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# THE ROLE OF THERMOPHORETIC EFFECT IN THE FORMATION OF SOOT FROM LIQUID FUELS

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## INTRODUCTION

In order to rationalize soot formation in two-phase combustion, the related dynamics can be conveniently studied in simpler systems. In the latest twenty years, experimental activity in drop towers and in the outer space have allowed to investigate the combustion of isolated droplets in microgravity conditions, i.e. spherically symmetric systems where buoyancy effects and slip velocity are absent, yet still containing the major phenomena affecting real combustion (unsteady evolution, convection, gas and soot radiation, heterogeneous properties and so on). In such conditions, it had been speculated [1] that a key role in soot formation is played by thermophoretic effect, because of which solid particles are transported towards the droplet surface, thus increasing their residence times in the fuel-rich area, where soot growth is kinetically favoured.

The spherical symmetry also allows to numerically study these systems with a relatively low computational weight. The importance of thermophoresis in the dynamics of soot formation can thus be investigated in a variety of operating conditions (droplet size, pressure, composition, etc.), which is the subject of this work. Starting from a description of the constitutive parts of the isolated-droplet model, the transient dynamics of soot formation in *n*-heptane droplets is analysed. The impact of the submodel describing thermophoresis is considered in detail, and indications about its possible refinements are provided.

## 1 MODELING SOOT FORMATION IN TWO-PHASE SYSTEMS

### 1.1 Isolated droplet model

The numerical model describing the transient evolution of an isolated droplet was developed by Cuoci et al. [4]. It is implemented through a finite-difference approach, and both gas-phase and liquid phase are spatially discretized, and thermodynamic and flux equilibrium is imposed at the interface. At initial conditions, the droplet is numerically ignited by simulating a spark: a temperature profile peaking at ~2000 K is imposed near the interface.

### 1.2 Kinetic model

The gas-phase kinetic model is based on the POLIMI mechanism [2]: the hierarchy, generality and modularity features behind it allow to easily isolate the part of interest for the purposes of this work. The coupling with solid-phase is carried out through the discrete sectional approach recently devised by Saggese and coworkers [3]. It represents the aerosol distribution through a 2-dimensional discretization into pseudo-species, called BINs, lumping a class of particles according to i) size and ii) composition in terms of H/C ratio. Soot model is conceived according to a reaction-class approach: doing so, the coupled system can be described in a pseudo-homogeneous way. The complete mechanism is made up of 297 species and 16797 reactions.

### 1.3 Thermophoretic effect

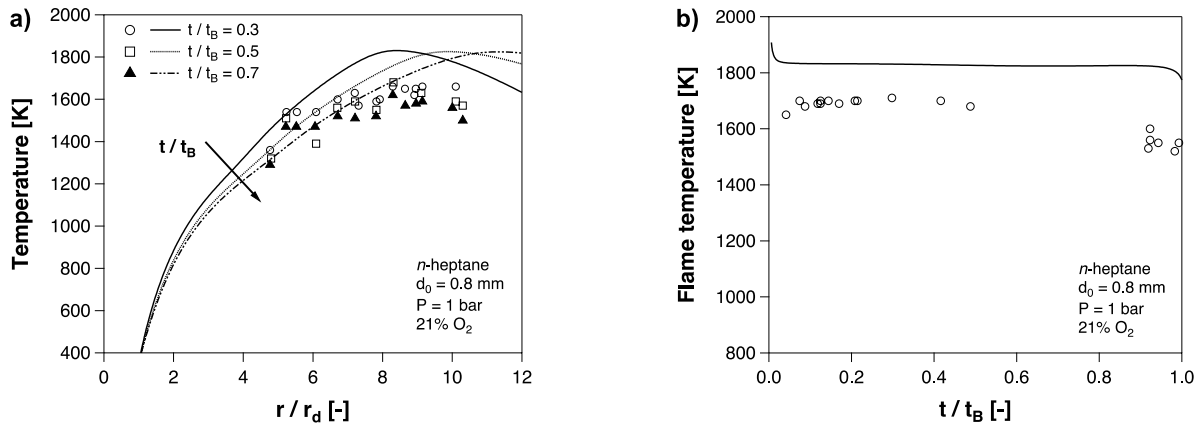
Thermophoresis is a phenomenon involving solid particles, which undergo a force field proportional to the temperature gradient. The most commonly accepted formulation of such effects follows the law proposed by Waldmann [5], according to which thermophoretic velocity is calculated as:

$$v_{th} = -\frac{3}{4 + \left(1 + \frac{\rho a}{8}\right)} \frac{m \nabla T}{r T} = -K_{th} \frac{m \nabla T}{r T} \quad (1)$$

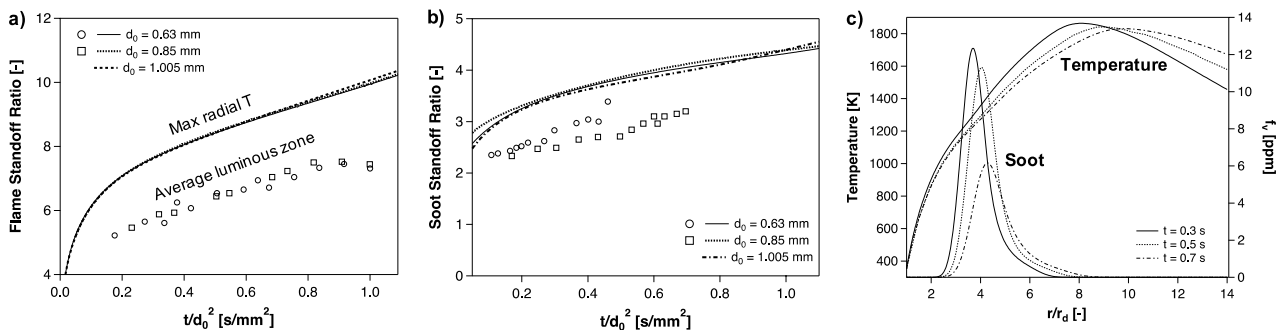
where  $\mu$  is the gas dynamic viscosity,  $\rho$  is gas density and  $\alpha$  is the accommodation factor, which is commonly accepted as 0.9, thus leading to an overall coefficient  $K_{th}$  equal to  $\sim 0.554$ . In the droplet model, such term is added to soot pseudo-species.

## 2 DROPLET COMBUSTION OF SOOTING FUELS

Based on the experimental activity carried out in the latest decades, the combustion of *n*-heptane droplets has been investigated in a wide range of operating conditions. The combustion of *n*-heptane droplets at ambient pressure was reproduced through the described 1-D model. Results are shown in Figure 1 for a sample droplet, and show that the model is able to replicate the shape of the radial temperature profile. An overestimation at the outer part of the temperature profile can be observed, but such profiles need to be corrected because of the heat loss from the thermocouple [6], estimated as equal to  $\sim 80$  K. Figure 1a also points out that the flame front, evaluated as the location of the maximum temperature profile) cannot be considered stationary, but rather it progressively gets farther from the droplet surface. The thickness of flame and soot shell is shown in Figure 2. They are expressed in terms of Flame Standoff Ratio (FSR) and Soot Standoff Ratio (SSR). The model is able to predict the progressive increase of both ratios over time. An offset is present between experimental and predicted FSR, which is most likely due to the different reference used for its evaluation: here, FSR has been calculated as the radial coordinate where maximum temperature is reached, while experimentally [6] its evaluation had been based on the position of the yellow luminous zone, i.e. the region where soot is present at sufficiently high temperatures (Figure 2c).



**Figure 1. Flame evolution over time in a n-heptane droplet: experimental data [6] vs numerical predictions. a) temperature profile at different time steps. b) flame temperature over time.**



**Figure 2. Experimental [7] vs predicted a) Flame and b) Soot Standoff Ratios. c) Correspondence between temperature and soot volume fraction profiles.**

On the other hand, an offset of about one diameter is present in the estimation of SSR (Figure 2b), which is numerically evaluated as the coordinate where the volume fraction  $f_v$  is maximum. In order to understand this disagreement, the different factors determining its position must be considered.

## 2.1 Role of thermophoretic effect in the transient soot evolution

The evolution of soot profile is mainly determined by the residence times of particles in the fuel-rich area, far from the oxidation zone where it is consumed (Figure 2c). Residence times depend on the different velocities acting on them: (i) the convective velocity due to evaporation, known as Stefan flow (Figure 3a); (ii) the diffusiophoretic velocity due to composition gradients, which is usually small for such large particles; (iii) thermophoretic velocity (Figure 3b). Therefore, the balance between (i) and (iii) determines the location of the equilibrium point inside the shell.

Therefore, a stronger thermophoretic effect would push the soot shell towards the droplet. This would lower SSR profile, but would also allow a longer permanence of soot in the favourable region, thus fostering its accumulation. As shown in Figure 3, the competition between (i) and (iii) generates two equilibrium points, out of which only the first is stable (because of its negative derivative). As a result, SSR is located in correspondence of it, and increases over time.

In order to quantify the role of thermophoresis in this balance, a sensitivity analysis of the model to the thermophoretic velocity has been carried out. Figure 4 shows the results for two different diameters. FSR slightly decreases at the end of droplet combustion, as a result of the radiative interaction with the soot layer. The higher amount of soot increases radiation and lowers the flame temperature. Instead, SSR is much more sensitive to such variation, and a higher thermophoretic velocity pushes the soot shell towards the droplet. This has an influence on the amount of produced soot, too, as shown in Figure 5. Here, the role of thermophoresis becomes apparent. Without considering it, soot concentrations are 1-2 ppm, comparable to gas-phase diffusion flames.

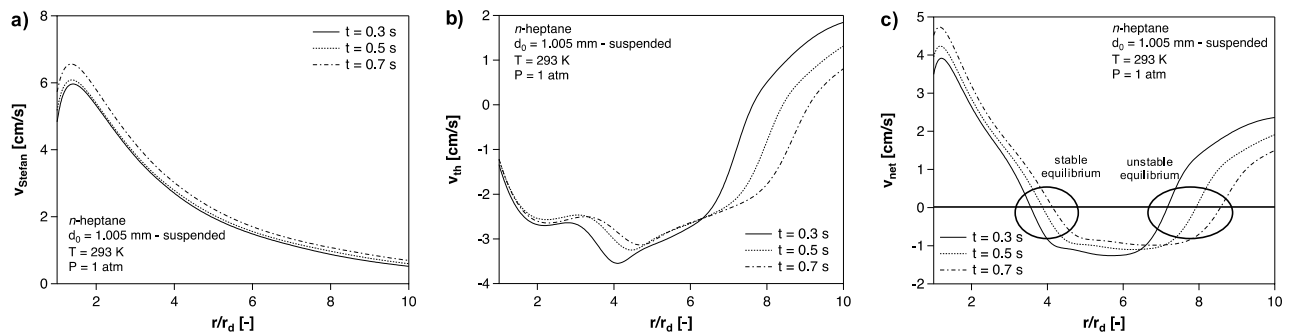


Figure 3. Predicted velocity profiles at different time steps: a) Stefan velocity. b) The thermophoretic velocity. c) Net velocity.

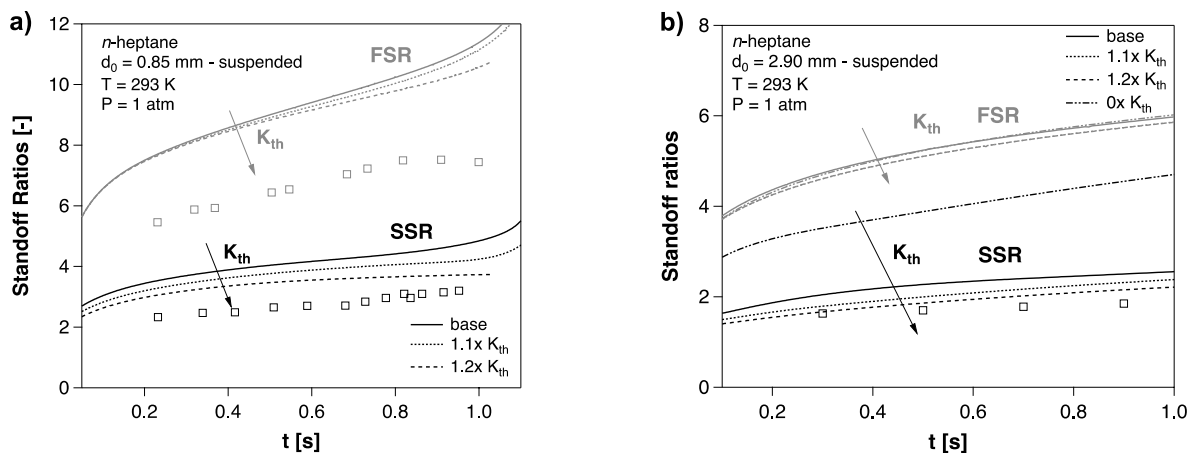


Figure 4. Sensitivity of FSR/SSR to  $K_{th}$  value (Eq. 1). a)  $d_0 = 0.85$  mm [7]. b)  $d_0 = 2.90$  mm [8].

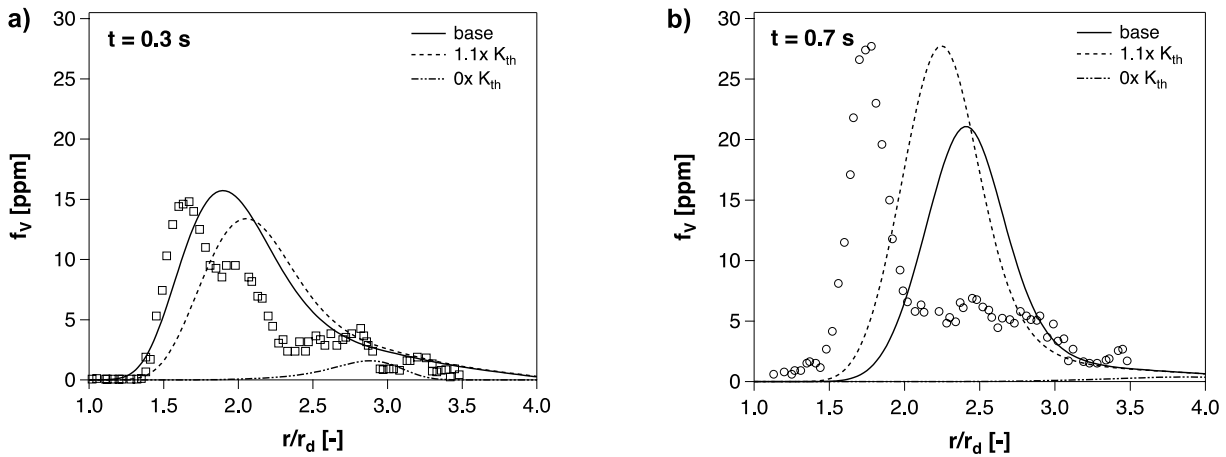


Figure 5. Sensitivity of  $f_v$  to  $K_{th}$  at different times.  $d_0 = 2.90$  mm [8].

### 3 CONCLUSIONS

This work has shed light on the role of thermophoresis in the dynamics of soot formation two-phase combustion. Two main conclusions have been drawn. First of all, it has been recognized as the determining factor causing the very high volumetric fractions, which have been obtained experimentally. Moreover, it has been found out that the simplified formulation of the thermophoretic law underestimates the actual volume fractions, and correspondingly overestimates the thickness of the soot shell. Therefore, further work is needed in this direction towards the development of a more detailed formulation.

### ACKNOWLEDGEMENTS

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