Non-equilibrium effects on thermal ignition using molecular dynamics simulations

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Abstract

The present study addresses the role of molecular non-equilibrium effects in thermal ignition problems. We consider a single binary reaction of the form A+B→C+C. Molecular dynamics calculations were performed for activation energies ranging between $RT$ and $7.5RT$ and heat release of $2.5RT$ and $10RT$. The evolution of up to 10,000 particles was calculated as the system undergoes a thermal ignition at constant volume. Ensemble averages of 100 calculations for each parameter set permitted to determine the ignition delay, along with a measure of the stochasticity of the process. A well behaved convergence to large system sizes is also demonstrated. The ignition delay calculations were compared with those obtained at the continuum level using rates derived from kinetic theory: the standard rate assuming that the distribution of the speed of the particles is the Maxwell-Boltzmann distribution, and the perturbed rates by Prigogine and Xhrouet \cite{1} for an isothermal system, and Prigogine and Mahieu \cite{2} for an energy releasing reaction, obtained by the Chapman-Enskog perturbation procedure. The molecular results were
found in very good agreement with the latter at low temperatures, confirming that non-equilibrium effects promote the formation of energetic particles, that serve as seeds for subsequent reaction events: i.e., hot spots. This effect was found to lower the ignition delay by up to 30%. At high temperatures, the ignition delay obtained from the standard equilibrium rate was found to be up to 60% longer than the molecular calculations. This effect is due to the rapidity of the reactive collisions that do not allow the system to equilibrate. For this regime, none of the perturbation solutions obtained by the Chapman-Enskog procedure were valid. This study thus clearly shows the importance of non-equilibrium effects in thermal ignition problems, for all temperatures of practical interest.

Keywords:
thermal ignition, molecular dynamics, non-equilibrium effects, hot spots

1. Introduction

Thermal ignition of a reactive gas involves the classical coupling between the temperature of a reactive mixture of gases and the rate of energy addition, which depends exponentially on temperature. A slight increase in the system’s temperature by reactions may bring the system in a runaway reaction occurring faster than any potential loss \[3\]. Although real systems involve the evolution of many reactive species in a complex sequence of elementary reactions, thermal ignition is particularly relevant to low temperature ignition in hydrogen, for example \[4\].

A proper account of the reaction rate of elementary reactions is essential in problems of thermal ignition. Although most reaction rates of elementary
reactions are obtained or calibrated from experiment, their assumed Arrhenius form is justified theoretically from arguments of kinetic theory of gases or transition state theory only if the gas can be assumed to be in thermodynamic equilibrium, i.e., the distribution of molecular speeds follows the Maxwell-Boltzmann distribution. While the assumption of a Maxwell-Boltzmann distribution is expected asymptotically in the limit of slow reactions, i.e., when the activation energy is large and the heat release is negligible, deviations from the Maxwell-Boltzmann (MB) distribution are expected otherwise. In this respect, over 60 years ago, Prigogine and co-workers extended the classical perturbation method of Chapman and Enskog to the case of reactive collisions of hard spheres. They investigated two separate problems: the non-equilibrium effects arising in an isothermal system [1] and in a reactive system, where the energy release may influence the rate of reactions explicitly by perturbing the local MB distribution [2]. The latter is particularly important for the problem of interest in the present paper, namely thermal ignition.

In the isothermal case, the non-equilibrium corrections to the MB-derived rate of standard kinetic theory of gases was found to be small in such Chapman-Enskog perturbations to the MB distribution [1]. Subsequent work by other groups confirmed this finding [3, 6], although problems have been raised regarding the uniformity of the Chapman-Enskog expansion. The advent of affordable calculations using molecular dynamics (MD) or Direct Simulation Monte Carlo (DSMC) techniques [7–10] permitted to evaluate the predictions of the kinetic theory results. Although a systematic comparison has not been performed over an entire parameter range of activation
energies and heats of reaction, the computational results confirmed that the corrections in the isothermal case tend to slow down the reactions.

More interestingly, however, is the reactive case treated in the perturbation theory of Prigogine and Mahieu. Their results indicate that the effect of heat release is to significantly accelerate the reaction rate through nonequilibrium effects: reactive collisions, through local energy addition, give rise to highly energetic particles that can serve to locally initiate other reactive collisions, before the effect is equilibrated in the entire system. The perturbation is proportional to the ratio $Q/E_A$, in that energetic systems will benefit the most of these effects. In spite of their utmost importance in thermal ignition problems, to the best of our knowledge, these effects have not been considered by the combustion community.

Recently, Sirmas et al. have investigated the role of nonequilibrium effects in the problem of thermal ignition in a model system characterized by a single binary reaction by molecular dynamics in two-dimensions [11]. They have identified large departures from the equilibrium prediction at both low and high activation energies. It was observed that systems with low activation energies exhibit a homogeneous ignition event with departure from thermal equilibrium prediction, yielding lower reaction rates and longer ignition delays. On the other hand, for systems with sufficiently high activation energies and heat of reaction, they have proposed that the thermal ignition is a stochastic process with ignition due to hot-spot formations which is associated with shorter ignition delay than predicted from continuum model by approximately 30%.

In the present communication, we wish to assess the role of non-equilibrium
effects in thermal ignition in a much more physical three-dimensional space, in order to compare with the analytical predictions of non-equilibrium kinetic theory for both isothermal and reactive collisions. We consider a single binary reaction in a hard sphere gas. The assumption of the hard sphere gas permits to not only compare with the available predictions from kinetic theory, but also to integrate the equations of motion of the spheres exactly and deterministically, given a set of initial conditions of positions and momenta. We make use of the classical algorithm of Alder and Wainright to evolve the system analytically, now known as the Event Driven Molecular Dynamics method [12].

2. Problem definition

The problem we solve is the evolution of a system of hard spheres evolving inside an insulated cube of side $L$, i.e., a constant volume ignition problem. Collisions with the boundaries are reflective. By hard spheres, we refer to particles which do not exert any force on others except at the instant of collision, where the laws of momentum and energy conservation apply to determine the post-collision velocities [13]. The gas contains three types of species, A, B and C, which may transform according to the model binary irreversible exothermic reaction:

$$A + B \rightarrow C + C + \text{heat} \quad (1)$$

As initial condition, we specify the number of type A and B spheres, denoted as $N_A$ and $N_B$, respectively. Both reactants and the product have identical mass and diameter, $d$. The initial condition of our problem also requires a
Figure 1: Schematic of interactions between particles A and B before impact (left), during impact (center) and after impact (right) along the line of action

specified temperature and species concentrations. The particles are expected to be in equilibrium, such that their average speed distributions are given by the Maxwell-Boltzmann distribution. The initial temperature of the system, defined from the mean speed of the particles, uniquely defines the initial condition in the thermodynamic sense. With these initial conditions, we allow the particle dynamics inside the box to evolve and undergo an overall thermal ignition process.

All collisions are assumed to be elastic with the exception of reactive collisions. The heat release $Q$ of a reactive collision increases the kinetic energy of each species C. The collision occurs along the line of action, i.e., the change in the speed can take place only in the normal direction while the tangential components remain unchanged (as seen in Fig. 1). The reactive collision can occur only when the relative speed between the two colliding reactants exceeds the minimum impact velocity, $u_{cr}$, satisfies the condition ($\left|u_{A(N)} - u_{B(N)}\right| > u_{cr}$). The impact velocity is related to the activation en-
ergy by $u_{cr} = (4E_A)^{1/2}$. The post collision speed of particle A (which becomes a particle C) after a reactive collision, is:

$$u'_{A(N)} = \frac{1}{2} \left( u_{A+B} + u_{A-B} \sqrt{1 + \frac{8Q}{m u^2_{A-B}}} \right)$$  \hspace{1cm} (2)

where, $u_{A-B} = u_{A(N)} - u_{B(N)}$ and $u_{A+B} = u_{A(N)} + u_{B(N)}$. Whereas, the tangential component of post collision velocities remains unchanged as per the line of action model.

For a given initial temperature and species concentrations, we are interested in the evolution of the system’s temperature. We define ignition as the time required for half of the energy of the system to be released, which corresponds to the depletion of half of the least abundant reactant.

3. Numerical Method

The evolution of the particles position and velocities follows the Event Driven Molecular Dynamics algorithm [12, 14]. The dynamics of hard sphere models can be determined analytically. For any pair of particles, the collision time can be determined analytically as

$$t^* - t = -\frac{\vec{r}_{ij} \cdot \vec{v}_{ij}}{v^2_{ij}} - \left[ \left( \frac{\vec{r}_{ij} \cdot \vec{v}_{ij}}{v^2_{ij}} \right)^2 + \frac{R^2_{ij} - r^2_{ij}}{v^2_{ij}} \right]^{0.5}$$  \hspace{1cm} (3)

where $t$ and $t^*$ are the current and next collision times, respectively; $\vec{r}_{ij}$, $\vec{v}_{ij}$ and $R_{ij} = R_i + R_j$ are the relative distance, relative velocity and sum of the radius of the colliding spheres, respectively. The system is evolved from collision to collision, or event to event, hence the name of the algorithm. Our implementation of the method follows Pöschel’s procedure [14].
Every calculation was initialized with the equal amounts of particles A and B having equal speeds and randomized trajectories. This permits to accurately control the initial temperature (energy) of the system, as it is conserved exactly through elastic collisions. The system is then allowed to evolve with all reactive collisions turned off, until all particles undergo a sufficient number of collisions such that their speed distribution converges to the Maxwell-Boltzmann (MB) distribution, given by:

\[ f(v) = \frac{m v^2}{2RT} \exp \left( -\frac{mv^2}{2RT} \right) \]  \hfill (4)

Figure 2 shows an example of the thermalization process. After one mean collision time (Fig. 2a), there is a large peak in the distribution, corresponding to the initial speed of the particles. This peak progressively disappears as collisions deplete this class of particles; energy is eventually partitioned in classes of the tails of the distribution. The distribution of speeds is seen to evolve towards the MB distribution within less than 10 mean collision times, \( \tau_o \). Once a thermal equilibrium is achieved among the reactants A and B, reactive collisions are allowed. This marks time 0 of the problem formulation. As very few particles have a high enough speed to give rise to a reactive collision, the rate of energy release in the box is initially slow. As time progresses and the energy released heats the system, more and more particles can undergo reactive collisions. This thermal ignition eventually raises the temperature of the system progressively faster, until depletion of the reactants moderates the rates. Figure 3 shows the evolution of the system’s temperature for two such calculations, which show the molecular noise, reflected by different configurations of the system at the same thermodynamic temperature give rise to a stochastic effect in the time of ignition. We conducted the
Figure 2: Probability distribution of speeds obtained from MD for different point in time for $N = 10000$ and compared with MB distribution.
calculations 100 times for each set of parameters of interest, such that the ignition delay reported is the mean value. Likewise, the standard deviation is also recorded, as a measure of the stochasticity. To test the influence of the system size, calculations have been performed by changing the total number of spheres, \( N \), ranging from 50 to 10000, corresponding to cubes with sides, \( L \), ranging from 1.103 to 6.45 mean free paths.

4. **Continuum level description from kinetic theory**

The results from molecular dynamics simulations described in the previous section were compared with those obtained from kinetic theory descriptions, where the reaction rate is either the standard form assuming thermal equilibrium at every instant, or its corrected versions to account for non-
equilibrium effects in the evolution of the speed distribution function \[1, 2\].

For the problem of an insulated system at constant volume, its macroscopic evolution is given by \[3\]:

\[
\rho c_V \frac{dT}{dt} = Q \omega_C \tag{5}
\]

\[
\rho \frac{dY_C}{dt} = \omega_C \tag{6}
\]

where \(Y_C\) and \(\omega_C\) are the mass fraction and the production rate of product C, respectively; \(c_V\) is the specific heat at constant volume. Given an initial temperature \(T_o\) and concentrations, the integration of these equations provide the evolution of the system’s temperature and concentrations, and hence permits to determine the ignition delay.

The standard rate of reaction, if one assumes a gas in local thermal equilibrium, takes the form \[13\]:

\[
\omega_C = 48 \frac{\eta}{\sqrt{\pi} d} \rho Y_A Y_B \sqrt{RT} \exp \left( -\frac{E_A}{RT} \right) \tag{7}
\]

where \(Y_A\) and \(Y_B\) are the mass fractions of reactants A and B, respectively. \(R\) is the gas constant and \(\rho\) is the density. The pair correlation function \(g(\eta)\) is

\[
g_2(\eta) = \frac{(2 - \eta)}{2(1 - \eta)^3} \tag{8}
\]

For the current study the length and the time scales are normalized by initial mean free path and initial mean free time of the gas with the volume fraction of \(\eta = 0.01\) (dilute, ideal gas regime). The initial mean free path and mean free time are

\[
\lambda = \frac{\sqrt{\pi} d}{8 \sqrt{3} \eta g_2(\eta)}; \quad \tau_o = \lambda / u_{\text{rms}(o)}
\]
With this scaling the homogeneous ignition description is independent of $\eta$, allowing $Q/RT_o$ and $E_A/RT_o$ to uniquely define the system’s evolution.

5. Results and discussion

The results for the ignition delay determined using the MD model described above are shown in Figs. 4 and 5 for the two values of heat release considered, respectively $Q/RT_o=2.5$ and 10. Each data point represents the average ignition delay among 100 calculations, while the error bar is the standard deviation. Each color band in the figure indicates the confidence zone of MD results for a particular activation energy for varying domain size. For all values of $Q$ and $E_A$, the calculated asymptote falls within the confidence zone of ignition delay time. It is prominent from the figure that the ignition delay and standard deviation decrease with increasing domain size. For low activation energies, regardless of heat release, the ignition delay time is very weakly influenced by the domain size effects. However, for increasing $Q$ and $E_A$, the trend line is steeper, showing a stronger influence of domain size. For all the calculations performed, the ignition delay was found to converge well to a system of infinite size (abscissa of 0 in the figures).

In order to determine the extrapolated value of ignition delay in an infinite system, the ignition delay dependence on system size was assumed to have the form

$$\ln(t_{ig}) = \ln(t_{ig,\infty}) + b \cosh \left( \frac{c\lambda}{L} \right)$$

(9)

where $b$, $c$ and $t_{ig,\infty}$ are fitting constants, the latter being the desired ignition delay time at infinite domain size. The fits are also shown in the Figs. 4 and 5.
Figure 4: Logarithm of ignition delay extrapolated to infinite domain size \( Q/RT_o = 2.5 \). The error bars indicate the standard deviation of ignition delay time. The color band represents the confidence zone of MD results for each activation energy. Solid line indicates the asymptote calculated from Eq. (9).

Figure 5: Logarithm of ignition delay extrapolated to infinite domain size for \( Q/RT_o = 10 \). Same description as Fig. 4.
Figure 6: Ignition delay time with varying $E_A$ obtained for $Q/RT_o = 2.5$ from MD (error-bars) are compared with equilibrium reaction rate (solid line) and non-equilibrium reaction rate calculated from Eqs. (10) (dashed red line) and (11) (dotted blue line).

Figure 7: Ignition delay time with varying $E_A$ obtained for $Q/RT_o = 10$. Same description as Fig. 6.
The ignition delays extrapolated to infinite domains are shown in terms of the activation energy in Figs. 6 and 7 for $Q/RT_o=2.5$ and 10, respectively. These are compared with three predictions of ignition delay calculated with expressions for the reaction rate from kinetic theory: the thermal equilibrium standard reaction rate $\omega_X$, the rate perturbed by Prigogine and Xhrouet for an isothermal system and the rate perturbed by Prigogine and Mahieu incorporating the effect of energy release. For the isothermal system, Prigogine and Xhrouet derived the rate $\omega_X$:

$$\omega_X = \omega_C \left\{ 1 - \frac{1}{32} e^{-\frac{E_A}{RT}} \left( \frac{E_A}{RT} \right)^3 \left[ \left( \frac{E_A}{RT} \right)^2 - 5 \frac{E_A}{RT} + \frac{17}{2} \right] \right\} \quad (10)$$

Incorporating the effects of reaction, the non-equilibrium reaction rate, $\omega_M$, derived by Prigogine and Mahieu is:

$$\omega_M = \omega_C \left\{ 1 + 1.2Y_A Y_B \left( \frac{Q}{E_A} \right) \right\} \quad (11)$$

The comparison of our molecular dynamics results for ignition delay in Figs. 6 and 7 with those obtained from kinetic theory permits to establish certain clear trends. First, we would like to compare with the results of standard kinetic theory. The differences from the standard kinetic theory are also shown in Fig. 8. For the low value of energy release of $Q/RT_o=2.5$, the standard equilibrium kinetic theory captures well, although slightly over-predicts the ignition delay obtained from the molecular dynamics calculations. Larger deviations are observed for low activation energies, below $E_A/RT_o$ of approximately 3. In this regime, the ignition delay was found to be longer than predicted by as much as 30% at low activation energies. For the high energy release of $Q/RT_o=10$ shown in Fig. 7, the predictions of the standard kinetic
rate is significantly deteriorated for all activation energies. The largest departure is seen for intermediate activation energies of $E_A/RT_o = 5$, where the ignition delay calculated from molecular dynamics is more than 30% shorter than anticipated from the standard equilibrium rate. Likewise, for low values of activation energy, the equilibrium model predicts an ignition delay longer by 60%.

The isothermal model prediction of Prigogine and Xhrouet, shown in red, systematically predicts an ignition delay longer than the one obtained from the equilibrium value. Nevertheless, it does not capture any of our molecular dynamic results. At large activation energies, this is the opposite trend from both our low heat release and high heat release results. At low activation energies, it provides a correction in the correct direction of lengthening the induction delay, but fails to capture the trend obtained with activation
energies approaching 1.

Interestingly, the model of Prigogine and Mahieu provides a much better approximation to both of our low heat release and high heat release results for sufficiently high activation energies only. For \( E_A/RT_o \) greater than 5, the prediction is within the standard deviation associated with the stochasticity of the ignition. This result is encouraging, as the model captures the data at the linear order correction in \( Q/E_A \), not requiring higher order terms in the Chapman-Enskog perturbation. At lower activation energies, however, the prediction significantly diverges from the molecular dynamic data for both low and high heat release.

At low temperatures, the good agreement between our calculations and those using the perturbed rate of Prigogine and Mahieu supports the validity of the physical mechanism proposed. Highly energetic particles resulting from reactive collisions promote local reactions. These do not have enough time to equilibrate with the rest of the system, thus giving rise to what we would like to call molecular hotspots. This result is also in accordance with the previous numerical results by Sirmas and Radulescu in the two-dimensional system [11]. In this regime of ignition, where non-equilibrium effects significantly promote ignition, we also observe a much higher stochasticity of ignition, as shown in Fig. 9. As the heat release and activation energy are increased, so is the stochasticity among our 100 realizations, measured by the standard deviation. Interestingly, this is also the regime where ignition is mild in practice: it takes the form of localized ignition spots [15, 16]. In this regime, the picture that emerges is the ever increasing role of molecular fluctuations.
6. Conclusion

Consistent with the two-dimensional study of Sirmas et al. [11], our current results confirm the existence of two non-equilibrium regimes important in thermal ignition problems, different at high low temperatures. At high temperatures, the ignition delay was longer than predicted by standard kinetic theory assuming local equilibrium. Although the trend was captured by Prigogine and Xhrouet qualitatively, the perturbation model failed at this extreme, as the perturbation assumes slow reactions in the limit of high activation energy. For low temperatures, particularly for high heat release, the ignition delay was found to be shorter than the one predicted by the standard kinetic theory. The perturbation scheme of Prigogine and Mahieu, which incorporates the effect of energy release in the perturbation of the distribution function, accurately captures the effect.
While the present study clearly highlights the necessity of incorporating non-equilibrium effects in kinetic predictions, particularly for systems where the kinetics are calibrated experimentally in nearly isothermal conditions. It also clearly shows that no existing perturbation scheme provides a uniformly valid approximation. Hence, molecular dynamic results, such as provided in the current paper, can be used to form an empirical correction factors to the existing reaction rates.

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