Work-in-progress: Thermal ignition revisited with three-dimensional molecular dynamics: role of fluctuations in activated collisions

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The current work investigates the problem of thermal ignition in a homogeonous gas using a three-dimensional molecular dynamics perspective. This is an extension of previous work which was completed in two dimensions [1]. The simple model that is adopted assumes a system of reactive spheres of type A and B in a fixed domain that react to form type C products if an activation threshold for impact is surpassed. The result for ignition delay are compared with those obtained from a continuum description with the reaction rate evaluated from kinetic theory assuming local thermodynamic equilibrium and Maxwell-Boltzmann statistics. This is done in order to assess the role played by molecular fluctuations on the ignition behaviour.

Results from two-dimensional simulations using this model shows two regimes of non-equilibrium ignition whereby ignition occurs at different times as compared to that for homogeneous ignition assuming local equilibrium. The first regime is at low activation energies, where the ignition time is found to be higher than that expected from theory for all values of heat release. The lower reaction rate is shown to occur due to a departure from local equilibrium for the different species, in agreement with predictions from Prigogine and Xhrouet [2]. In this low activation energy regime, the ignition times from molecular dynamics are also found to be independent of domain size and there is little variance between different realizations under similar conditions, which suggests that the ignition is spatially homogeneous. The second regime occurs at high activation energies and sufficiently large heat release values. In this high activation energy regime, ignition times are found to be dependent on domain size. Results for larger systems agree with the expectations by Prigogine and Mahieu [3], who demonstrate that the inclusion of a sufficiently large heat of reaction can yield a non-equilibrium reaction rate larger than expected for a homogeneous system in equilibrium. Results yield a large variance for ignition times under these conditions, which combined with the dependence on the domain size suggests a departure from homogeneous combustion. The results obtained are in qualitative agreement with experimental observations of auto-ignition at relatively low temperatures, where hot-spot ignition and associated ignition delays lower than predicted are generally observed.

The current work investigates whether a similar three-dimensional model can replicate the non-equilibrium ignition behavior observed by this previous work in two dimensions.

[1] Sirmas. N., Radulescu, MI. (2017). Thermal ignition revisited with two-dimensional molecular dynamics: Role of fluctuations in activated collisions. Combust. Flame. 177: 79-88.

[2] Prigogine, I., Xhrouet, E. (1949). On the perturbation of Maxwell distribution function by chemical reactions in gases. Physica. 15(11-12):913-932.

[3] Prigogine, I., Mahieu, M. (1950). Sur la perturbation de la distribution de Maxwell par des réactions chimiques en phase gazeuse. Physica. 16(1):51-64.