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Implementation of bivariate population balance equations in CFD codes for modelling nanoparticle formation in turbulent flames

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1 Introduction

Formation of nanoparticles in flames

- Combustion synthesis (production of tailored materials)
- <u>**Soot formation**</u> (undesired particulate matter)

Soot formation

Where:	**How:**
• Rich premixed and non-premixed flames (High equivalence ratio). • All the situations in which the combustion process cannot be completed.	• Products of incomplete combustion → benzene molecules • The benzene molecules grow to high molecular weight aromatic compounds (including Polycondensate Aromatic Hydrocarbons, **PAH**). • The larger PAHs coagulate to form soot nuclei. • The nuclei grow by surface reactions and aggregate.

• Epidemiological studies have demonstrated that particulate matter has an impact on **human health** even at low concentrations.

• Both aggregates with size of the order of micrometers and smaller particles formed in the early stages of the process (**nanoparticles**) can be toxic.

• Radiative properties of soot nanoparticles (**greenhouse effect**)

It is important to be able to accurately predict the evolution of the **size distribution** and **morphology** of soot particles during the combustion process.

2 Turbulent combustion and CFD

The accurate modelling of soot formation requires the accurate modelling of velocity, temperature and composition profiles in the flame: **Computational Fluid Dynamics**

• continuity $\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial}{\partial x_i}\left(\bar{\rho}\tilde{U}_i\right) = 0$

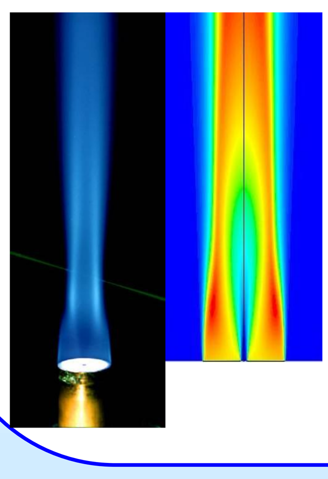
• momentum $\frac{\partial}{\partial t}\bar{\rho}\tilde{U}_i + \frac{\partial}{\partial x_i}\bar{\rho}\tilde{U}_i\tilde{U}_j + \frac{\partial}{\partial x_i}\bar{\rho}u_i u_j = -\frac{\partial \bar{p}}{\partial x_i} + \nu\frac{\partial^2 \bar{\rho}\tilde{U}_i}{\partial x_j \partial x_j}$

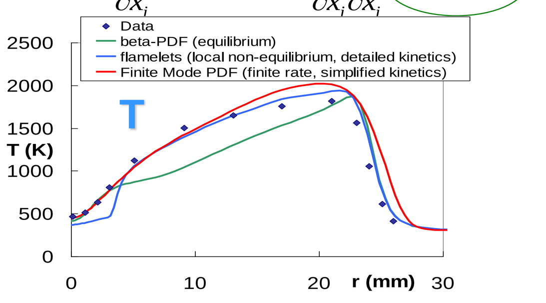
• scalars $\frac{\partial}{\partial t}\bar{\rho}\tilde{\Phi}_\alpha + \frac{\partial}{\partial x_i}\bar{\rho}\tilde{\Phi}_\alpha\tilde{U}_i + \frac{\partial}{\partial x_i}\bar{\rho}\phi_\alpha u_i = \Gamma_t\frac{\partial^2 \bar{\rho}\tilde{\Phi}_\alpha}{\partial x_i \partial x_i} + S(\Phi)$

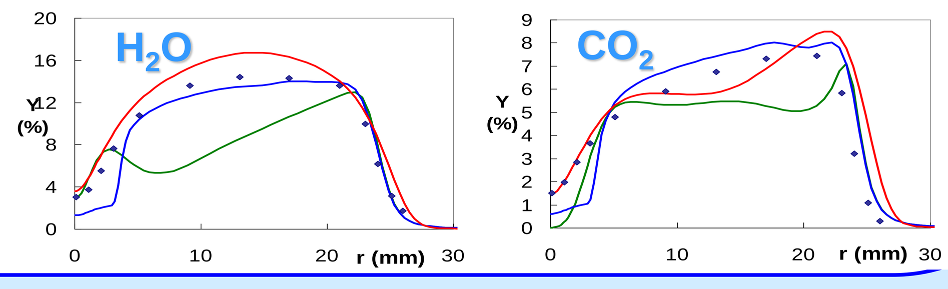
Turbulence modelling (Reynolds Averaged Navier-Stokes equations)

Modelling of **turbulence-chemistry interactions** → **Presumed PDF methods**

The knowledge of the **probability density function** of composition and temperature allows to compute the averaged chemical source term.







3 The Population Balance Equation (PBE)

$$\frac{\partial \tilde{n}(\boldsymbol{\xi};\mathbf{x},t)}{\partial t} + \frac{\partial}{\partial x_i}U_i\tilde{n}(\boldsymbol{\xi};\mathbf{x},t) - \frac{\partial}{\partial x_i}\left[\left(\Gamma+\Gamma_t\right)\frac{\partial \tilde{n}(\boldsymbol{\xi};\mathbf{x},t)}{\partial x_i}\right] = S(\boldsymbol{\xi};\mathbf{x},t)$$

$\tilde{n}(\boldsymbol{\xi};\mathbf{x},t)$ is the **number density function** of the particle population, in terms of a number of **internal coordinates (ξ)**, which are properties identifying the status of each particle (e.g., diameter, volume, surface area, velocity, composition, age…).

The solution of the PBE is not trivial. When it has to be coupled with CFD computations, the solution technique has to be <u>simple</u> and to have <u>low computational cost</u> (number of additional transport equations to be solved).

Only methods based on the **moments approach** are suitable to be coupled with CFD for the solution of PBEs.

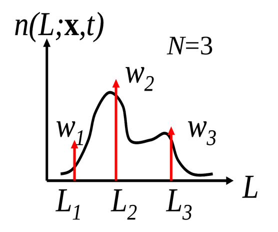
$$m_k(\mathbf{x},t) = \int_0^{+\infty}\tilde{n}(\xi;\mathbf{x},t)\xi^k d\xi \Longrightarrow \frac{\partial m_k(\mathbf{x},t)}{\partial t} + U_i\frac{\partial m_k(\mathbf{x},t)}{\partial x_i} - \frac{\partial}{\partial x_i}\left[\Gamma_t\frac{\partial m_k(\mathbf{x},t)}{\partial x_i}\right] = S(\mathbf{x},t)$$

The source term $S(\mathbf{x},t)$ determines the evolution of moments due to **nucleation**, **aggregation**, **molecular growth**, **oxidation** and **restructuring**.

4 The Direct Quadrature Method of Moments (DQMOM)

Let us consider only one internal coordinate (**monovariate PBE**)

Closure of the source term → Quadrature approximation



$$\tilde{n}(L;\mathbf{x},t) = \sum_{\alpha=1}^{N} w_\alpha(\mathbf{x},t)\,\delta\left[L - L_\alpha(\mathbf{x},t)\right] \Longrightarrow m_k(\mathbf{x},t) = \int_0^{+\infty}\tilde{n}(L;\mathbf{x},t)L^k dL \approx \sum_{\alpha=1}^{N} w_\alpha L_\alpha^k$$

Given 2N moments of the distribution is it possible to calculate the values of N **weights** w_α and N **abscissas** L_α of the delta functions, forcing them to yield known values of the moments, directly solving the transport equation of weights and abscissas (**Direct Quadrature Method of Moments**).

$$\frac{\partial w_\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\tilde{U}_{i\alpha}w_\alpha\right) - \frac{\partial}{\partial x_i}\left[\left(\Gamma+\Gamma_t\right)\frac{\partial w_\alpha}{\partial x_i}\right] = a_\alpha\ ; \quad \frac{\partial \mathcal{L}_\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\tilde{U}_{i\alpha}\mathcal{L}_\alpha\right) - \frac{\partial}{\partial x_i}\left[\left(\Gamma+\Gamma_t\right)\frac{\partial \mathcal{L}_\alpha}{\partial x_i}\right] = b_\alpha\ , \quad \text{where} \quad \mathcal{L}_\alpha = L_\alpha w_\alpha$$

The source terms for weights and abscissas are calculated solving a ***linear algebraic system*** obtained from the population balance written as a balance equation for moments, after the application of the quadrature approximation:

$$(1-k)\sum_{\alpha=1}^{N}L_\alpha^k a_\alpha + k\sum_{\alpha=1}^{N}L_\alpha^{k-1}b_\alpha = \bar{S}_k^{(N)} + \bar{C}_k$$

$\bar{S}_k^{(N)}$: Source terms for moments

$\bar{C}_k$: Spurious terms due to the finite-mode representation

For N=2:

$$\begin{array}{c} m_0 \rightarrow \\ m_1 \rightarrow \\ m_2 \rightarrow \\ m_3 \rightarrow \end{array}\begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ -L_1^2 & -L_2^2 & 2L_1 & 2L_2 \\ -2L_1^3 & -2L_2^3 & 3L_1^2 & 3L_2^2 \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \\ b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} \bar{S}_0 \\ \bar{S}_1 \\ \bar{S}_2 + \bar{C}_2 \\ \bar{S}_3 + \bar{C}_3 \end{pmatrix}$$

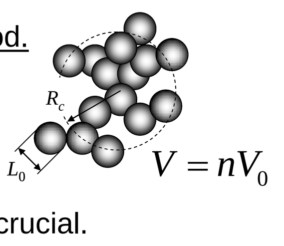
5 Modelling of particle morphology

The algorithm is simple and has low computational cost (solution of a linear system of rank (1+M)*N, and of (1+M)*N transport equations, where M is the number of internal coordinates

<u>Accounting for two internal coordinates does not increase the complexity of the method.</u>

• Soot aggregates have fractal properties: **fractal dimension, D_f (scaling exponent)**

• The collision radius of the aggregate can be calculated as $R_c = k_f\frac{L_0}{2}\left(\frac{V}{V_0}\right)^{1/D_f}$



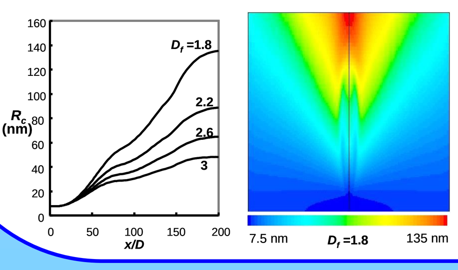
• The accurate modelling of D_f, which affects both **morphology** and **collision rate**, is crucial.

The solution of a **bivariate PBE**, in terms of particle volume and surface area, is important to model the evolution of soot particle morphology.

When the **monovariate PBE** is solved, we have to make some simplifying assumptions:

a) Superimposition of constant D_f in the whole domain

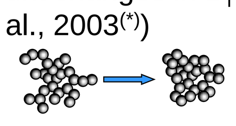
Collision radius



b) Use of an algebraic model to take into account changes in D_f due to aggregation and restructuring (Artelt et al., 2003(*))

Collision time: $t_c = \left(\bar{\beta}\cdot m_0\right)^{-1}$

Restructuring time: $t_r = \sqrt{15\nu/\varepsilon}$ $\Rightarrow \tau = \frac{t_c}{t_r}$



$$D_f = \begin{cases} D_{f,\min} + \left(D_{f,0} - D_{f,\min}\right)^{1/\tau^s} & \tau \le 1 \\ D_{f,\max} - \left(D_{f,\max} - D_{f,0}\right)^{\tau^s} & \tau > 1 \end{cases} \qquad D_{f,0} = \frac{1}{2}\left(D_{f,\min} + D_{f,\max}\right)$$

(*) Artelt C., Schmid H.J., Peukert W. (2003). On the relevance of accounting for the evolution of the fractal dimension in aerosol process simulations. *Journal of Aerosol Science*, **34**, 511-534.

6 The Bivariate Population Balance

Two internal coordinates: **Particle Volume** (V) and **Surface Area** (A)

The number density function is approximated as follows:

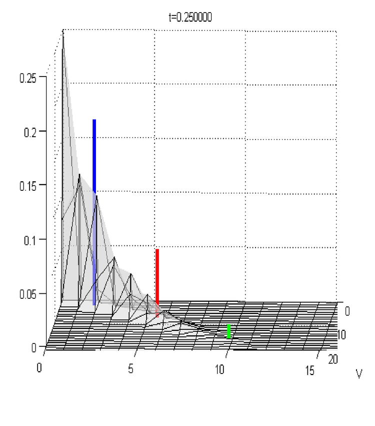
$$\tilde{n}(V,A;\mathbf{x},t) \approx \sum_{\alpha=1}^{N} w_\alpha(\mathbf{x},t)\delta\left[V - V_\alpha(\mathbf{x},t)\right]\delta\left[A - A_\alpha(\mathbf{x},t)\right]$$

Aggregation:

• Volume is additive: $V_{i+j} = V_i + V_j$

• Surface Area is, for each particle, the area of the sphere of radius R_c, the particle collision radius:

$$A_{i+j} = \left(A_i^{\frac{D_f}{2}} + A_j^{\frac{D_f}{2}}\right)^{\frac{2}{D_f}}$$



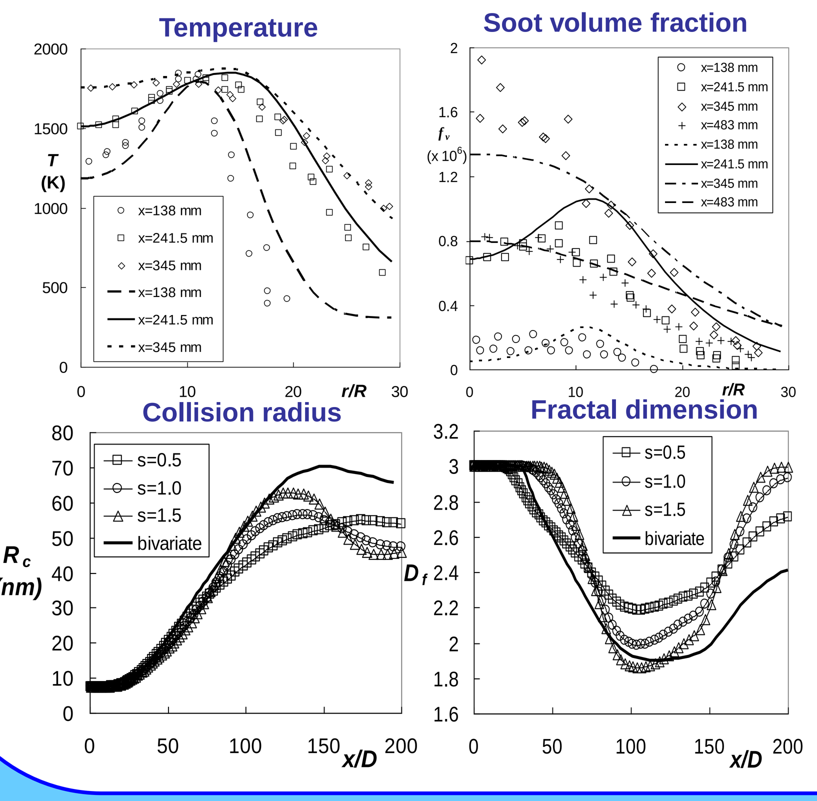
Two internal coordinates → **Mixed moments** $m_{k,l} = \int_0^\infty\int_0^\infty V^k A^l n(V,A)\,dVdA$

For a given number of nodes, the choice of the moments to be tracked is not unique, and affects both accuracy and numerical stability.

The method has been validated by comparison with the results of a **Direct Simulation Monte Carlo** code, for simple homogenous aggregating and restructuring systems.

7 Results

Case study: the non-premixed ethylene-air turbulent flame A (Kent & Honnery, 1987(*))



Simplified kinetics was implemented for nucleation, surface growth and oxidation of soot particles.

A Brownian kernel was used for aggregation

• Only modelling the evolution of fractal dimension it is possible to describe the restructuring process

• The algebraic model used with the monovariate population balance seem to overpredict the rate of restructuring, and the tuning parameter *s* is not effective to improve the prediction

• The algebraic model does not allow to take into account the distribution of fractal dimension.

(*) Kent J. H., and Honnery D. (1987). Soot and mixture fraction in turbulent diffusion flames. *Combustion Science and Technology*, **54**, 383-397.

8 Conclusions

• The **DQMOM** is a valid approach for the solution of the population balance equation within a CFD code, both in the monovariate and in the bivariate case.

• Simplified kinetics for nucleation, growth, oxidation and aggregation lead to good results in the flame under investigation.

• In order to take into account properly the evolution of **particle morphology** (fractal dimension) it is important to solve the **bivariate population balance**, i.e. to follow the evolution of both particle volume and surface area.

… Future Developements

• More detailed investigation of nucleation, growth, oxidation and aggregation rates, with particular attention to the dynamics of **nanoparticles**, and validation with other turbulent flames.

• Validation of the model with experimental data on soot **particle size distribution** in <u>laminar flames</u>.