Radial dependence of TiO$_2$ nanoparticles synthesised in jet-wall stagnation flames

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released: April 28, 2021

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Keywords: jet-wall stagnation flame, spherical particle model, detailed particle model, 2D simulations, TiO$_2$ nanoparticles
Abstract

The formation of titanium dioxide (TiO$_2$) nanoparticles from titanium tetraisopropoxide (TTIP) in premixed, jet-wall stagnation flames was simulated to investigate the variation of the particle properties as a function of deposition radius. Two different TTIP loadings (280 and 560 ppm) were studied in two flames: a lean flame (equivalence ratio, $\phi = 0.35$) and a stoichiometric flame ($\phi = 1.0$). First, the growth of particles was described using a spherical particle model that was fully coupled to the conservation equations of chemically reacting flow and solved in 2D using the finite volume method. Second, particle trajectories were extracted from the 2D simulations and post-processed using a hybrid particle-number/detailed particle model solved using a stochastic numerical method. In the 2D simulations, the particles were predicted to have mean diameters in the range 3–10 nm, which is consistent with, but slightly less than experimental values observed in the literature. Off-centreline particle trajectories experienced longer residence times at higher temperatures downstream of the flame front. Two particle size distribution (PSD) shapes were observed. In the lean flame, a bimodal PSD was observed due to the high rates of inception and surface growth. In contrast, the stoichiometric flame was dominated by coagulation and the particles quickly attained a self-preserving size distribution. The PSDs were found to be different beyond a deposition radius of approximately one and a half times the nozzle radius due to a small degree of aggregation; this may impact the synthesis of nanoparticles using jet-wall stagnation flames for novel applications.

Highlights

- TiO$_2$ nanoparticles synthesis in jet-wall stagnation flames were studied in 2D.
- A two-step method resolved TiO$_2$ with two models: spherical and detailed.
- Particles deposited at $r \leq 1$ cm have similar properties and size distributions.
- The degree of aggregation was responsible for changes in the size distributions.
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1 Introduction

Production of inorganic materials by flame synthesis is an important process because it provides a simple, continuous and scalable route for particle production. During flame synthesis of nanoparticles, gas is doped with liquid or vapour precursors that are oxidised to produce solid materials [39]. One such material, for example, is titania (TiO$_2$). Current experimental work investigating the flame synthesis of TiO$_2$ aims to produce novel materials for a wide array of applications, including the deposition of catalytic surfaces to serve as dye sensitised solar cells [57, 58], photocatalysts [12, 80] and antimicrobial coatings [19]. The flames can be turbulent, such as in flame spray pyrolysis [16, 69] or industrial reactors [3, 9, 11], or laminar, such as jet-wall stagnation flames [44, 71].

Premixed laminar jet-wall stagnation flames have several advantages when employed to study the fundamental physics of nanoparticle synthesis. First, they are a stable laminar system with a well-defined stagnation plane. This makes them easy to model and to study experimentally. Second, they provide short residence times and high temperature gradients between the flame and a cooled stagnation surface. This facilitates the thermophoretic deposition and the production of small particles. Third, changing experimental parameters has been shown to produce nanoparticles with different properties, such as average particle size [43], crystalline phase [43, 44, 47], and oxygen-vacancies [81]. This provides a simple, repeatable route to produce particles with specific properties.

The temperature-residence time profile is a key variable and a widely researched topic [1, 36, 68, 73, 77]. Ulrich [73] discussed that the final particle size was dependent on temperature and residence time when proposing Brownian motion to drive particle growth. In addition to particle size, other properties are known to be affected by the temperature-residence time profile. The titania phase transformation from anatase to rutile is dependent on the temperature-residence time [1, 36, 47]. The crystal phase and particle size were shown to be sensitive to the temperature-residence times in a lab-scale swirl-stabilised tubular burner [77].

The temperature-residence time profile along the centreline of premixed laminar jet-wall stagnation flames is able to be controlled. First, the premixed gas can be varied by changing its composition (e.g. fuel; equivalence ratio, $\phi$; and dilution) or total flow rate [47]. Second, the ability to cool the stagnation surface [46, 71] drives thermophoretic deposition, affecting the residence time. The stagnation surface can be air-cooled or water-cooled. In the air-cooled systems, the stagnation surface is rotated such that it is cooled by forced convection. This system is known as a flame stabilised on a rotating surface (FSRS) system [44, 53, 71, 80]. Alternatively, a water-cooled stagnation surface with sampling orifices can be used [20, 46].

Studies that model nanoparticle synthesis in premixed laminar jet-wall stagnation flames [37, 40, 41, 45, 47, 53, 71] frequently describe the flame environment using a pseudo 1D model [35]. The 1D model uses a stream function to describe the flow, resulting in a formulation that is dependent on the axial distance alone. This reduces the overall computational effort required to acquire a description of the flame. It has been shown that the 1D model can accurately describing the flame properties for wide nozzle diameters [7, 34] when the boundary conditions are properly described [5, 6].
Although the 1D model provides a computationally efficient approach to describing jet-wall stagnation flames, it has its limitations. First, the model only resolves centreline information, leaving radial information unresolved. Second, the radial pressure gradient is assumed to be constant, which may not always be valid [13]. Lastly, some important physics, like buoyancy [63, 84], radial diffusion of light species (e.g. H₂) [63], and the heat transfer with shielding co-flows [72], cannot be resolved.

When premixed, jet-wall stagnation flames are used to produce new materials, nanoparticles are collected from a finite area under the flame. It is important to assess how ‘uniform’ these nanoparticles are. The one-dimensional model is unable to describe particles at different deposition radii. In order to simulate the off-centreline particle growth, it is necessary to solve the full set of Navier-Stokes equations. Three dimensional simulations of jet-wall stagnation flames have shown that the total residence time and deposition temperature vary along different particle trajectories depending on their starting inlet radius [32]. How this impacts nanoparticle growth is an open question.

The simulation of the evolution of nanoparticles requires the solution of a population balance equation (PBE). This requires three components. First, a particle model (i.e. a mathematical description of the particles) is required. This can be univariate (e.g. particle size [45, 65]), bivariate (e.g. surface area-volume [82]), or a more multivariate description (e.g. primary-aggregate [42, 66]). The additional structural information offered by multivariate models is needed to describe the growth of polydisperse particles when coagulation and sintering are competitive [54]. Second, models are required to capture the important physics of the system, such as precursor chemistry, coagulation, and surface growth. Third, a numerical method is needed to solve the PBE. Different families of methods can be used depending on the complexity of the particle model, including moment [22, 23, 48, 52, 56], sectional [31, 38], and Monte Carlo methods [2, 60, 83]. Monte Carlo methods are required to keep the problem computationally tractable when the dimensionality of the particle model is large.

The purpose of this paper is to explore the properties of TiO₂ particles synthesised along different radial trajectories in a laminar, jet-wall stagnation flame. A spherical particle model was fully coupled to the governing reacting flow equations and solved in 2D. Particle trajectories extracted from the 2D simulations were post-processed with a detailed particle model to resolve particle properties including size distributions, primary particle sizes, and particle morphology. The paper is structured as follows: Section 2 provides a description of the jet-wall stagnation flame and simulated boundary conditions. Sections 3 present the models and numerical methods used to describe the jet-wall stagnation flame and evolution of nanoparticle growth. Section 4 presents the results and discussion of the flame and particle simulations. The conclusions are presented in Section 5.

## 2 Burner geometry and boundary conditions

Figure 1 presents the premixed, jet-wall stagnation burner that was simulated in this work. The setup is similar to those used in previous studies of the synthesis of titania from titanium(IV) tetraisopropoxide (TTIP) [45–47, 85] as well as in experiments measuring 2D temperature fields by thin-filament pyrometry [20].
Figure 1: Burner geometry and computational domain (red) for the premixed, jet-wall stagnation flame modelled in this work.

The burner consists of a nozzle with two concentric outlets and a water-cooled stagnation surface. The central outlet consists of an aerodynamic nozzle used to accelerate the gases, while the annular outlet provides a sheath flow of nitrogen to separate the premixed gases from the ambient atmosphere. The burner is open to the atmosphere and at ambient pressure (101.325 kPa). The burner and stagnation surface are separated by 14 mm, corresponding to a unity ratio between nozzle-surface separation distance and nozzle diameter as is frequently used when characterising jet-wall stagnation experiments [5].

The gases used for the simulations in this work were mixtures of ethylene-oxygen-argon at two different equivalence ratios: a lean flame with an equivalence ratio of $\phi = 0.35$ and a stoichiometric flame with an equivalence ratio of $\phi = 1.0$. For the purpose of this study, the two equivalence ratios provide two different backgrounds for TiO$_2$ synthesis. A premixed gas flow rate of 28 slpm was used for both equivalence ratios. The sheath flow rate of 13.6 slpm of nitrogen was kept constant for all conditions studied. Two TTIP loadings were studied in this work: 280 and 560 ppm of TTIP. Argon was assumed to be displaced by the presence of TTIP, which changes the mass fraction of argon by less than 0.5%. The full list of mass fractions at the inlet boundary are tabulated in Table 1. The boundary conditions for other species mass fractions at the inlets were fixed at 0. All other species boundary conditions were specified as zero-gradient.

The remaining boundary conditions used are as follows: The inlet gas temperature was specified as 423 K for both the gas and sheath flow. The gas and sheath flow inlet velocities were fixed to match the volumetric flow rates assuming uniform velocity profiles. Zero gradient pressure boundary conditions were assigned to the inlets while ambient pressure outlets were specified at the boundaries open to the atmosphere (fixed 101.325 kPa). Isothermal and no-slip boundary conditions were specified at walls. The temperature of the burner walls was assumed to be equal to that of the inlet gas ($T = 423$ K), while the stagnation surface was assumed to have a uniform temperature of 500 K. The inlet bound-
Table 1: Mass fraction boundary conditions.

<table>
<thead>
<tr>
<th>φ (-)</th>
<th>C₂H₄</th>
<th>O₂</th>
<th>Ar</th>
<th>TTIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>2.27</td>
<td>25.94</td>
<td>71.79</td>
<td>0</td>
</tr>
<tr>
<td>2.27</td>
<td>25.94</td>
<td>71.58</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>2.27</td>
<td>25.94</td>
<td>71.36</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>3.45</td>
<td>11.79</td>
<td>84.35</td>
<td>0.21</td>
</tr>
<tr>
<td>3.45</td>
<td>11.79</td>
<td>84.13</td>
<td>0.43</td>
<td></td>
</tr>
</tbody>
</table>

Boundary condition of the particle fields corresponded to no particles; for all other particulate field boundaries, a zero gradient boundary condition was used.

3 Physical models and numerical methods

This section describes relevant details of the models and numerical methods used in this work. Table A.1 in the supporting information gives details of the model parameters. Full details can be found in the references given in the text and in the supporting information.

3.1 Governing equations

The governing equations for chemically reacting flow [64, 75] are convective-diffusive-reactive partial differential equations in space and time. The domain is axisymmetric around the centreline, reducing the problem to two spatial dimensions. The conservation equations of mass, momentum, species, and enthalpy were used to describe the gas phase. The diffusion of species was described using mixture-averaged transport [27]. The thermochemical coefficients are determined using JANAF polynomials [26]. The particulate phase was described by additional transport equations for the moments of the particle size distribution [49]. The finite volume method was used to discretise the governing equations into algebraic equations. OpenFOAM [70] was used to solve the discretised equations using the transient PISO Algorithm [33]. The kinetics Application Programming Interface [17] was used to calculate the transport coefficients and source terms of the species and moment fields. The OpenFOAM-kinetics solver has previously been used to study premixed, jet-wall stagnation flames [20] and has been updated to account for the addition of the particle phase for this work. The mesh is this work is similar to that used in previous work [20], containing 200,000 cells with local refinement at the walls and flame front.

The combustion chemistry was described using the San Diego Mechanism [79]. A reduced TTIP mechanism [41] based on a mechanism produced from first principles [14, 15] was coupled to the combustion mechanism. It captures the decomposition of TTIP via C₃H₆ abstraction and CH₃/H abstractions to form Ti(OH)₄ which may further decompose. In total, the overall mechanism comprised 65 species and 240 reactions.
3.2 Spherical particle model

A spherical particle model [45] was used to describe the growth of the TiO\textsubscript{2} particles in the 2D simulations. The model assumes that the particles are spherical and uses a single quantity – the number of TiO\textsubscript{2} units, \( k \) – to describe the particles. Coagulation was described by the Smoluchowski equation [67] with an assumption of instantaneous coalescence for particles to remain spherical. The inception (IN) reaction is

\[
2\text{Ti(OH)}_4(\text{g}) \xrightarrow{k_{\text{IN}}} \text{Ti}_2\text{O}_4(\text{s}) + 4\text{H}_2\text{O}(\text{g}).
\]  

(1)

Surface growth (SG) is modelled as

\[
\text{Ti(OH)}_4(\text{g}) + [\text{Ti}_x\text{O}_y]_s(\text{s}) \xrightarrow{k_{\text{SG}}} [\text{Ti}_{x+1}\text{O}_{y+2}](\text{s}) + 2\text{H}_2\text{O}(\text{g}).
\]  

(2)

The inception and surface growth rates constants are

\[
k_{\text{IN}} = \varepsilon \sqrt{\frac{\pi k_B T}{m_{\text{Ti(OH)}_4} \left(2d_{c,\text{Ti(OH)}_4}\right)^2}},
\]  

(3)

and

\[
k_{\text{SG}} = \varepsilon \left( \frac{6k_B T}{\rho_{\text{TiO}_2}} \right)^{\frac{1}{3}} \left( \frac{3m_{\text{Ti(OH)}_4}}{4\pi \rho_{\text{TiO}_2}} \right)^{\frac{1}{3}} \left( k^{2/3} \right).
\]  

(4)

The method of moments with interpolative closure (MoMIC) [22] was used to transform and solve the resulting population balance equations for the first six integer moments \( M_0 \) to \( M_5 \) of the particle number distribution. The top panel of Figure 2 illustrates the essential features of the approach. A list of the numerical parameters used by the spherical particle model can be found in Table A.1. The full model equations and a description of MoMIC can be found in references [22, 45].

3.3 Detailed particle model

Lagrangian particle trajectories extracted from the results of the 2D simulations were post-processed using a hybrid particle-number/detailed particle model [10, 42] to gain insight into the particle morphology and particle size distribution. The bottom panel of Figure 2 illustrates the essential features of the model. The particle-number part of the particle model tracks the number particles of each size, up to a specified maximum size, \( N_{\text{thresh}} \) [10, 11]. These are the smallest particles in the population and are assumed to be spherical. This approach improves numerical efficiency and reduces systematic error without loss of information [10, 11]. The detailed particle model describes aggregate particles, \( P_q \), as a list of primary particles and their connectivity, \( C \). Each primary particle, \( p_i \), is mathematically described by its radius, \( r \), composition, \( \eta \), and position, \( x \). The model describes the evolution of the particles due to inception, surface growth, coagulation and rounding of the particles both due to mass addition and sintering. The inception and surface growth model equations are the same as for the spherical particle model.
Spherical Particle

$$P = \sum_{k=1}^{\infty} k^2 N(k)$$

for small, spherical particles:

$$P = \sum_{k=1}^{K_{\text{thresh}}} k^2 N(k)$$

for large, aggregate particles:

$$P = P_q \left( p_1, p_2, \ldots, p_n, \eta, C \right)$$

$$p_i = p_i(\tau, \eta, x_i)$$

Solved with MoMIC [22]

Lagrangian post-processing

Figure 2: Visualisation of particle descriptions used in this work when coupled to the governing equations and when post-processed.

The method used to post-process the Lagrangian particle trajectories is analogous to that used elsewhere [40]: the profiles of gas phase composition, temperature and pressure as a function of Lagrangian time were held constant while the population balance was solved. The hybrid particle-number/detailed particle model was solved using a direct simulation Monte Carlo (DSMC) method [21, 25, 59, 61]. The method approximates the solution of the PBE by evolving an ensemble of representative stochastic particles in a Lagrangian control volume. The full mathematical description of particles, model equations and DSMC method can be found in references [10, 42].

To facilitate visualisation of the particle size distributions (PSDs), kernel density estimates (KDE) (calculated using Sci-kit Learn [62] with a Gaussian kernel and bandwidth of 0.3 nm) were used to produce a continuous estimate of the PSD. To assess the similarity between distributions, binary comparisons of the PSDs were made using a two sample, non-parametric Kolmogorov-Smirnov (KS) test [30, 50] as implemented in the Sci-Py numerical computing package [76]. The null hypothesis, $H_0$, was that the two underlying distributions from which the samples were taken are equal. The confidence threshold used in this work is $\alpha = 0.01$. 
4 Results and discussion

4.1 Thermochemical environment

Figure 3 presents the thermochemical environments in each flame for the two different TTIP loadings, 280 and 560 ppm. The centreline profiles of temperature and Ti(OH)$_4$, the gas phase species involved in inception and surface growth reactions, are shown at the bottom of the figure.

**Figure 3:** 2D mass fraction and temperature fields for the 280 ppm (left sub-panel) and 560 ppm (right sub-panel) TTIP loadings in the $\phi = 0.35$ (left) and $\phi = 1.0$ (right) flames. The centreline (d) temperature and (e) Ti(OH)$_4$ mass fraction are plotted to assist visual clarity.
It can be observed that the shapes of all the flames are very similar: the flames contain a flat central region with up-turned wings at \( r/r_0 \approx 1.5 \) (1 cm). The TTIP loading affected the location of the flame front of the lean flame as determined by the peak CH mass fraction (Fig. 3a). This can also be seen in Fig. 3d, where the flame front of the lean flame was located at \( h = 1.7 \) mm (dotted line) without TTIP. The addition of TTIP shifted the flame front closer to the burner. The flame was found to rest at \( h = 1.9 \) mm (solid line) above the stagnation surface for the 280 ppm loading and \( h = 2.2 \) mm (dashed line) for the 560 ppm loading. The lean flame location is predicted to be closer to the surface than past experiments which reported the flame front around 3 mm above the stagnation plate [41, 45]. In the stoichiometric flame, the flame front remained located at \( h = 4.5 \) mm for both loadings (Fig. 3d). This is in good agreement with measurements reported in literature: a stoichiometric flame was found to rest 3.5 mm from the stagnation surface [44] when the nozzle-surface separation was smaller than in this work. This will create a higher strain rate at the flame front and push the flame closer to the surface. The 1 mm difference in flame position is consistent with the change seen in previous work when changing the nozzle-surface ratio [20].

Figure 3 also shows the temperature (Fig. 3b) and the mass fraction of Ti(OH)_4 (Fig. 3c), the gas phase species involved in inception and surface growth reactions. The TTIP loading affected the lean and stoichiometric flames differently. The \( \phi = 0.35 \) flame had a peak temperature around 1840 K for 580 ppm TTIP, which was 160 K higher than without TTIP (1680 K, Fig. 3d). For 280 ppm TTIP in the lean flame, the peak temperature was 1760 K, which was 90 K higher than without TTIP. The \( \phi = 1.0 \) flame had a peak temperature around 2340 K for 560 ppm TTIP, which was 20 K higher than without TTIP. The two flames show very different Ti(OH)_4 fields. In the lean flame (Fig. 3c left column), Ti(OH)_4 was present downstream of the flame front with two peaks (Fig. 3e). This is consistent with centreline profiles predicted by the reduced mechanism in 1D simulations [41]. In contrast, Ti(OH)_4 was produced and consumed at the flame front of the stoichiometric flame (Fig. 3e).

### 4.2 Spherical particle model

Figure 4 shows fields for TiO_2 nanoparticles as predicted by the spherical model in the 2D simulations. The quantities in the figure are integral quantities of the distribution calculated from the moments.

The particle number density field (Fig. 4a) mirrors that of the precursor, Ti(OH)_4 (Fig. 3c). In the \( \phi = 0.35 \) flame (left column), the number density has two peaks, indicating that the rate of inception downstream of the flame front is competitive with that of coagulation. The \( \phi = 1.0 \) flame, in contrast, has a well defined peak in the number density at the flame front. The number density decreases moving downstream of the flame front, indicating that the rate of coagulation far exceeds the rate of inception downstream of the flame front.

Figure 4b shows the particle mass density field. There was a significantly slower transfer of mass from the gas phase to the particle phase in the \( \phi = 0.35 \) flame than in the \( \phi = 1.0 \) flame. In the lean flames, the particle mass density was very low at the flame front and peaked \( \approx 1 \) mm above the stagnation surface. In the stoichiometric flames, the particle
$\phi = 0.35$

280 ppm  560 ppm

$\phi = 1.0$

280 ppm  560 ppm

(a) Particle Number Density [$m^{-3}$]

(b) Particle Mass Density [$kg \, m^{-3}$]

(c) Average Particle Diameter, $\bar{d}_{ph}$, [nm]

Figure 4: 2D particle fields for the 280 ppm (left sub-panel) and 560 ppm (right sub-panel) TTIP loadings in the $\phi = 0.35$ (left) and $\phi = 1.0$ (right) flames. The centreline (d) average particle diameter and (e) number density are plotted to assist visual clarity.

mass density rapidly approached its peak value at the flame front ($\approx 4$ mm above the surface); downstream of the flame front, the particle density changed with temperature due to thermal expansion and contraction of the gas (see temperature change downstream of flame front in Fig. 3d).

The average particle diameter (Fig. 4c) shows two different trends as a function of equivalence ratio. In the lean flames, the particles remain small ($< 2$ nm) until they approach the surface (Fig. 4c left column). In the 280 ppm case, the average diameter on the surface was 3 nm. In the 560 ppm case, it was 10 nm. In the stoichiometric flames, the particles have an average diameter of approximately 3 nm near the flame front and continue to
grow until they reach the stagnation surface. In the 280 ppm case, the average diameter on the surface was 5 nm. In the 560 ppm case, it was 8 nm.

4.3 Residence time distributions

Figure 5 shows the total residence time and deposition radius of the trajectories sampled from the 2D simulations as a function of the radial starting point of each trajectory. The trajectories were calculated considering both convective and thermophoretic transport. Without the thermophoretic transport, the trajectories would not impinge (see Fig. C.2). The total residence time is approximately constant up to an inlet radius of \(r/r_0 = 1/7\) (1 mm), after which it begins to grow, leading to more time for particles to evolve. The deposition radius is approximately linearly dependent on the initial radius. Additionally, it can be observed that the 560 ppm TTIP loading results in a residence time that is 0.5 ms shorter than the 280 ppm TTIP loading in the \(\phi = 0.35\) flame. The TTIP loading did not affect the residence time distributions in the \(\phi = 1.0\) flame because the predicted temperature profiles were almost the same.

![Figure 5](image)

\textbf{Figure 5:} Total residence time (left) and deposition radius (right) as a function of starting radial point, \(r\). The total nozzle outlet radius is \(r_0 = 7\) mm. The markers indicate the starting radii of the sampled trajectories used in the subsequent analysis.

Figure 6 shows the temperature as a function of residence time along different particle trajectories. The profiles are very similar at the flame fronts, but trajectories originating from larger starting radii spend more time at higher temperatures, with some trajectories leaving the computational domain before depositing on the stagnation surface. This produces different rates of cooling as the particles move from the flame front to the stagnation surface. Figure 7 shows the mole fraction of Ti(OH)$_4$, the particle precursor, as a function of residence time. In the \(\phi = 0.35\) flames, Ti(OH)$_4$ was present downstream of the flame front. This leads to increased inception and surface growth rates in the lean flames. In contrast, the \(\phi = 1.0\) flames have a delta-like profile at the flame front. The terminal values of the trajectories approached zero, indicating that Ti(OH)$_4$ was consumed through mass transfer to the particle phase. This is also the reason why the trajectories that leave the computational domain observed in Fig. 6 are not visible in Fig. 7.
Figure 6: Temperature as a function of residence time along particle trajectories at different starting radii (solid to transparent moving outwards). The ends of the trajectories are marked with bars indicating that the trajectories deposited on the stagnation surface (blue) or exit the simulation domain (orange).

Figure 7: Ti(OH)$_4$ as a function of residence time along particle trajectories at different starting radii (solid to transparent moving outwards). The profiles are found to be very similar and are seen to overlap.
Fig. 7 shows that the Ti(OH)$_4$ mole fraction does not significantly change with the increased residence time of the trajectories that impinged on the stagnation surface. A similar trend was observed for other species (not shown). However, it is worth noting that trajectories originating from an inlet radius of $r/r_0 > 1/2$ (3.5 mm) begin to experience dilution from diffusion of the sheath flow. This changes the local thermochemical environment in these trajectories. These trajectories do not impinge on the stagnation surface due to the flow divergence at large radii and are not considered further in this study. However, these trajectories may be important if large flow re-circulation is experienced.

4.4 Detailed particle model

4.4.1 Particle size distributions

The particle size distributions along the particle trajectories were examined. Like the chemical environment, the particle size distributions at the flame front were nearly identical. Differences begin to occur near the end of the trajectories (see Figs. C.3 and C.4), and are most easily seen by examining the particles that impinge on the stagnation surface. Figure 8 shows the size distributions of the particles that impinge on the stagnation surface for each trajectory of each flame. The sphere-equivalent diameter is used to characterise particle size. Note that Fig. 8 includes all particles tracked by the hybrid model, some of which are smaller than what may be experimentally observed.

Figure 8: Particle size distribution at the end of trajectories (solid to transparent moving radially outwards from the centre of the flame) that deposit on the stagnation surface. The arrows mark the trend moving radially outwards. The equivalent spherical diameter is used to characterise the particle size.
The two equivalence ratios present different particle size distributions. In the lean flames (top row), the particle size distributions are bimodal with an inception mode and a coagulation mode. In the stoichiometric flames (bottom row), the particle size distributions are monomodal. The monomodal distributions are approximately log-normal. The lean flames produce larger particles due to the longer residence times (Fig. 5).

Table 2 shows the centreline values of the median diameter and geometric standard deviation for the primary particles and aggregates, alongside comparable experimental data from the literature. The primary particle sizes are determined experimentally by transmission electron microscopy (TEM), whereas aggregate particle sizes are determined from mobility size measurements. A small level of aggregation in the simulated particles can be inferred in the cases where the median aggregate diameter is observed to be larger than the median primary particle diameter, though this comparison is not conclusive.

### Table 2: A comparison between experimentally determined primary and aggregate particle sizes in the literature and sizes predicted by the simulations in this work at similar TTIP loadings.

<table>
<thead>
<tr>
<th>Reference</th>
<th>( \phi )</th>
<th>TTIP ppm</th>
<th>Primary Particle</th>
<th>Aggregate Particle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Median nm</td>
<td>GSD</td>
</tr>
<tr>
<td>This work</td>
<td>0.35</td>
<td>280</td>
<td>6.1</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>560</td>
<td>7.8</td>
<td>1.24</td>
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<tr>
<td></td>
<td>1.0</td>
<td>280</td>
<td>6.0</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>560</td>
<td>7.5</td>
<td>1.35</td>
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<td>Manuputty et al. [46]</td>
<td>0.35</td>
<td>190</td>
<td>5.7</td>
<td>1.50</td>
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<td></td>
<td></td>
<td>580</td>
<td>9.7</td>
<td>1.62</td>
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<td></td>
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<td>190</td>
<td>7.1</td>
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<td></td>
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<td>580</td>
<td>9.8</td>
<td>1.63</td>
</tr>
<tr>
<td>Manuputty et al. [47]</td>
<td>1.0</td>
<td>365</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tolmachoff et al. [71]</td>
<td>0.45</td>
<td>300</td>
<td>5.8</td>
<td>1.31</td>
</tr>
</tbody>
</table>

The quantities predicted by the simulations are in reasonable agreement with the experimental data. In the simulation of the lean flame, the median aggregate particle sizes were found to be 6.0 nm and 9.0 nm for 280 ppm and 560 ppm TTIP respectively. These values compare well with the median particle sizes of 5.7 nm and 10.4 nm measured by Manuputty et al. [46] in \( \phi = 0.35 \) flames with 190 ppm and 580 ppm TTIP.

In the work of Tolmachoff et al. [71], the primary and aggregate particle properties were measured with stagnation surfaces at difference temperatures. This was originally thought to be responsible for the difference between the primary and aggregate sizes [71]. It has since been shown that the difference in surface temperature does not explain the difference between the primary and aggregate sizes [45] and there is experimental evidence to suggest that the difference is due to a small degree of aggregation [40, 46].

A less direct comparison can be made for the stoichiometric flame simulated in this work. An aggregate particle size of 8.0 nm was measured by Manuputty et al. [47] for a TTIP loading of 365 ppm. This loading falls in between the values studied in the simulations in this work, which predicted aggregate particle sizes of 5.9 nm and 7.7 nm at 280 ppm.
and 560 ppm TTIP respectively. The results of this work appear to slightly under-predict the experimental aggregate sizes of Manuputty et al. [47], but are nevertheless in the right range and are considered to be physically reasonable.

The following section examines the particle morphology. The radial dependency of the particle properties is discussed in Section 4.4.3.

### 4.4.2 Particle morphology

Particle morphology is important for many applications. In the analyses that follow, particles from the particle-number model \( d(N_{\text{thresh}}) < 2 \text{ nm} \) are excluded because they are smaller than the lower limit of the experimental TEM measurements (3 nm) [46]. In addition, the model parameters are such that rapid sintering causes small primaries \( (d < 4 \text{ nm}) \) to coalesce with their larger neighbours. This makes the analysis consistent with experimental measurements of primary particle size by TEM.

**Figure 9** shows the size distributions of the primary particles that impinge on the stagnation surface for each trajectory of each flame. As the particle trajectories move radially outwards, the frequency of the primary particles at 4 nm (the sintering limit) decreases, and the number of large primaries grow. This is most apparent in the flames with 280 ppm TTIP (left column). In the stoichiometric flames (bottom row), the distribution moves to the right. This is explained by coagulation and sintering of small primaries.

![Figure 9](image)

**Figure 9**: Primary particle size distributions at the end of trajectories (solid to transparent moving radially outwards from the centre of the flame) that deposited on the stagnation surface. The arrows mark the trend moving radially outwards.

The median and geometric standard deviation of the primary particle sizes are tabulated in
Table 2. The lean and stoichiometric flames have a median primary particle size of 6.1 nm and 6.0 nm at 280 ppm TTIP respectively. This is in good agreement with the available experimental data, which reports values of 5.69 nm [46] and 5.8 nm [71] in lean flames.

Figure 10 shows joint distributions of aggregate collision diameter and average primary diameter, number of primaries, and average sintering level for three different trajectories for the lean flame with 560 ppm TTIP. The sintering level is defined as the ratio of the ‘neck’ radius and the radius of the smaller primary [42]. The averages are calculated as the arithmetic mean of the corresponding quantities for the primaries within each aggregate. The trajectories are selected to represent the centreline, an off-centreline trajectory that shows similar trends to the centreline, and an off-centreline trajectory that shows significant differences. The black dotted lines in the figure show the corresponding values for values spherical particles. The fraction of spherical particles is reported for each trajectory. Results for the other flames showed similar trends and can be found in the appendix (Fig. C.5).

Figure 10: Joint distributions of average primary diameter, number of primaries, and average sintering level with collision diameter at different deposition radii, \( r_d \), for the lean flame with 560 ppm TTIP. The averages are arithmetic means are taken over the primary particles within each aggregate. The fraction of particles that are spherical are reported as a percentage. The dotted black line corresponds to spherical particles, while the dot-dash lines (column 3) mark the collision diameter of large aggregates that form at large deposition radii.
Figure 10 shows that aggregates are comprised of larger primary particles that are near the median size. Additionally, that the number of primaries in point contact grows as the deposition radius increases (moving left to right). This is most strongly affected by the TTIP loading (cf. Fig. C.5) as higher TTIP loadings results in more aggregated particles. These particles are not strongly sintered, suggesting that they coagulate at the end of the trajectories and do not have time to fully coalesce when above the sintering critical diameter. This is further supported by the observation that the average number of primaries remains small until larger residence times (Fig. C.4).

While the previous analysis has considered joint distributions between the properties of the primary particles and the aggregates, the shape information provided by the detailed particle model allows for individual particles to be analysed. Figure 11 shows simulated TEM images for the stoichiometric flame with 560 ppm of TTIP for trajectories with three deposition radii. For each trajectory, the simulated TEMs are produced for particles with collision diameters in the range: 3 nm < $d_c$ ≤ 10 nm, 10 nm < $d_c$ ≤ 20 nm, and 20 nm < $d_c$ to aid visual clarity. Particles with small collision diameters are observed to be largely spherical with very few aggregates. Between 10 and 20 nm, there is a mix of spherical particles ($n_p = 1$) and aggregates. Above 20 nm, the particles are aggregates with the constituent primaries mostly in point contact or weakly sintered. Similar trends were observed for the other flames (not shown).

**Figure 11:** Simulated TEM images of particles with different collision diameters, $d_c$ at different deposition radii, $r_d$, in the stoichiometric flame with 560 ppm TTIP. The scale bar is 20 nm in width. The TEM images are ‘supervised’ such that the particles do not overlap. The largest particles are aggregates composed of primary particles that are in similar in size to the primary particles seen in the smaller particles.
4.4.3 Radial dependency of the particle properties

Statistics of the aggregate and primary particles are compared as a function of the deposition radius to examine the effect of different trajectories on nanoparticle formation. Figure 12 shows the median sphere-equivalent diameter, \( \langle d_{\text{sph}} \rangle \), and geometric standard deviation, GSD, of the terminal particle size distribution of the aggregates as a function of deposition radius. The trend observed in the median particle size is analogous to that seen in the total residence time (Fig. 5): the median particle size is approximately constant over a central region before growing with deposition radius. The radius at which the distributions begin to differ from the centreline \( (r_d = 0 \text{ mm}) \) was determined using a two-sample Kolmogorov-Smirnov test (confidence threshold \( \alpha = 0.01 \), see Appendix B for details), and is marked by the width of the shaded bar on Fig. 12a. For the lean flames (black), the distributions begin to differ at a deposition radius of 7.5 mm and 12 mm for 280 ppm and 560 ppm, respectively. For the stoichiometric flames (green), the distributions begin to differ at a deposition radius of 8.5 mm and 9.3 mm for 280 ppm and 560 ppm, respectively. The geometric standard deviation of the particle size distribution was between 1.4 and 1.47 for all deposition radii and all flames, which is very close to the self-preserving size distribution value of 1.45 (Fig. 12b). The observation that the distributions achieve a GSD close to that of the self-preserving size distribution is consistent with empirical rules for the time required for an ensemble of particles undergoing coagulation to reach the self-preserving distribution [74]. This indicates that the distributions are coagulation driven as the particles approach the stagnation surface.

Figure 12: The (a) median aggregate diameter, \( \langle d_{\text{sph}} \rangle \) and (b) geometric standard deviation (GSD) as a function of deposition radius, \( r_d \). The median aggregate diameters at \( r_d = 0 \text{ mm} \) are marked by semi-transparent bars; the horizontal extent of the bars shows where the size distributions begin to deviate from the distribution observed at \( r_d = 0 \text{ mm} \) as determined by a two-sample Kolmogorov-Smirnov test (confidence threshold \( \alpha = 0.01 \)). The GSD of a self-preserving size distribution is marked in pink.

Figure 13 shows the median primary diameter and (arithmetic) average number of primaries per particle as a function of deposition radius. The width of the semi-transparent bars in Fig. 13 indicate the range of deposition radii where the aggregate particle size dis-
The distribution was determined to be similar (see Appendix B). The median primary diameter remains constant across the trajectories studied, consistent with the observations made during the analysis of Fig. 10. The particles were found to aggregate more as the deposition radius increases (Fig. 13b). This is due to the increased residence time of trajectories originating from larger radii (Fig. 5). In the stoichiometric flames and lean flame with 280 ppm TTIP, the average number of primaries ranges between 1.1 and 1.5, indicating some aggregation. In the lean flame with 560 ppm TTIP, the mean number of primaries per particle is between 1.7 and 2.6, indicating a higher level of aggregation.

\[ \phi = 0.35, 190 \text{ ppm [46]} \]
\[ \phi = 0.45, 300 \text{ ppm [71]} \]

\[ \phi = 0.35, 580 \text{ ppm [46]} \]

![Figure 13:](image)

The small increase in residence time experienced by trajectories originating from larger radii is the key factor driving the differences observed in this work. Coagulation has been shown to be the main process responsible for the radial differences in the particles, with the most pronounced difference being the increase in aggregation at larger radii. The observation that the particles deposited at different radii on the stagnation surface are different has implications for the experimental synthesis of materials in jet-wall stagnation flames. As particle size is an important parameter for the application of materials, it is important to understand the extent of the region in which the particles are expected to be uniform \([r/r_0 < 1.5, r \lesssim 1 \text{ cm in this case}].\) Experimentally, this may be overly restrictive. Nonetheless, it is worth considering the impact of the radial dependence of the particle properties on the suitability of the particles for a given application. Further, the disruption of the temperature-residence time profiles in flame configurations with rotating stagnation surfaces should be considered in the context of particle synthesis. As it has been shown that the increase in residence time produces differences in the size distribution, it is possible that disruption to the particle trajectories from a rotating surface could interfere with this effect. This combination of effects warrants further study to ensure that particles collected at different deposition radii do indeed have sufficiently similar properties.
5 Conclusions

The synthesis of TiO$_2$ nanoparticles in jet-wall stagnation flames was studied to explore the radial dependence of the particle properties. The 2D structure of the flame was resolved with the particles described by a spherical particle model; the moments of the population balance describing the particles were transported in 2D space. The results were post-processed using a detailed particle model solved using a direct simulation Monte Carlo method. Two flames, a lean flame (equivalence ratio, $\phi = 0.35$) and a stoichiometric flame ($\phi = 1.0$), were studied to explore the particle formation under two different, but experimentally relevant, thermochemical environments. The $\phi = 0.35$ flame was predicted to rest 1.7 mm above the stagnation surface while the $\phi = 1.0$ flame was predicted to rest 4.5 mm above the stagnation surface. The stoichiometric flame position was in good agreement with experimental data [47], while the lean flame slightly underpredicted the experimentally observed flame position [41, 45]. Two titanium(IV) tetraisopropoxide (TTIP) metal oxide precursor loadings were used in this study: 280 ppm and 560 ppm. The addition of TTIP has a small effect on the thermochemical environment, shifting the lean flame front by 0.3 cm and raising the temperature by 160 K (1840 K). The location of the stoichiometric flame was unaffected and the temperature raised by 20 K (2340 K).

Integral properties of the particle population were shown to vary between the two flames. In the $\phi = 0.35$ flame, the Ti(OH)$_4$ particle precursor was observed downstream of the flame front, which was consistent with previous work [40]. In the $\phi = 1.0$ flame, the precursor was generated and consumed near the flame front. Particle number density profiles mirror those of the precursor. In the $\phi = 0.35$ flame, high number densities were observed downstream of the flame front, whereas the number density peaked at the flame front in the $\phi = 1.0$ flame. The average particle diameters show similar trends to previous studies [40]. In the lean flame, the particle diameter remained constant at the flame front before growing as the particles approached the stagnation surface to reach a final average size of 3 to 10 nm. In the stoichiometric flame, the particles rapidly grew to 3 mm at the flame front and continued to grow throughout the flame to reach a final average size of between 5 and 8 mm.

Trajectories originating from different initial radial positions at the burner outlet (radius, $r_0 = 7$ mm) were examined. Trajectories that originated from $r/r_0 \leq 1/7$ had similar residence times for both flames and deposited particles at radii up to $r_d/r_0 \lesssim 1.5$ ($\approx 1$ cm). Trajectories that originated from $1/7 < r/r_0 \leq 1/2$ spent more time at elevated temperatures due to flow divergence, but experienced similar chemical environments. Trajectories that originated from $r/r_0 > 1/2$ experienced significant changes in their chemical environment due to the dilution from the sheath flow, but did not deposit on the stagnation surface.

The trajectories were post-processed to study TiO$_2$ nanoparticle growth using a hybrid particle-number/detailed particle model solved using a direct simulation Monte Carlo method. The detailed particle model resolves details about the aggregate size distribution, morphology and composition. The aggregates were predicted to have collision diameters between 6 and 12 nm, whereas the spherical model predicted (spherical) diameters between 3 and 10 nm. This is in close agreement with experimental values of 5 to 10 nm measured at the centreline [46, 71]. The differences in the thermochemical environments
between the flames led to different processes influencing the particle growth. In the lean flame, the simulated temperatures were lower and the particle precursor persisted further into the flame, leading to higher rates of inception and surface growth compared to the stoichiometric flame. This resulted in bimodal PSDs with a large inception mode at small diameters (< 2 nm). In the stoichiometric flame, the size distributions were found to be approximately log-normal and had GSDs of approximately 1.45, consistent with the particles reaching a self-preserving distribution. Experiments have reported that the particle size distribution produced in jet-wall stagnation flames is narrow, but the simulations suggest that the narrowness is a consequence of the small size of the particles.

The particle size distributions were shown to vary as a function of deposition radius. For the cases studied, differences in the observed particle size distribution began to occur at a deposition radius of \( r/r_0 \approx 1.5 \) (\( \approx 1 \) cm). The differences were due to an increase in aggregation resulting from an increase in residence time at larger radii. Moving forward, it is suggested that applications that use stagnation flames for nanoparticle synthesis should consider any radial variation in the performance of the particles for the intended application.

**Research data**

Additional data and the source code for solving the governing equations are available to download from the University of Cambridge data repository (doi:10.17863/CAM.66854). The source code relies on the OpenFOAM library [70] and kinetics Application Programming Interface (API) [17]. OpenFOAM is freely available online; contact CMCL Innovations [17] regarding the kinetics API. The source code for the hybrid particle-number/detailed particle model [18] used in this work is available on GitHub (https://github.com/ucam-ceb-como/MOpS) under an open source licence.

**Acknowledgements**

This research was supported by the National Research Foundation, Prime Minister’s Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme. EJB was funded by a Gates Cambridge Scholarship (OPP1144). GL was funded by a CONACYT Cambridge Scholarship and acknowledges the National Council of Science and Technology and the Cambridge Commonwealth Trust. MK gratefully acknowledges the support of the Alexander von Humboldt foundation. The authors are grateful to the University of Cambridge Research Computing Service for their technical support.
A Governing equations

The governing equations for laminar reacting flow [64, 75] are partial differential equations in space and time, $t$, which describe the conservation of mass,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) = 0; \quad (A.1)$$

momentum,

$$\frac{\partial \rho \mathbf{U}}{\partial t} + \nabla \cdot (\rho \mathbf{UU}) = -\nabla p - \mu \left( \nabla \mathbf{U} + (\nabla \mathbf{U})^T \right); \quad (A.2)$$

species,

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho \mathbf{U} Y_i) + \nabla \cdot (\rho V_i^c Y_i) = \dot{\omega}_i \quad \text{for } i = 1, \ldots, N_{sp}; \quad (A.3)$$

and energy,

$$c_p \frac{\partial \rho T}{\partial t} + c_p \nabla \cdot (\rho \mathbf{U} T) = \nabla \cdot (\lambda \nabla T) - \left( \rho \sum_{i=1}^{N} c_p Y_i V_i^c \right) \cdot \nabla T + \dot{\omega}_T; \quad (A.4)$$

where $\rho$ is density, $\mathbf{U}$ is velocity, $Y_i$ is the mass fraction of species $i$, $T$ is temperature, $p$ is pressure, $V_i^c$ is the corrected diffusive velocity of species $i$, $\dot{\omega}_i$ is the mass rate of formation of species $i$, $\dot{\omega}_T$ is the enthalpy heat release, $\mu$ is mixture viscosity, $\lambda$ is the mixture thermal conductivity, and $c_p$ is the mixture heat capacity.

Transport equations are required to describe the particle phase. Even for particles that are described by a single internal coordinate (e.g. particle size, $k$), an infinite number of transport equations would be required to describe the number of particles of each possible size, making such an approach intractable. In this work, the transport equations to describe the population of univariate, spherical $\text{TiO}_2$ particles are transformed using the method of moments. The particles are assumed to be spherical, have very low volume fraction, have negligible mass, and have no influence on the momentum or enthalpy of the gas-phase. The evolution of the moments of the distribution per unit mass, $\hat{M}_j = M_j \rho$, is governed by

$$\frac{\partial \rho \hat{M}_j}{\partial t} + \nabla \cdot (\rho \mathbf{U} \hat{M}_j) + \nabla \cdot (\rho V_T \hat{M}_j) = \nabla \cdot \left( \rho D_{p1} \nabla \hat{M}_j - \frac{2}{3} \hat{M}_j \right) + \dot{\omega}_j \quad \text{for } j = 0, \ldots, N_{\text{mom}} - 1. \quad (A.5)$$

In this equation, $D_{p1}$ is the diffusion coefficient of the smallest particle (of size $k = 1$), $V_T$ is the thermophoretic velocity, and $N_{\text{mom}}$ is the number of moments solved for ($N_{\text{mom}} = 6$ in this case). The source terms of the moment equations $\dot{\omega}_j$ include terms describing inception, coagulation and surface growth processes [22, 45]. The source terms and the $\hat{M}_{j-\frac{1}{2}}$ field are unclosed. The equations are closed using interpolative closure (MoMIC) [23].

The ideal (perfect) gas law [4] was additionally used to close the above equations. The heat capacities, $c_{pi}$; enthalpy, $h_i$; and entropy, $s_i$ of species $i$ are described using JANAF polynomials [26]. Mixture-averaged properties are calculated as mass-weighted sums of $N_{sp}$ species with molecular weight $W_i$. The mixture viscosity is defined by a semi-empirical formula by Wilke [78] that has been modified by Bird et al. [8]:

$$\mu = \frac{\sum_{i=1}^{N_{sp}} X_i \mu_i}{\sum_{i=1}^{N_{sp}} X_i \phi_i \mu_i}, \quad (A.6)$$
where \( X_i, W_i, \) and \( \mu_i \) are the mole fraction, molecular weight, and viscosity of species \( i \), and

\[
\phi_{i_1,i_2} = \frac{1}{\sqrt{8}} \left( 1 + \frac{W_{i_1}}{W_{i_2}} \right)^{-\frac{1}{2}} \left( 1 + \left( \frac{\mu_{i_1}}{\mu_{i_2}} \right)^{\frac{1}{2}} \left( \frac{W_{i_1}}{W_{i_2}} \right)^{\frac{1}{4}} \right)^2. \tag{A.7}
\]

The mixture thermal conductivity is given by Mathur et al. [51]:

\[
\lambda = \frac{1}{2} \left( \sum_{i=1}^{N_{sp}} X_i \lambda_i + \left[ \sum_{i=1}^{N_{sp}} X_i / \lambda_i \right]^{-1} \right), \tag{A.8}
\]

where \( \lambda_i \) is the thermal conductivity of species \( i \).

A model is needed to describe the mass flux due to concentration gradients in a multicomponent gas mixture. A mixture-averaged approach [29] is used to calculate a single diffusion coefficient for each species. The binary diffusion coefficient, \( D_{i_1,i_2} \), given below, is a function of temperature; pressure; the reduced molecular weight, \( \bar{W}_{i_1,i_2} \); the reduced collision diameter, \( \bar{\sigma}_{i_1,i_2} \); and a collision integral, \( \Omega^{(1,1)} \), based on reduced temperature [55]:

\[
D_{i_1,i_2} = \frac{3}{16} \frac{\sqrt{2\pi k_B T^3 / W_{i_1,i_2}}}{p \pi \sigma_{i_1,i_2}^2 \Omega^{(1,1)}}, \tag{A.9}
\]

where

\[
\bar{W}_{i_1,i_2} = \left( W_{i_1}^{-1} + W_{i_2}^{-1} \right)^{-1}. \tag{A.10}
\]

The mixture-averaged approach of Hirschfelder and Curtiss [28] is used to calculate the mixture diffusion coefficient, \( D_i \). This approach is not inherently mass conserving, so a corrective velocity, \( V_c \), is applied to each species to ensure that mass conservation is followed. The final, corrected diffusion velocity, \( V_i^c \), is the sum of the mass flux and the corrective velocity.

\[
D_i = \frac{1}{N_{sp}} \sum_{i_2 \neq i} X_{i_2} \frac{1}{D_{i_1,i_2}}, \tag{A.11}
\]

\[
V_i^c = V_i + V_c, \quad V_i = -D_i \frac{\nabla X_i}{X_i}, \quad V_c = -\sum_i X_i V_i \tag{A.12}
\]

The diffusion coefficient of particles of size \( k \) due to Brownian motion in the free-molecular regime, \( D_{p_k} \), can be expressed as [24]:

\[
D_{p_k} = \frac{3}{2 \rho} \left( 1 + \frac{\pi \alpha_T}{8} \right)^{-1} \sqrt{\frac{W k_B T}{2 \pi N_A d_k^2}}, \tag{A.13}
\]

where \( \alpha_T \) is a thermal accommodation factor (fraction of gas molecules that leave the surface in equilibrium), \( N_A \) is Avagadro’s constant, and \( d_k \) is the diameter of a particle of size \( k \). The thermal accommodation factor usually takes a value of 0.9 [24]. Under the
spherical particle assumption, the diameter of a particle of size \( k \) scales by \( k^{1/3} \). This can be used to describe \( D_{p_k} \) as a function of \( k \) and \( D_{p_1} \):

\[
D_{p_k} = \frac{3}{2\rho} \left( 1 + \frac{\pi \alpha_T}{8} \right)^{-1} \sqrt{\frac{W k_B T}{2\pi N_A} \frac{1}{(d_1 k^{1/3})^2}} \\
= \frac{3}{2\rho} \left( 1 + \frac{\pi \alpha_T}{8} \right)^{-1} \sqrt{\frac{W k_B T}{2\pi N_A} \frac{1}{d_1^2 k^{-2/3}}} \\
= D_{p_1} k^{-2/3}. \tag{A.14}
\]

When applying the definition of moments to the infinite number of particle transport equations, the diffusion transport term of moment \( \hat{M}_j \) results in the

\[
\nabla \cdot \left( \rho D_{p_1} \nabla \hat{M}_{j; i} \right)
\]

term in Eqn. A.5. The thermophoretic velocity of the particles, \( V_T \), is assumed to be independent of particle size and is expressed as [24]:

\[
V_T = -\frac{3}{4} \left( 1 + \frac{\pi \alpha_T}{8} \right)^{-1} \frac{\mu}{\rho T} \nabla T. \tag{A.15}
\]

\( V_T \) acts as an additional convective flux term in Eqn. A.5.

Figure A.1 shows the algorithm used in this work. The algorithm is rooted in the PISO algorithm [33] for handling the velocity-pressure coupling, with the addition of solving scalar fields for chemistry and particle fields. The chemical and moment source terms are calculated by treating each cell as a constant-pressure batch reactor and is solved by integrating the system using ordinary differential equations solvers. The solver is parallelised using a domain decomposition method, where the domain is split into smaller domains for each processor to solve for. Adjacent domains are connected using halo cells.
Figure A.1: A diagram of the implemented algorithm. The governing transport equations are solved using OpenFOAM [70] while detailed coefficients and source terms are calculated using kinetics [17].
Table A.1 gives details of all the model parameters.

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<th>Value</th>
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<td>3.84 kg m$^{-3}$</td>
<td>Density of titania (anatase)</td>
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B  Assessment of particle size distribution similarity

The similarity of the PSDs are assessed using the two sample Kolmogorov-Smirnov (KS) test [30, 50, 76] for each distribution pair. The null hypothesis, $H_0$, was that the two underlying distributions from which the samples were taken are equal.

Figure B.1 presents the results of the two sample KS tests as reject (blue) or fail-to-reject (yellow) the null hypothesis of equivalent distributions. Similar trends are observed in all four cases. The PSDs of trajectories are mostly similar up to a critical radius beyond which the distributions become statistically different. In the lean flame, the critical radius was $r/r_0 \approx 1$ (0.7 cm) for the 280 ppm loading and $r/r_0 \approx 1.5$ (1.1 cm) for the 560 ppm loading. In the stoichiometric flame, the critical radius was $r/r_0 \approx 1$ (0.7 cm) for both TTIP loadings.

Figure B.1: Results of two sample Kolmogorov-Smirnov test between particle ensembles from different trajectories. The null hypothesis, $H_0$, was that the two underlying distributions from which the samples were taken are equal. Results marked with yellow fail to reject $H_0$: the two distributions are equal at the $\alpha = 0.01$ confidence level; results marked with blue provide evidence to reject $H_0$ ($p < 0.005$).
C Additional figures

Figure C.1: 2D mass fraction and temperature fields for the $\phi = 0.35$ (left) and $\phi = 1.0$ (right) flames without TTIP.

Figure C.2: Trajectories with (left) and without (right) thermophoretic drift. The trajectories that include thermophoretic drift impinge on the stagnation plate whereas trajectories without it do not.
Figure C.3: Mean aggregate diameter as a function of residence time along different trajectories (dark to light moving radially outwards from the centre of the flame) in (a) $\phi = 0.35$, 280 ppm flame, (b) $\phi = 0.35$, 560 ppm flame, (c) $\phi = 1.0$, 280 ppm flame, and (d) $\phi = 1.0$, 560 ppm flame. The inception mode is excluded in this figure.

Figure C.4: Mean number of primaries per aggregate as a function of residence time along different trajectories (dark to light moving radially outwards from the centre of the flame) in (a) $\phi = 0.35$, 280 ppm flame, (b) $\phi = 0.35$, 560 ppm flame, (c) $\phi = 1.0$, 280 ppm flame, and (d) $\phi = 1.0$, 560 ppm flame.
(a) Part 1: Lean flame with 280 ppm TTIP.

**Figure C.5:** Joint distributions of average primary diameter, number of primaries, and average sintering level with collision diameter at different deposition radii, $r_d$. The averages are arithmetic means are taken over the primary particles within each aggregate. The fraction of particles that are spherical are reported as a percentage. The dotted black line corresponds to spherical particles, while the dot-dash lines (column 3) mark the collision diameter of large aggregates that form at large deposition radii.
Part 2: Stoichiometric flame with 280 ppm TTIP.

**Figure C.5**: Cont.
(c) Part 3: Stoichiometric flame with 560 ppm TTIP.

**Figure C.5:** Cont.
References


