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Thermal ignition revisited with two-dimensional molecular dynamics: Role of fluctuations in activated collisions

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ABSTRACT

The problem of thermal ignition in a homogeneous gas is revisited from a molecular dynamics perspective. A two-dimensional model is adopted, which assumes reactive disks of types A and B in a fixed domain that react to form type C products if an activation threshold for impact is surpassed. Such a reaction liberates kinetic energy to the product particles, representative of the heat release. The results for the ignition delay are compared with those obtained from the continuum description with the reaction rate evaluated from kinetic theory assuming local thermodynamic equilibrium and Maxwell–Boltzmann statistics, in order to assess the role played by molecular fluctuations. Ignition times obtained using molecular dynamics are ensemble averaged over 100 simulations to address the statistics of the ignition event. Results show 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. 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, where small domains of 2.87×2.87 mean free paths yielded longer ignition delays than predicted, while for larger domain sizes, with 9.06×9.06 and 28.73×28.73 mean free paths, shorter ignition delays than those expected were observed. Results for larger systems agree with the expectations by Prigogine and Mahieu, 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.

1. Introduction

Ignition phenomena are central to combustion problems [1]. Experimentally, hot-spot ignition is generally observed at low temperatures [2,3], with ignition delays typically lower than predicted from classical chemical kinetic descriptions in a homogeneous system. Recently, detailed experiments suggest that spark induced ignition, for example, is an intrinsically stochastic process [4] when observed at the continuum scale. At low temperatures, ignition phenomena are typically of the thermal type [5]. The present paper focuses on this type of thermal ignition in a model system.

It has been proposed that the source of stochasticity in ignition phenomena may be attributed to fluctuations within the reactive medium, ranging from thermal fluctuations, to fluctuations in the number of activated collisions yielding ignition, hydrodynamic fluctuations from macroscopic effects [6] and hydrodynamic instabilities. Departures from equilibrium have also been considered, especially for small-scale systems [7,8].

Previous authors have demonstrated that exothermicity can play a strong role in introducing non-equilibrium effects and

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modifying the macroscopic rate of reactions from that obtained from the standard kinetic theory evaluation assuming local thermodynamic equilibrium (e.g., see [9]). Some of the earliest work by Prigogine and Xhrouet [10] estimated the change of the reaction rate by perturbation of the Maxwellian distribution for reactions with low levels of heat release, concluding that the non-equilibrium reaction rate is lower than the equilibrium rate for low activation energies.

In contrast, Prigogine and Mahieu [11] demonstrated that the inclusion of a sufficiently large heat of reaction can yield a non-equilibrium reaction rate larger than the one derived with the assumption of local equilibrium, using the same perturbation method. Similar results have been reported by others using comparable perturbation methods to a reactive system, demonstrating the roles that both activation energy and heat release in exothermic reactions have on the departure from equilibrium [12–14].

Microscopic models have been used to investigate the role that fluctuations and non-equilibrium effects have on reactive systems, whereby such models naturally account for fluctuations in reactive systems. Such studies have been conducted using Molecular Dynamics (MD) simulations [7,15,16] and models using the Direct Simulation Monte Carlo (DSMC) method [8,17–20]. Recently, models involving Landau's *fluctuating hydrodynamics* formalism [21] that bridges the molecular and continuum descriptions have been formulated to address problems in reactive systems [22], although the authors argue that particle based models are still needed in order to capture physics at the molecular scale.

Despite the extent of the previous work, few studies have addressed the arguments made by Borisov [6] regarding the role that fluctuations and hot-spot formations have on the ignition delay in auto-ignition phenomena. The present work addresses these issues by revisiting the classical problem of thermal ignition [1] via MD simulations in a simplified binary system of reactive gases. Such a system is suitable to look at low temperatures ignition, whereby the chemistry is shown to follow a thermal ignition process [5]. The MD description used in the present paper addresses the potential role of spatial non-homogeneities in the ignition problem, which is typically more difficult to consider in a continuum description using corrections of the type initiated by Prigogine and Xhrouet [10], as discussed above.

The present paper reports the results obtained from microscopic simulations of the molecular dynamics using the two-dimensional hard particle method with activated reactive collisions. Such hard particle models are attractive to study because of their low computational price, while still yeilding similar results to models implementing realistic inter-particle force potentials [9]. Since the pioneering work of Alder and Wainright [23], the dynamics of hard particles can be solved by solely solving for the time of collisions among different pairs of particles, where each successive collision can be predicted analytically. The system is evolved from collision to collision, or event to event, hence the name of the algorithm, the Event Driven Molecular Dynamics method (EDMD). The method can be readily applied to hundreds of thousands of particles on today's personal computers. In the current study, simulations are limited to 2D, as 3D simulations would require significantly more computational time using this method. It can be shown that in order to replicate a 2D system with N_{2D} disks in an area of $l \times l$, approximately $N_{3D} = N_{2D}^{3/2}$ spheres would be needed in a volume with similar length scales of $l \times l \times l$ in 3D. The computational time required to advance for a specified number of collisions per particle scales with $N \log N$ using the described method [24], thus requiring a 3D system to run for at least $\frac{3}{2}N_{2D}^{1/2}$ times longer than a system with similar scaling in 2D. Despite the idealization of a system in 2D, such a simplified model using EDMD is insightful and has been used for some of the earliest investigations of non-equilibrium reactive phenomena, such as ignition [15] and detonation wave propagation [25], albeit with a limited number of particles.

The present paper uses similar reactive dynamics assumed in these earlier papers to study the problem of homogeneous thermal ignition and compare with the predictions made from the continuum description, where the reaction rate is evaluated from classical kinetic theory arguments assuming local equilibrium [9]. Calculations are done in a fixed area, where the thermal ignition problem in the continuum regime is well understood [1]. In order to address the statistics of the ignition phenomena, especially at low temperatures, ensemble averaging is completed over multiple realizations for different parameters.

The paper is organized as follows. The first part describes the reactive system that is investigated, with the details regarding the MD simulations and the continuum description. In the second part, the results from MD are compared with those obtained from the continuum description in order to draw a conclusion of whether molecular fluctuations may be responsible for departures from homogeneous ignition and changes in the ignition delay times.

2. Methodology

2.1. Model description

The present model assumes an irreversible exothermic reaction of the form

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{C} + \text{heat} \tag{1}$$

in which only collisions among the reactants A and B can yield two product species C. This reactive model is similar to that presented by previous authors [7,15,16,18], with modified chemistry to allow for depletion of two distinct reactants. Such a description is desirable since fluctuations of species can be considered, and gives the flexibility of varying the ratio of reactants to study the effect of dilution on ignition.

The model assumes N_A and N_B number of type A and B reactive disks, respectively. Disks have a diameter d occupying a prescribed volume fraction η within a 2D fixed domain. In the reactive collision, each existing particle A and B transform into two reacted particles C. Disks A, B, and C have identical masses. All collisions are assumed to be elastic with the exception of a reactive collision, which gives an amount of chemical energy Q to each reacted particle in order to increase their kinetic energies. The changes in speeds of the reacting particles after impact occur along the line of action, while the tangential components remain unchanged. A schematic of this process is shown in Fig. 1. The activation energy necessary for reactions is taken as E_A. The activation energy can be related to the minimum impact velocity, u_{cr}, necessary for a reactive collision to occur between particles A and B,

$$\left| u_{\mathrm{A}(N)} - u_{\mathrm{B}(N)} \right| > u_{cr}, \tag{2}$$

which for a 2D system the relationship between E_A and u_{cr} is

$$u_{cr} = \sqrt{4E_\mathrm{A}}. \tag{3}$$

Video 1 in the supplementary material demonstrates the dynamics of the disks for such a system.

2.2. Molecular dynamics details

The MD model was established by implementing the collision rules for reactive and non-reactive encounters into an Event Driven Molecular Dynamics algorithm, as pioneered by Alder and Wainright [23], as also described by Pöschel and Schwager [24]. For each simulation, N_A and N_B disks of diameter d are initialized in a square domain with equal speeds and randomized trajectories.