aerosol dynamics. *Journal of Colloid and Interface Science*, 76(2):541–556, 1980.
- D. T. Gillespie. An exact method for numerically simulating the stochastic coalescence process in a cloud. *Journal of Atmospheric Sciences*, 32(10):1977–1989, 1975.
- S. L. Girshick and C. P. Chiu. Homogeneous nucleation of particles from the vapor phase in thermal plasma synthesis. *Plasma Chemistry and Plasma Processing*, 9(3):355–369, 1989.
- S. Goto and J. C. Vassilicos. Local equilibrium hypothesis and taylor’s dissipation law. *Fluid Dynamics Research*, 48(2):021402, 2016.

- E. Goudeli and S. E. Pratsinis. Gas-phase manufacturing of nanoparticles: Molecular dynamics and mesoscale simulations. *Particulate Science and Technology*, 34(4):483–493, 2016.
- E. Goudeli, M. L. Eggersdorfer, and S. E. Pratsinis. Aggregate characteristics accounting for the evolving fractal-like structure during coagulation and sintering. *Journal of Aerosol Science*, 89:58–68, 2015.
- P. R. Griffiths and J. A. De Haseth. *Fourier transform infrared spectrometry*. John Wiley & Sons, 2007.
- A. J. Gröhn, B. Buesser, J. K. Jokiniemi, and S. E. Pratsinis. Design of turbulent flame aerosol reactors by mixing-limited fluid dynamics. *Industrial & Engineering Chemistry Research*, 50(6):3159–3168, 2011.
- A. J. Gröhn, S. E. Pratsinis, and K. Wegner. Fluid-particle dynamics during combustion spray aerosol synthesis of ZrO_2 . *Chemical Engineering Journal*, 191:491–502, 2012.
- W. L. Grosshandler. Radcal: a narrow band model for radiation. *Calculations in a Combustion Environment, NIST Technical Note*, 1402, 1993.
- E. Gutmark and I. Wygnanski. The planar turbulent jet. *Journal of Fluid Mechanics*, 73(3):465–495, 1976.
- W. R. Heinson, C. M. Sorensen, and A. Chakrabarti. Does shape anisotropy control the fractal dimension in diffusion-limited cluster-cluster aggregation? *Aerosol Science & Technology*, 44(12):i–iv, 2010.
- J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird. Molecular theory of gases and liquids. *Physics today*, 8(3):17, 1955.
- S. S. Iyer, T. A. Litzinger, S. Y. Lee, and R. J. Santoro. Determination of soot scattering coefficient from extinction and three-angle scattering in a laminar diffusion flame. *Combustion and Flame*, 149(1-2):206–216, 2007.
- F. A. Jaberi, P. J. Colucci, S. James, P. Givi, and S. B. Pope. Filtered mass density function for large-eddy simulation of turbulent reacting flows. *Journal of Fluid Mechanics*, 401:85–121, 1999.

- H. D. Jang. Experimental study of synthesis of silica nanoparticles by a bench-scale diffusion flame reactor. *Powder Technology*, 119(2-3):102–108, 2001.
- H. Jasak, H. G. Weller, and A. D. Gosman. High resolution NVD differencing scheme for arbitrarily unstructured meshes. *International Journal for Numerical Methods in Fluids*, 31(2):431–449, 1999.
- P. E. Jenkins and V. W. Goldschmidt. Mean temperature and velocity in a plane turbulent jet. *Journal of Fluids Engineering, Transactions of the ASME*, 95(4):581–584, 1973.
- Y. Ji, H. Y. Sohn, H. D. Jang, B. Wan, and T. A. Ring. Computational fluid dynamic modeling of a flame reaction process for silica nanopowder synthesis from tetraethylorthosilicate. *Journal of the American Ceramic Society*, 90(12):3838–3845, 2007.
- T. Johannessen, S. E. Pratsinis, and H. Livbjerg. Computational fluid-particle dynamics for the flame synthesis of alumina particles. *Chemical Engineering Science*, 55(1):177–191, 2000.
- T. Johannessen, s. E. Pratsinis, and H. Livbjerg. Computational analysis of coagulation and coalescence in the flame synthesis of titania particles. *Powder Technology*, 118(3):242–250, 2001.
- W. P. Jones and S. Navarro-Martinez. Large eddy simulation of autoignition with a subgrid probability density function method. *Combustion and Flame*, 150(3):170–187, 2007.
- W. P. Jones and V. N. Prasad. Large eddy simulation of the sandia flame series (D–F) using the eulerian stochastic field method. *Combustion and Flame*, 157(9):1621–1636, 2010.
- W. P. Jones, F. di Mare, and A. J. Marquis. Les-boffin: users guide. *Imperial College London, Department of Mechanical Engineering, London*, 2002.
- W. P. Jones, A. J. Marquis, and F. Wang. Large eddy simulation of a premixed propane turbulent bluff body flame using the eulerian stochastic field method. *Fuel*, 140:514–525, 2015.
- Z. Junzong, Q. Haiying, and W. Jinsheng. Nanoparticle dispersion and coagulation in a turbulent round jet. *International Journal of Multiphase Flow*, 54:1–9, 2013.

- H. K. Kammler, S. E. Pratsinis, P. W. Morrison Jr, and B. Hemmerling. Flame temperature measurements during electrically assisted aerosol synthesis of nanoparticles. *Combustion and Flame*, 128(4):369–381, 2002.
- H. K. Kammler, G. Beaucage, D. J. Kohls, N. Agashe, and J. Ilavsky. Monitoring simultaneously the growth of nanoparticles and aggregates by in situ ultra-small-angle x-ray scattering. *Journal of Applied Physics*, 97(5):054309, 2005.
- I. M. Kennedy and S. J. Harris. Enhancement of silica aerosol coagulation by van der waals forces. *Aerosol Science & Technology*, 12(4):869–875, 1990.
- H. J. Kim, J. I. Jeong, Y. Park, Y. Yoon, and M. Choi. Modeling of generation and growth of non-spherical nanoparticles in a co-flow flame. *Journal of Nanoparticle Research*, 5(3-4): 237–246, 2003.
- H. W. Kim and M. Choi. In situ line measurement of mean aggregate size and fractal dimension along the flame axis by planar laser light scattering. *Journal of Aerosol Science*, 34(12):1633–1645, 2003.
- K. S. Kim and S. E. Pratsinis. Manufacture of optical waveguide preforms by modified chemical vapor deposition. *AIChE journal*, 34(6):912–921, 1988.
- K. S. Kim and S. E. Pratsinis. Modeling and analysis of modified chemical vapor deposition of optical fiber preforms. *Chemical Engineering Science*, 44(11):2475–2482, 1989.
- M. J. Kirchhof, H. Förster, H. J. Schmid, and W. Peukert. Sintering kinetics and mechanism of vitreous nanoparticles. *Journal of Aerosol Science*, 45:26–39, 2012.
- M. Klein, A. Sadiki, and J. Janicka. A digital filter based generation of inflow data for spatially developing direct numerical or large eddy simulations. *Journal of Computational Physics*, 186(2):652–665, 2003a.
- M. Klein, A. Sadiki, and J. Janicka. Investigation of the influence of the reynolds number on a plane jet using direct numerical simulation. *International Journal of Heat and Fluid Flow*, 24(6):785–794, 2003b.
- P. E. Kloeden and E. Platen. Stochastic differential equations. In *Numerical solution of stochastic differential equations*, pages 103–160. Springer, 1992.

- W. Koch and S. K. Friedlander. The effect of particle coalescence on the surface area of a coagulating aerosol. *Journal of Colloid and Interface Science*, 140(2):419–427, 1990.
- F. E. Kruis, K. A. Kusters, S. E. Pratsinis, and B. Scarlett. A simple model for the evolution of the characteristics of aggregate particles undergoing coagulation and sintering. *Aerosol Science & Technology*, 19(4):514–526, 1993.
- M. Kulmala, H. Vehkamäki, T. Petäjä, M. Dal Maso, A. Lauri, V.-M. Kerminen, W. Birmili, and P. H. McMurry. Formation and growth rates of ultrafine atmospheric particles: a review of observations. *Journal of Aerosol Science*, 35(2):143–176, 2004.
- J. D. Landgrebe and S. E. Pratsinis. A discrete-sectional model for particulate production by gas-phase chemical reaction and aerosol coagulation in the free-molecular regime. *Journal of Colloid and Interface Science*, 139(1):63–86, 1990.
- C. Le Ribault, S. Sarkar, and S. A. Stanley. Large eddy simulation of a plane jet. *Physics of Fluids*, 11(10):3069–3083, 1999.
- B. W. Lee, S. Oh, and M. Choi. Simulation of growth of nonspherical silica nanoparticles in a premixed flat flame. *Aerosol Science & Technology*, 35(6):978–989, 2001.
- J. Lee. Estimation of emission properties for silica particles using thermal radiation spectroscopy. *Applied Optics*, 50(22):4262–4267, 2011.
- V. G. Levich. *Physicochemical Hydrodynamics*. Prentice-Hall, Inc., 1962.
- L. M. Levin and Y. S. Sedunov. Gravitational coagulation of charged cloud drops in turbulent flow. *Pure and Applied Geophysics*, 64(1):185–196, 1966.
- L. M. Levin and Y. S. Sedunov. The theoretical model of the drop spectrum formation process in clouds. *Pure and Applied Geophysics*, 69(1):320–335, 1968.
- C. S. Lindberg, M. Y. Manuputty, J. Akroyd, and M. Kraft. A two-step simulation methodology for modelling stagnation flame synthesised aggregate nanoparticles. *Combustion and Flame*, 202:143–153, 2019.
- A. Liu and S. Rigopoulos. A conservative method for numerical solution of the population balance equation, and application to soot formation. *Combustion and Flame*, 205:506–521, 2019.

- D. L. Marchisio and R. O. Fox. Solution of population balance equations using the direct quadrature method of moments. *Journal of Aerosol Science*, 36(1):43–73, 2005.
- S. Mathur and S. C. Saxena. Methods of calculating thermal conductivity of binary mixtures involving polyatomic gases. *Applied Scientific Research*, 17(2):155–168, 1967.
- F. Meierhofer and U. Fritsching. Synthesis of metal oxide nanoparticles in flame sprays: review on process technology, modeling, and diagnostics. *Energy & Fuels*, 35(7):5495–5537, 2021.
- E. Michaelides, C. T. Crowe, and J. D. Schwarzkopf. *Multiphase flow handbook*. CRC Press, 2016.
- S. E. Miller and S. C. Garrick. Nanoparticle coagulation in a planar jet. *Aerosol Science & Technology*, 38(1):79–89, 2004.
- M. F. Modest. *Radiative Heat Transfer*. Academic Press: Cambridge MA, USA, 2nd edition, 2003.
- P. Moin and K. Mahesh. Direct numerical simulation: a tool in turbulence research. *Annual Review of Fluid Mechanics*, 30:539–578, 1998.
- P. W. Morrison Jr, R. Raghavan, A. J. Timpone, C. P. Artelt, and S. E. Pratsinis. In situ fourier transform infrared characterization of the effect of electrical fields on the flame synthesis of TiO_2 particles. *Chemistry of Materials*, 9(12):2702–2708, 1997.
- R. Mueller, H. K. Kammler, S. E. Pratsinis, A. Vital, G. Beaucage, and P. Bartscher. Non-agglomerated dry silica nanoparticles. *Powder Technology*, 140(1):40–48, 2004.
- H. Mühlenweg, A. Gutsch, A. Schild, and S. E. Pratsinis. Process simulation of gas-to-particle-synthesis via population balances: Investigation of three models. *Chemical Engineering Science*, 57(12):2305–2322, 2002.
- R. Mustata, L. Valiño, C. Jiménez, W. P. Jones, and S. Bondi. A probability density function eulerian monte carlo field method for large eddy simulations: Application to a turbulent piloted methane/air diffusion flame (sandia d). *Combustion and Flame*, 145(1-2):88–104, 2006.

- K. Netzell, H. Lehtiniemi, and F. Mauss. Calculating the soot particle size distribution function in turbulent diffusion flames using a sectional method. *Proceedings of the Combustion Institute*, 31(1):667–674, 2007.
- G. Neuber, C. E. Garcia, A. Kronenburg, B. A. Williams, F. Beyrau, O. T. Stein, and M. J. Cleary. Joint experimental and numerical study of silica particulate synthesis in a turbulent reacting jet. *Proceedings of the Combustion Institute*, 37(1):1213–1220, 2019.
- T. T. Nguyen, F. Laurent, R. O. Fox, and M. Massot. Solution of population balance equations in applications with fine particles: mathematical modeling and numerical schemes. *Journal of Computational Physics*, 325:129–156, 2016.
- E. E. O’Brien. The probability density function (pdf) approach to reacting turbulent flows. *Turbulent Reacting Flows*, pages 185–218, 1980.
- M. Olin, T. Rönkkö, and M. Dal Maso. CFD modeling of a vehicle exhaust laboratory sampling system: sulfur-driven nucleation and growth in diluting diesel exhaust. *Atmospheric Chemistry & Physics*, 15(9):5305–5323, 2015.
- M. Olivas-Martinez, H. Y. Sohn, H. D. Jang, and K.-I. Rhee. Computational fluid dynamic modeling of the flame spray pyrolysis process for silica nanopowder synthesis. *Journal of Nanoparticle Research*, 17(7):324, 2015.
- D. O’Sullivan and S. Rigopoulos. A conservative finite volume method for the population balance equation with aggregation, fragmentation, nucleation and growth. *Chemical Engineering Science*, 263:117925, 2022.
- H. K. Park and K. Y. Park. Control of particle morphology and size in vapor-phase synthesis of titania, silica and alumina nanoparticles. *KONA Powder and Particle Journal*, 32:85–101, 2015.
- I. Pasmazoglou, A. M. Kempf, and S. Navarro-Martinez. Large eddy simulation of particle aggregation in turbulent jets. *Journal of Aerosol Science*, 111:1–17, 2017.
- N. Peters. *Turbulent combustion*. Cambridge University Press, 2000.
- U. Piomelli and J. Liu. Large-eddy simulation of rotating channel flows using a localized dynamic model. *Physics of Fluids*, 7(4):839–848, 1995.

- H. Pitsch. Large-eddy simulation of turbulent combustion. *Annual Review of Fluid Mechanics*, 38:453–482, 2006.
- T. Poinso and D. Veynante. *Theoretical and numerical combustion*. RT Edwards, Inc., 2005.
- S. B. Pope. PDF methods for turbulent reactive flows. *Progress in Energy and Combustion Science*, 11(2):119–192, 1985.
- S. B. Pope. *Turbulent Flows*. Cambridge University Press, 2000.
- V. N. Prasad. *Large eddy simulation of partially premixed turbulent combustion*. PhD thesis, Imperial College London (University of London), 2011.
- S. E. Pratsinis. Simultaneous nucleation, condensation, and coagulation in aerosol reactors. *Journal of Colloid and Interface Science*, 124(2):416–427, 1988.
- S. E. Pratsinis. History of manufacture of fine particles in high-temperature aerosol reactors. *Aerosol science and technology: History and reviews*, pages 475–507, 2011.
- S. E. Pratsinis and K.-S. Kim. Particle coagulation, diffusion and thermophoresis in laminar tube flows. *Journal of Aerosol Science*, 20(1):101–111, 1989.
- N. Rajaratnam. *Turbulent jets*. Elsevier, 1976.
- V. Raman and R. O. Fox. Modeling of fine-particle formation in turbulent flames. *Annual Review of Fluid Mechanics*, 48:159–190, 2016.
- B. R. Ramaprian and M. S. Chandrasekhara. LDA measurements in plane turbulent jets. *Journal of Fluids Engineering, Transactions of the ASME*, 107(2):264–271, 1985.
- D. Ramkrishna. Analysis of population balance—iv: The precise connection between monte carlo simulation and population balances. *Chemical Engineering Science*, 36(7):1203–1209, 1981.
- W. C. Reade and L. R. Collins. A numerical study of the particle size distribution of an aerosol undergoing turbulent coagulation. *Journal of Fluid Mechanics*, 415:45–64, 2000.
- S. Rigopoulos. PDF method for population balance in turbulent reactive flow. *Chemical Engineering Science*, 62(23):6865–6878, 2007.

- S. Rigopoulos. Population balance modelling of polydispersed particles in reactive flows. *Progress in Energy and Combustion Science*, 36(4):412–443, 2010.
- S. Rigopoulos. Modelling of soot aerosol dynamics in turbulent flow. *Flow, Turbulence and Combustion*, 103(3):565–604, 2019.
- A. Rittler, L. Deng, I. Wlokas, and A. M. Kempf. Large eddy simulations of nanoparticle synthesis from flame spray pyrolysis. *Proceedings of the Combustion Institute*, 36(1):1077–1087, 2017.
- P. Rodrigues, B. Franzelli, R. Vicquelin, O. Gicquel, and N. Darabiha. Coupling an LES approach and a soot sectional model for the study of sooting turbulent non-premixed flames. *Combustion and Flame*, 190:477–499, 2018.
- S. N. Rogak. Modeling small cluster deposition on the primary particles of aerosol agglomerates. *Aerosol Science and Technology*, 26(2):127–140, 1997.
- D. E. Rosner. Flame synthesis of valuable nanoparticles: Recent progress/current needs in areas of rate laws, population dynamics, and characterization. *Industrial & Engineering Chemistry research*, 44(16):6045–6055, 2005.
- P. Roth. Particle synthesis in flames. *Proceedings of the Combustion Institute*, 31(2):1773–1788, 2007.
- P. G. Saffman and J. S. Turner. On the collision of drops in turbulent clouds. *Journal of Fluid Mechanics*, 1(1):16–30, 1956.
- J. H. Scheckman, P. H. McMurry, and S. E. Pratsinis. Rapid characterization of agglomerate aerosols by in situ mass- mobility measurements. *Langmuir*, 25(14):8248–8254, 2009.
- A. Schild, A. Gutsch, H. Mühlenweg, and S. E. Pratsinis. Simulation of nanoparticle production in premixed aerosol flow reactors by interfacing fluid mechanics and particle dynamics. *Journal of Nanoparticle Research*, 1(2):305–315, 1999.
- F. Schneider, S. Suleiman, J. Menser, E. Borukhovich, I. Wlokas, A. Kempf, H. Wiggers, and C. Schulz. Spraysyn—a standardized burner configuration for nanoparticle synthesis in spray flames. *Review of Scientific Instruments*, 90(8):5090232, 2019.

- W. T. Scott. Poisson statistics in distributions of coalescing droplets. *Journal of the Atmospheric Sciences*, 24(2):221–225, 1967.
- T. Seto, A. Hirota, T. Fujimoto, M. Shimada, and K. Okuyama. Sintering of polydisperse nanometer-sized agglomerates. *Aerosol Science & Technology*, 27(3):422–438, 1997.
- N. Settumba and S. C. Garrick. Direct numerical simulation of nanoparticle coagulation in a temporal mixing layer via a moment method. *Journal of Aerosol Science*, 34(2):149–167, 2003.
- F. Sewerin and S. Rigopoulos. An LES-PBE-PDF approach for modeling particle formation in turbulent reacting flows. *Physics of Fluids*, 29(10):105105, 2017.
- F. Sewerin and S. Rigopoulos. An LES-PBE-PDF approach for predicting the soot particle size distribution in turbulent flames. *Combustion and Flame*, 189:62–76, 2018.
- F. Sewerin and S. Rigopoulos. Algorithmic aspects of the LES-PBE-PDF method for modeling soot particle size distributions in turbulent flames. *Combustion Science and Technology*, 191(5–6):766–796, 2019.
- J. V. Shebalin and S. L. Woodruff. Kolmogorov flow in three dimensions. *Physics of Fluids*, 9(1):164–170, 1997.
- S. Shekar, M. Sander, R. C. Riehl, A. J. Smith, A. Braumann, and M. Kraft. Modelling the flame synthesis of silica nanoparticles from tetraethoxysilane. *Chemical Engineering Science*, 70:54–66, 2012a.
- S. Shekar, A. J. Smith, W. J. Menz, M. Sander, and M. Kraft. A multidimensional population balance model to describe the aerosol synthesis of silica nanoparticles. *Journal of Aerosol Science*, 44:83–98, 2012b.
- J. Smagorinsky. General circulation experiments with the primitive equations: I. the basic experiment. *Monthly Weather Review*, 91(3):99–164, 1963.
- M. D. Smooke, M. B. Long, B. C. Connelly, M. B. Colket, and R. J. Hall. Soot formation in laminar diffusion flames. *Combustion and Flame*, 143(4):613–628, 2005.
- S. A. Stanley and S. Sarkar. Influence of nozzle conditions and discrete forcing on turbulent planar jets. *AIAA journal*, 38(9):1615–1623, 2000.

- S. A. Stanley, S. Sarkar, and J. P. Mellado González. A study of the flow-field evolution and mixing in a planar turbulent jet using direct numerical simulation. *Journal of Fluid Mechanics*, 450:377–407, 2002.
- B. Sun and S. Rigopoulos. Modelling of soot formation and aggregation in turbulent flows with the LES-PBE-PDF approach and a conservative sectional method. *Combustion and Flame*, 242:112152, 2022.
- B. Sun, S. Rigopoulos, and A. Liu. Modelling of soot coalescence and aggregation with a two-population balance equation model and a conservative finite volume method. *Combustion and Flame*, 229:111382, 2021.
- Y. Sung, V. Raman, and R. O. Fox. Large-eddy-simulation-based multiscale modeling of TiO_2 nanoparticle synthesis in a turbulent flame reactor using detailed nucleation chemistry. *Chemical Engineering Science*, 66(19):4370–4381, 2011.
- Y. Sung, V. Raman, H. Koo, M. Mehta, and R. O. Fox. Large-eddy simulation modeling of turbulent flame synthesis of titania nanoparticles using a bivariate particle description. *AIChE Journal*, 60(2):459–472, 2014.
- P. R. Suresh, K. Srinivasan, T. Sundararajan, and S. K. Das. Reynolds number dependence of plane jet development in the transitional regime. *Physics of Fluids*, 20(4):044105, 2008.
- M. Sztucki, T. Narayanan, and G. Beaucage. In situ study of aggregation of soot particles in an acetylene flame by small-angle x-ray scattering. *Journal of Applied Physics*, 101(11):114304, 2007.
- H. Y. Tang, S. Rigopoulos, and G. Papadakis. A methodology for coupling DNS and discretised population balance for modelling turbulent precipitation. *International Journal of Heat and Fluid Flow*, 86:108689, 2020.
- G. I. Taylor. Statistical theory of turbulence. *Proc. R. Soc. Lond. A*, 23(2):421–444, 1935.
- F. O. Thomas and H. C. Chu. An experimental investigation of the transition of a planar jet: Subharmonic suppression and upstream feedback. *Physics of Fluids A*, 1(9):1566–1587, 1989.
- S. Tsantilis and S. E. Pratsinis. Evolution of primary and aggregate particle-size distributions by coagulation and sintering. *AIChE Journal*, 46(2):407–415, 2000.

- S. Tsantilis and S. E. Pratsinis. Narrowing the size distribution of aerosol-made titania by surface growth and coagulation. *Journal of Aerosol Science*, 35(3):405–420, 2004.
- S. Tsantilis, S. E. Pratsinis, and V. Haas. Simulation of synthesis of palladium nanoparticles in a jet aerosol flow condenser. *Journal of Aerosol Science*, 30(6):785–803, 1999.
- S. Tsantilis, H. Briesen, and S. E. Pratsinis. Sintering time for silica particle growth. *Aerosol Science & Technology*, 34(3):237–246, 2001.
- S. Tsantilis, H. K. Kammler, and S. E. Pratsinis. Population balance modeling of flame synthesis of titania nanoparticles. *Chemical Engineering Science*, 57(12):2139–2156, 2002.
- G. D. Ulrich. Theory of particle formation and growth in oxide synthesis flames. *Combustion Science and Technology*, 4(1):47–57, 1971.
- G. D. Ulrich and J. W. Rieh. Aggregation and growth of submicron oxide particles in flames. *Journal of Colloid and Interface Science*, 87(1):257–265, 1982.
- L. Valiño. A field monte carlo formulation for calculating the probability density function of a single scalar in a turbulent flow. *Flow, Turbulence and Combustion*, 60(2):157–172, 1998.
- W. M. Van Rees, A. Leonard, D. I. Pullin, and P. Koumoutsakos. A comparison of vortex and pseudo-spectral methods for the simulation of periodic vortical flows at high reynolds numbers. *Journal of Computational Physics*, 230(8):2794–2805, 2011.
- L. van Veen and S. Goto. Sub critical transition to turbulence in three-dimensional kolmogorov flow. *Fluid Dynamics Research*, 48(6):061425, 2016.
- S. Vemury and S. E. Pratsinis. Self-preserving size distributions of agglomerates. *Journal of Aerosol Science*, 26(2):175–185, 1995.
- S. Vemury, K. A. Kusters, and S. E. Pratsinis. Time-lag for attainment of the self-preserving particle size distribution by coagulation. *Journal of Colloid and Interface Science*, 165(1):53–59, 1994.
- S. Vo, A. Kronenburg, O. T. Stein, and M. J. Cleary. Multiple mapping conditioning for silica nanoparticle nucleation in turbulent flows. *Proceedings of the Combustion Institute*, 36(1):1089–1097, 2017.

- L. P. Wang, A. S. Wexler, and Y. Zhou. On the collision rate of small particles in isotropic turbulence. i. zero-inertia case. *Physics of Fluids*, 10(1):266–276, 1998.
- M. Warshaw. Cloud droplet coalescence: Statistical foundations and a one-dimensional sedimentation model. *Journal of the Atmospheric Sciences*, 24(3):278–286, 1967.
- T. Watanabe, Y. Sakai, K. Nagata, Y. Ito, and T. Hayase. Vortex stretching and compression near the turbulent/non-turbulent interface in a planar jet. *Journal of Fluid Mechanics*, 758:754–785, 2014.
- K. Wegner and S. E. Pratsinis. Nozzle-quenching process for controlled flame synthesis of titania nanoparticles. *AIChE Journal*, 49(7):1667–1675, 2003a.
- K. Wegner and S. E. Pratsinis. Scale-up of nanoparticle synthesis in diffusion flame reactors. *Chemical Engineering Science*, 58(20):4581–4589, 2003b.
- E. R. Whitby and P. H. McMurry. Modal aerosol dynamics modeling. *Aerosol Science & Technology*, 27(6):673–688, 1997.
- C. R. Wilke. A viscosity equation for gas mixtures. *The Journal of Chemical Physics*, 18(4):517–519, 1950.
- K. Willeke. Temperature dependence of particle slip in a gaseous medium. *Journal of Aerosol Science*, 7(5):381–387, 1976.
- M. M. R. Williams and S. K. Loyalka. *Aerosol Science - Theory and Practice: With Special Applications to the Nuclear Industry*. Pergamon Press, Oxford, 1991.
- P. Wollny, S. Angel, H. Wiggers, A. M. Kempf, and I. Wlokas. Multiscale simulation of the formation of platinum-particles on alumina nanoparticles in a spray flame experiment. *Fluids*, 5(4):201, 2020.
- D. Xiao and G. Papadakis. Nonlinear optimal control of transition due to a pair of vortical perturbations using a receding horizon approach. *Journal of Fluid Mechanics*, 861:524–555, 2019.
- Y. Xiong and S. E. Pratsinis. Gas phase production of particles in reactive turbulent flows. *Journal of Aerosol Science*, 22(5):637–655, 1991.

- Y. Xiong and S. E. Pratsinis. Formation of agglomerate particles by coagulation and sintering—part i. a two-dimensional solution of the population balance equation. *Journal of Aerosol Science*, 24(3):283–300, 1993.
- Y. Yang and D. I. Pullin. Evolution of vortex-surface fields in viscous taylor–green and kida–pelz flows. *Journal of Fluid Mechanics*, 685:146–164, 2011.
- M. Yu, J. Lin, and T. Chan. Numerical simulation of nanoparticle synthesis in diffusion flame reactor. *Powder Technology*, 181(1):9–20, 2008a.
- M.-Z. Yu, J.-Z. Lin, and T.-L. Chan. Effect of precursor loading on non-spherical TiO_2 nanoparticle synthesis in a diffusion flame reactor. *Chemical Engineering Science*, 63(9):2317–2329, 2008b.
- M. R. Zachariah, D. Chin, H. G. Semerjian, and J. L. Katz. Silica particle synthesis in a counterflow diffusion flame reactor. *Combustion and Flame*, 78(3-4):287–298, 1989.