

A THERMODYNAMICALLY CONSISTENT METHODOLOGY TO DEVELOP PREDICTIVE SIMPLIFIED KINETICS FOR DETONATION SIMULATIONS

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Abstract

The number of species and elementary reactions needed for describing the oxidation of fuels increases with the size of the molecule, and in turn, the complexity of detailed mechanisms. Although the kinetics for conventional fuels (H_2 , CH_4 , C_3H_8 ...) are somewhat well-established, chemical integration in detonation applications remains a major challenge. Significant efforts have been made to develop reduction techniques that aim to keep the predictive capabilities of detailed mechanisms intact while minimizing the number of species and reactions required. However, as their starting point of development is based on homogeneous reactors or ZND profiles, reduced mechanisms comprising a few species and reactions are not predictive. The methodology presented here relies on defining virtual chemical species such that the thermodynamic equilibrium of the ZND structure is properly recovered thereby circumventing the need to account for minor intermediate species. A classical asymptotic expression relating the ignition delay time with the reaction rate constant is then used to fit the Arrhenius coefficients targeting computations carried out with detailed kinetics. The methodology was extended to develop a three-step mechanism in which the Arrhenius coefficients were optimized to accurately reproduce the one-dimensional laminar ZND structure and the $D-\kappa$ curves for slightly-curved quasi-steady detonation waves. Two-dimensional simulations performed with the three-step mechanism successfully reproduce the spectrum of length scales present in soot foils computed with detailed kinetics (i.e., cell regularity and size). Results attest for the robustness of the proposed methodology/approximation and its flexibility to be adapted to different configurations.

1. INTRODUCTION

To date, numerical simulation of detonations lacks predictive capabilities (e.g. cell sizes, quenching limits, etc.). Despite having achieved partial success using detonation solvers with detailed kinetics for *simple* fuels such as hydrogen (9 species/21 reactions) [1–3], the stringent resolution requirements make multidimensional simulations of detonations very time consuming and thus restricted to research groups with extraordinary computational resources. For hydrocarbons with more elaborate chemical kinetics, it is still prohibitively expensive, as they may include hundreds of species and thousands of reactions [4].

As a consequence, the detonation community very often resorts to reduced chemical schemes. The most widespread models are based on one-step Arrhenius-like chemistry that only accounts for reactants and products. The complexity of the constructs can increase [5–8], including additional steps (e.g., 3-step, 5-step) and/or species surrogates (e.g., radical pool). The methodology to design them is basically to perform a fitting exercise of the parameters thought to control the detonation physics. Namely, conventional approaches are to match the constant volume or pressure induction time obtained with a 0-D reactor, or to mimic the ZND profiles calculated with a 1-D ideal model; always using detailed chemistry as a reference. Recently, alternative methodologies [9, 10] propose to include the physics that is expected to play a role in the problem considered (e.g. propagation in tubes, initiation, quenching, etc.) into the fitting procedure. The latter use extensions to the ZND model adding loss terms due to front curvature (κ) [9] and/or friction to walls (c_f) [10] aiming to reproduce the critical conditions that these models yield ($\kappa_{crit} / c_{f,crit}$); so far the results reported by the authors are encouraging.

In this work, we propose a new method to obtain simplified kinetics of predictive nature. The methodology entails creating a virtual species that recovers temperature-dependent thermodynamic properties and a kinetic scheme that mimics the induction and reaction times measured in canonical 0/1-D configurations. In addition, the capability of the simplified kinetic scheme to reproduce 1-D detonations with curvature losses (i.e., $D - \kappa$ curves) and 2-D detonations propagating in channels (e.g., cell size and instantaneous detonation fields) is assessed by comparing the results with those obtained using a detailed chemical scheme for stoichiometric H_2-O_2 mixtures.

2. FITTING PROCEDURE

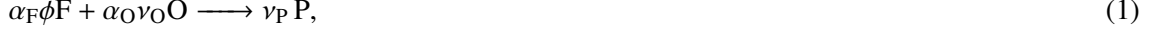
In developing simplified kinetic models two main objectives emerge. First, obtaining the correct heat release in the combustion process, and second, getting a specific set of kinetic properties, e.g. induction time. The purpose of this work is to present a methodology to construct simplified mechanisms where these two objectives are independent of each other. To that end, we first outline the constraints that a product specie should follow to mimic the detailed mechanism’s behavior. Thereafter, we propose a fitting procedure to match reference results for thermodynamic and kinetic properties.

2.1. Virtual Species definition

In the present work, we extend the original formulation developed by M. Cailler et al. [11] for virtual species. Let us consider an initial mixture of F, fuel, and O, oxidizer, at a given equivalence ratio ϕ . By imposing an equilibrium condition to the system, e.g. constant volume and internal energy, the final state will be described by the mass fraction of the product species Y_i . The number of product species

considered in the equilibrium is determined by the reference kinetic model employed.

The virtual species formulation considers that the two reactants, F and O, will combust into a single species P which represents the original mixture Y_i through the global reaction



where α_i , is the consumption ratio and ν_i is the stoichiometric coefficient for the i th specie in the global reaction.

In the reference mechanism, the initial mixture composed by $N^0 = \sum_{i=1}^{N_{sp}} n_i^0$ moles (with $n_F^0 = \phi$ and $n_O^0 = \nu_O$) will react into the final concentration $n_i^f = \frac{W^0}{W^f} X_i^f N^0$, being X_i the mole fraction of the i th specie and W the mean molecular weight. Superscripts 0 and f refer to the initial and equilibrium states, respectively. The global reaction coefficients are defined as

$$\alpha_i = (n_i^0 - n_i^f) / \nu_i^0, \quad \nu_P = \sum_{i=1}^{N_{sp}} \max(n_i^f - n_i^0, 0). \quad (2)$$

From this assumption, the mass, enthalpy, and free Gibbs energy conservation equations give the following constraints:

$$W_P = \sum_{i=1}^{N_{sp}} \frac{\max(n_i^0 - n_i^f, 0)}{\nu_{P_c}} W_i \quad (3)$$

$$Y_P = \sum_{i=1}^{N_{sp}} \max(Y_i^0 - Y_i^f, 0) \quad (4)$$

$$H_P^f = \sum_{i=1}^{N_{sp}} \frac{Y_i^f - (1 - \alpha_i) Y_i^0}{Y_P} H_i^f \quad (5)$$

$$S_P^f = \sum_{i=1}^{N_{sp}} \frac{Y_i^f - (1 - \alpha_i) Y_i^0}{Y_P} S_i^f + \frac{\mathcal{R}}{W_P} \ln X_P^f - \sum_{i=1}^{N_{sp}} \frac{Y_i^f - (1 - \alpha_i) Y_i^0}{Y_P} \frac{\mathcal{R}}{W_i} \ln X_i^f. \quad (6)$$

Where \mathcal{R} is the universal gas constant, H_i and S_i are the enthalpy and entropy of the i th specie.

2.2. Thermodynamic fitting

We will restrict our attention to stoichiometric hydrogen-oxygen mixtures at atmospheric conditions. The San Diego mechanism [12] will be employed as the reference chemistry. The standard thermodynamic dependence of Gordon and McBride [13] relates the i^{th} specie properties with a temperature

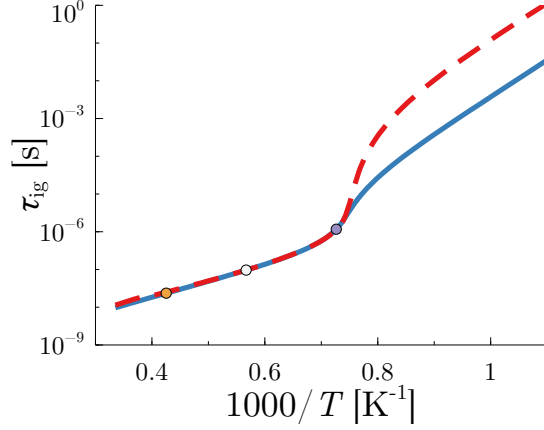


Figure 1: Ignition delay times versus inverse of temperature for $\text{H}_2\text{-O}_2$ mixtures with equivalence ratio of $\phi = 1$ at initial conditions defined by the *Von Neumann* state of a laminar detonation propagating at D_{CJ} in an ambient of initial temperature $T_0 = 300$ K and pressure $P_0 = 1$ bar. Solid line represents computations made with the reference mechanism; dashed line represents results obtained with 3-step mechanism; markers represent initial conditions of $D/D_{CJ} = [1.2, 1, 0.85]$, from left to right respectively.

polynomial as follows

$$\frac{C_{p,i}}{\mathcal{R}W_i} = \sum_{k=0}^4 a_{i,k} T^k \quad (7)$$

$$\frac{H_i}{\mathcal{R}TW_i} = \sum_{k=0}^4 \frac{a_{i,k}}{k+1} T^k + \frac{a_{i,5}}{T} \quad (8)$$

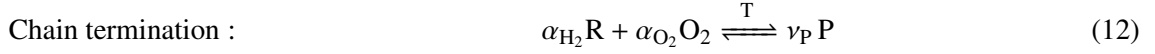
$$\frac{S_i}{\mathcal{R}W_i} = a_{i,0} \ln T + \sum_{k=1}^4 \frac{a_{i,k}}{k} T^k + a_{i,6}. \quad (9)$$

Although this formulation allows us to express polynomial coefficients of the virtual species as a linear combination of the original species, see [14], in the present work we propose a different approach. The behavior of unsteady multidimensional cellular detonations results in a wide range of postshock states (*von Neumann* conditions) due to the leading shock velocity oscillations (over/under driven cycles) observed during their propagation. We thus fit the polynomial coefficients for a set of equilibrium conditions obtained for postshock states in the normalized leading shock velocity range $D/D_{CJ} \in [0.8, 1.2]$. $C_{p,i}$, H_i , and S_i are fitted considering a single value of W_p for the product specie. This approach allows us to correctly reproduce the burnt gas conditions in ZND profiles as well as the steady *Chapman-Jouguet* speed, D_{CJ} , for three representative D/D_{CJ} values [0.85, 1.0, 1.2].

2.3. Kinetic fitting

In kinetic modeling, two classical approaches arise when a single product specie is considered: the single-step mechanism or the three-step chain-branching mechanism. More sophisticated approaches (including more intermediate steps) or customized functions that do not follow the Chemkin format (e.g. a switch that decouples the heat release reaction from the induction time, see [15]) have not been considered in this work. We will focus on the more generic 3-step chain-branching kinetics, however, it should be noted that the present formulation is capable of correctly predicting D_{CJ} for single-step kinetics as well.

A generic chain-branching mechanism can be defined as



with their corresponding reaction rates given by

$$\omega_{\text{I}} = C_{\text{H}_2}^2 B_{\text{I}} e^{-T_{\text{I}}/T} \quad (13)$$

$$\omega_{\text{B}} = C_{\text{H}_2} C_{\text{R}} B_{\text{B}} e^{-T_{\text{B}}/T} \quad (14)$$

$$\omega_{\text{T}} = \left(C_{\text{H}_2} C_{\text{O}_2} - C_{\text{P}}^{\nu_{\text{P}}} \frac{1}{K_{\text{T},e}} \right) B_{\text{T}} e^{-T_{\text{T}}/T} \quad (15)$$

where C_i is the molar concentration of the i th specie and $K_{\text{T},e}$ is the equilibrium constant for the termination reaction. A total of six free parameters appear in the formulation (the pair (B_k, T_k) for each reaction). Assuming that B_{T} controls the induction length, l_{ind} , or ignition delay time, τ_{ig} , for the ideal detonation propagation velocity ($D = D_{\text{CJ}}$), 5 parameters need to be determined in the fitting procedure.

A high activation energy analysis of the previous 3-step chain-branching kinetics scheme yields the following relations

$$\frac{B_{\text{B}}}{B_{\text{T}}} = \frac{1}{2\phi} e^{(T_{\text{B}} - T_{\text{T}})/T_{\text{C}}}, \quad \tau_{\text{ig}}^{\text{high}} \sim \frac{e^{T_{\text{B}}/T_{\text{vN}}}}{B_{\text{B}}}, \quad \tau_{\text{ig}}^{\text{low}} \sim \frac{T_{\text{vN}}^2}{(T^f - T_{\text{vN}})T_{\text{I}}} \frac{e^{T_{\text{I}}/T_{\text{vN}}}}{B_{\text{I}}}, \quad (16)$$

where T_{C} is the crossover temperature. After computing constant volume ignition delay times with the reference mechanism, see fig. 1, T_{I} , T_{B} , and T_{C} are directly obtained using the $\log \tau_{\text{ig}} - 1/T$ slopes. Here, the initial conditions of the homogeneous reactor are defined as the *von Neumann* state for each D/D_{CJ} . The fitting procedure is finalized by assuming that $B_{\text{I}}/B_{\text{B}} = \epsilon \ll 1$ and finding the appropriate value for T_{T} that recovers the maximum thermicity value in the ZND profiles; see Figure 2. It should be noted that fuel is fully converted into radical species R by equations (10) & (11) but R is not completely burned in equation (12). In the burned gas condition, R represents the amount of H_2 that remains unburned whereas in the fresh mixture, that is before ignition occurs, it denotes the amount of H_2 plus radical ignition precursor present in the system or just an ‘‘activated’’ H_2 species.

3. 1-D RESULTS

3.1. ZND profiles

The 3-step chain-branching kinetics just developed is first used to compute the ideal ZND profiles of a stoichiometric $\text{H}_2\text{-O}_2$ mixture at initial temperature and pressure of $T_0 = 300$ K and $P_0 = 100$ kPa respectively. The results in Figure 2 show that the new 3-step model is able to capture quite well the *von Neumann* (vN) conditions, the induction length, and the thermicity profiles. These features were expected to match as some of the fitting parameters were tuned against these parameters, namely, the pre-exponential factor, B_{T} , with the former and the termination crossover temperature, T_{T} , with the latter. Note that only minor differences are observed after the main energy release stage. This is because the product species in the detailed mechanism computations are not constant while in the simplified scheme, only a single product specie is considered. In the end, when all the reactants reach chemical equilibrium, the differences become rather minor.

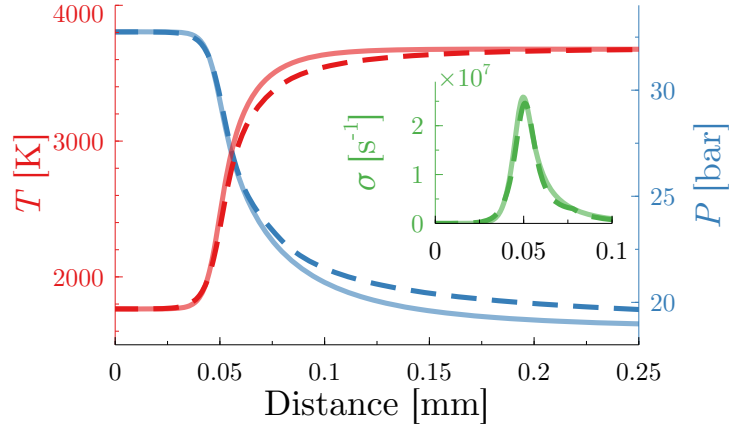


Figure 2: Temperature, pressure and thermicity profiles of a steady laminar detonation for $\text{H}_2\text{-O}_2$ mixtures with an equivalence ratio of $\phi = 1$ propagating in an ambient gas of initial temperature $T_0 = 300$ K and pressure $P_0 = 1$ bar. Solid lines represent computations made with the reference mechanism and dashed lines represent results obtained with the 3-step mechanism.

3.2. D - κ curves

One of the simplest extensions to the ZND model is derived by including curvature losses to the reactive Euler equations. The code developed by Veiga-López et al. [9, 16] is used in this work to compute $D/D_{CJ} - \kappa$ curves, where κ represents the average curvature of the detonation front. The system of equations reads:

$$\begin{aligned} \frac{d\rho}{dt} &= -\rho \frac{(\dot{\sigma} - w(1 - \eta)\alpha)}{\eta}, \\ \frac{dw}{dt} &= w \frac{(\dot{\sigma} - w\alpha)}{\eta}, \\ \frac{dp}{dt} &= -\rho w^2 \frac{(\dot{\sigma} - w\alpha)}{\eta}, \\ \frac{dY_i}{dt} &= \frac{W_i \dot{\omega}_i}{\rho}, \quad (i = 1, \dots, N), \\ \dot{\sigma} &= \sum_{i=1}^N \left(\frac{\bar{W}}{W_i} - \frac{h_i}{c_p T} \right) \frac{dY_i}{dt}, \quad \alpha = \frac{1}{A} \frac{dA}{dx} = \kappa \left(\frac{D}{w} - 1 \right), \end{aligned}$$

where, ρ , w , p , and t are the mixture density, axial velocity in the wave-attached frame, pressure, and time, respectively. The mass fraction, molecular weight and net production/consumption rate per unit mass of species i are given by Y_i , W_i and $\dot{\omega}_i$. Here $\eta = 1 - M^2$ is the sonic parameter and $M = w/a_f$ is the Mach number relative to the leading shock computed using the frozen speed of sound, a_f . $\dot{\sigma}$ is the thermicity, α the axial area change, \bar{W} is the mean molar mass of the mixture, c_p the mixture specific heat at constant pressure, and h_i is the specific enthalpy of species i .

For each detonation speed below D_{CJ} there is only a possible value of front curvature κ that yields a steady solution with no numerical singularities at the sonic point (i.e., $\eta = 0$). The resulting $D/D_{CJ} - \kappa$ curve is shown in Fig. 3 for the range of detonation velocities of interest $D/D_{CJ} \in [0.8, 1.0]$.

Previous analyses with simplified kinetics obtained assuming calorically perfect gases and simply using the constant volume ignition delay time as a fitting target, fail to reproduce these curves [9]. The 3-step kinetics proposed here yields $D/D_{CJ} - \kappa$ curves that are almost indistinguishable from those obtained with the detailed mechanism throughout the range of velocity deficits, D/D_{CJ} , considered. Most importantly, it yields the same critical curvature value, κ_{crit} .

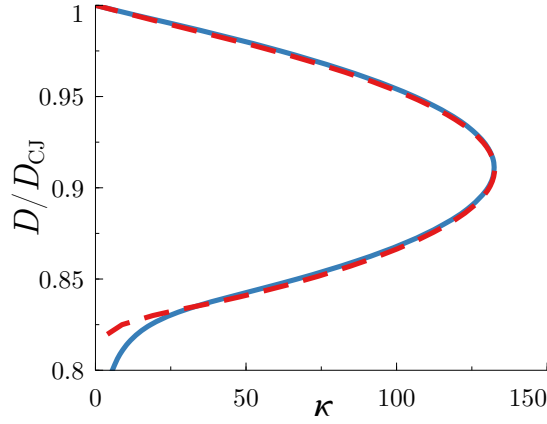


Figure 3: D/D_{CJ} versus κ curve. Solid line represent computations made with the present reference mechanism, dashed line represent results obtained with 3-step mechanism.

4. 2-D RESULTS

The capability of the new simplified kinetic scheme to reproduce the dynamics of multidimensional cellular detonations propagating in 2- D channels is assessed next. RESIDENT, a high-order compressible reacting Euler solver with detailed kinetics [2] will be used for the calculation. A computational domain of $L_x \times L_y = 50 l_{ind} \times 250 l_{ind} = 10 \text{ mm} \times 2 \text{ mm}$ is chosen to have ample space for the development of several detonation cells along the height of the channel. The spatial resolution is fixed at $l_{ind}/10$ which has been found to be sufficient to ensure that the inductions region is adequately resolved. The detonations are propagated until they reach a steady propagation velocity of about $D_{CJ} \pm 2\%$.

4.1. Temperature fields

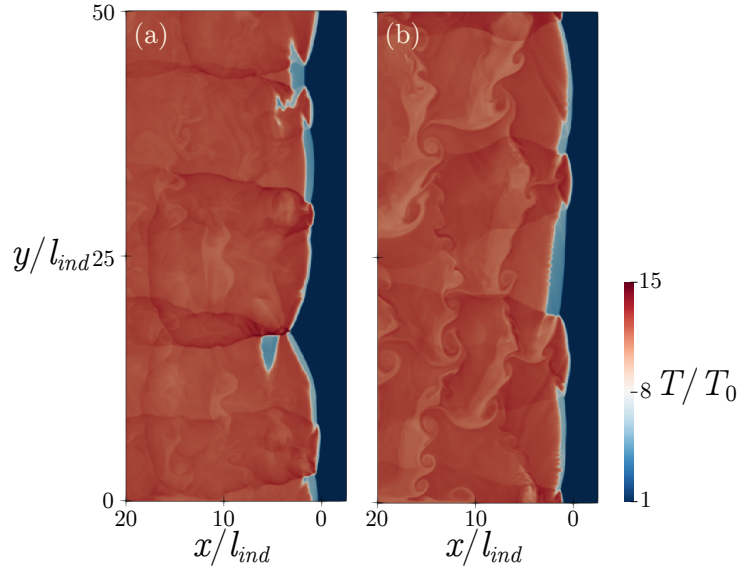


Figure 4: Temperature fields obtained with (a) detailed kinetics and (b) the 3-step reduced scheme, for a quasi-steady propagating wave at D_{CJ} .

The dimensionless instantaneous temperature fields are shown in Fig. 4, taken at $14.57 \mu\text{s}$ after ignition corresponding with a distance $x/l_{ind} = 1036.5$ from the ignition source. The resulting fields are quite

similar and capture the final equilibrium temperature ($T \sim 12T_0$) behind the front. Note that for the H_2 - O_2 system, this was one of the worst features of the simplified schemes used in [2] as a result of the constant molecular weight approximation. The presence of additional unburned pockets in the detailed chemistry field for the timestep shown is anecdotal as these are present in the 3-step chain-branching results as well but at different time instances.

4.2. Detonation cellular structure

The numerical *soot-foils* obtained with both mechanisms are included in Fig. 5.

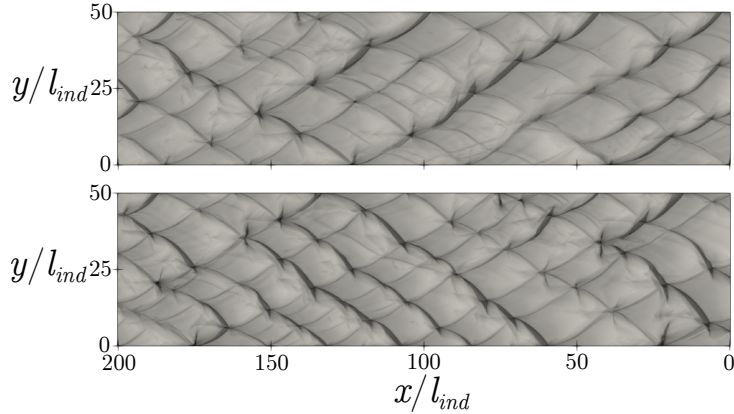


Figure 5: Numerical *soot-foils* showing the distribution of cell sizes (λ). Top represents computations made with the 3-step mechanism, bottom represents results obtained with the reference mechanism. Channel width $h = 2\text{mm}$.

The detonation cell sizes were manually measured from the *soot-foils* by selecting a sample size of 100 cells and counting the amount of times that a certain cell size, λ , appears. The probability density function (PDF) of the resulting distribution is given in Fig. 6 together with its approximation to a normal distribution. The average cell size of the detailed and 3-step chain-branching kinetics are $\lambda_\mu = 15.26 l_{ind}$ and $\lambda_\mu = 15.01 l_{ind}$, respectively, exhibiting a deviation of $\sim 1.6\%$. The standard deviation, λ_σ , is underpredicted by 1 unit, 3.11 instead of 4.13, due to the presence of a larger spectrum of cell sizes (i.e., slightly-smaller cells) in the results obtained with the detailed mechanism. It is important to emphasize that the cell size was not a target in the fitting procedure and arises naturally as an output of the computations.

5. CONCLUSIONS AND FUTURE DIRECTIONS

A new methodology to obtain simplified 3-step mechanisms for detonation applications is presented in this work. The idea is to combine (i) a virtual species that accounts for the temperature variation of the thermodynamic properties of the mixture and (ii) a kinetic scheme that reproduces the induction time and detonation ZND profiles.

Comparison of the 2-D results using the simplified scheme for detonations propagating in channels with those obtained using a reference detailed chemical mechanism reveal that the instantaneous temperature profiles, numerical *soot-foils*, and the statistics of the detonation cell sizes are in excellent agreement.

Future directions are (i) to assess the performance of the simplified kinetics to capture limiting behaviors (i.e. quenching, re-initiation, propagation under yielding confinement), and (ii) to extend the methodology to hydrocarbon-based fuels such as methane, ethylene or dimethyl-ether (DME).

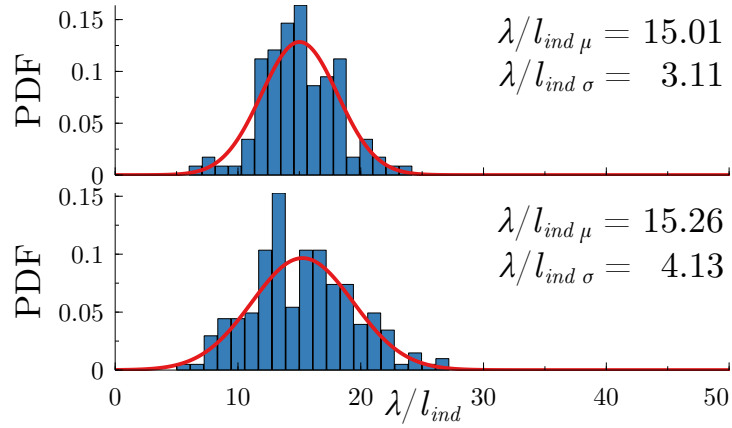


Figure 6: Numerical cell size distribution (λ). The top represents computations made with the 3-step mechanism, the bottom represents results obtained with the reference mechanism. PDF has been fitted into a normal distribution function with its mean value, μ , and its standard deviation, σ .

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