Non-Equilibrium Effects in Detonations Initiation using Hard Spheres

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1 Introduction

In the present study, Molecular Dynamics (MD) simulations using hard spheres have been used to investigate the non-equilibrium effects due to the piston initiated shock wave in a reactive system. Molecular models using a media composed of colliding hard spheres (3D) serve as good approximations for gases and liquids. It is to be noted that for a dilute gas, relevant to ideal gases, that a hard sphere potential yields accurate results [1], for which the kinetic theory is well established [2]. It is therefore chosen due to its adaptability into an event driven algorithm which significantly lowers the computational time. For this purpose, we make use of the classical algorithm of Alder and Wainright to evolve the system analytically from collision to collision, or event to event, now known as the Event Driven Molecular Dynamics method (EDMD) [3].

Not surprisingly, the first molecular dynamic investigations of non-equilibrium reactive phenomena, such as ignition [4] and detonation wave propagation [5] were conducted using the EDMD method. Brenner et al. investigated the detonation structure for condensed-phase detonations by using MD, in which the 2D energetic molecules are described by many body complex force potential, Reactive Empirical Bond Order (REBO) [6]. It has been shown to support a chemically sustained shock waves with properties consistent with planar detonations. In the similar manner, Heim et al. [7] investigated the detonation instability in condensed phase medium by making modifications to the original REBO potential for MD. They reported that the instability increases with increasing activation energies and noticed that the reaction zone structure is convoluted with the structure of the transverse waves and unreacted pockets. In the essence, Heim and co-workers conclude that the reaction zone overlaps with the compression shock in condensed phase detonations.

In our previous 3D study [10] on a constant volume thermal ignition process of hard sphere gases, we have found that the non-equilibrium effects (eg: molecular hotspots) tend to play an crucial rule with increase in activation energy and heat release. This in turn predicts the reaction rate higher than the standard equilibrium reaction rate and other kinectic theory predictions by Prigogine and co-workers [11]. Most of the current detonation models employing MD are limited to the condensed phase and the numerical solutions

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for detonations in gas-phase are limited to continuum level. Therefore, in the present communication, we aim to explore this phenomena at an microscopic level for gas-phase detonations. The physical significance of these non-equilibrium effects in detonation problems is emphasized by making a comparison and quantifying our present molecular dynamics calculations with the existing continuum models used for treating detonation waves problems with strong non-equilibrium effects.

The present study begins by clearly formulating the model used to study reactive collisions, for which well-defined activation energy, heat of reaction and reaction rate pre-exponential factor can be defined in order to particularly consider the case where the shockwave relaxation and reaction zone overlap. We then present calculations of reactive waves initiated by the motion of a piston, and study the structure of these waves, by first averaging over the particles motion in order to recover hydrodynamic descriptions, and secondly investigating the structure of the waves and quantifying any potential anomalous non-equilibrium effects using existing continuum models.

2 Model Description

The problem that we solve is the shock to detonation transition, that is generated by the sudden motion of a piston into a reactive system of hard spheres. The model that we consider is the binary irreversible exothermic reaction of the form:

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

where the species, A and B react to form two species of C. 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. Collisions with the boundaries are considered as 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 [1]. As an 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 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. 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 ($|u_{\text{A(N)}} - u_{\text{B(N)}}| > u_{\text{cr}}$). The impact velocity is related to the activation energy by $u_{\text{cr}} = (4E_{\text{A}})^{1/2}$. The post collision speed of particle A (which becomes a particle C) after a reactive collision, is:

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

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

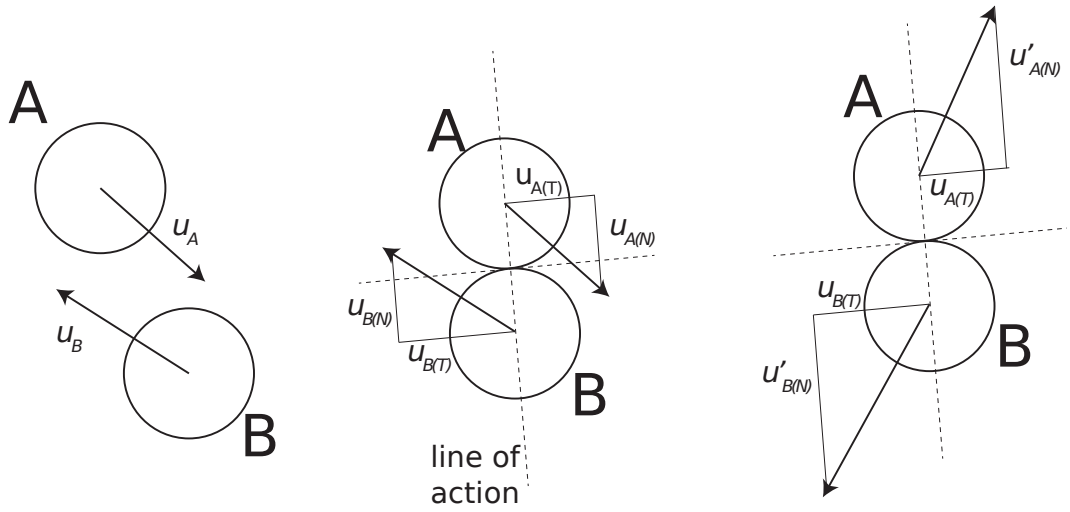


Figure 1: Schematic of interactions between particles A and B before impact (left), during impact (center) and after impact (right) along the line of action

3 Molecular Dynamics Description

The evolution of the particles position and velocities follows the Event Driven Molecular Dynamics algorithm [3, 8]. The dynamics of hard sphere models can be determined analytically. For any pair of particles, the collision time can be determined analytically as

$$t^* - t = -\frac{\vec{r}_{\rm ij} \cdot \vec{v}_{\rm ij}}{\vec{v}_{\rm ij}^2} - \left[\left(\frac{\vec{r}_{\rm ij} \cdot \vec{v}_{\rm ij}}{\vec{v}_{\rm ij}^2} \right)^2 + \frac{R_{\rm ij}^2 - \vec{r}_{\rm ij}^2}{\vec{v}_{\rm ij}^2} \right]^{0.5} \tag{3}$$

where t and t^* are the current and next collision times, respectively; $\vec{r}_{\rm ij}$, $\vec{v}_{\rm ij}$ and $R_{\rm ij} = R_{\rm i} + R_{\rm j}$ 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 [8]. Each calculation was initialized with the equal amounts of particles A and B having speeds equal to the Maxwell-Boltzmann (MB) distribution. This energy provided to the system corresponds to the initial specific energy of the system e_1:

$$e_1 = \frac{1}{2}\langle U_1^2 \rangle \tag{4}$$

The initial mean free path and mean free time are ,

$$\lambda = \frac{\sqrt{\pi} d}{8\sqrt{3}\eta g_2(\eta)}; \quad \tau_{\rm o} = \lambda / u_{\rm rms(o)}$$

where g(η) is the pair correlation function given by

$$g_2(\eta) = \frac{(2-\eta)}{2(1-\eta)^3} \tag{5}$$

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 η = 0.01, respectively. With this scaling the homogeneous ignition description is independent of η, allowing Q/RT_1 and E_A/RT_1 to uniquely define the system's evolution.

Table 1: Parameters considered for molecular dynamics simulations

Initial conditions and parameters	Dimensionless values
$(L_x \times L_y \times L_z)/\lambda$	$36.848 \times 10.236 \times 2.844$
d/λ	0.08
η	0.01
No. of particles	40000
Q/RT_1	8 and 38
E_A/RT_1	19

4 Continuum level description from kinetic theory

The compressible motion of a reactive medium, after neglecting slow processes involving molecular transport, are governed by the Euler equations.

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} = -\rho\nabla\cdot\mathbf{u} \tag{6}$$

$$\rho\frac{\mathrm{D}u}{\mathrm{D}t} = -\nabla\mathrm{p} \tag{7}$$

$$\rho\frac{\mathrm{D}e}{\mathrm{D}t} + \nabla\cdot pu = Q\omega_C \tag{8}$$

$$\rho\frac{\mathrm{D}Y_C}{\mathrm{D}t} = \omega_C \tag{9}$$

where Y_C and ω_C are the mass fraction and the production rate of product C, respectively. Given the initial conditions, 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 [1]:

$$\omega_C = 48\frac{\eta}{\sqrt{\pi}d}\rho Y_A Y_B\sqrt{RT}\exp\left(-\frac{E_A}{RT}\right) \tag{10}$$

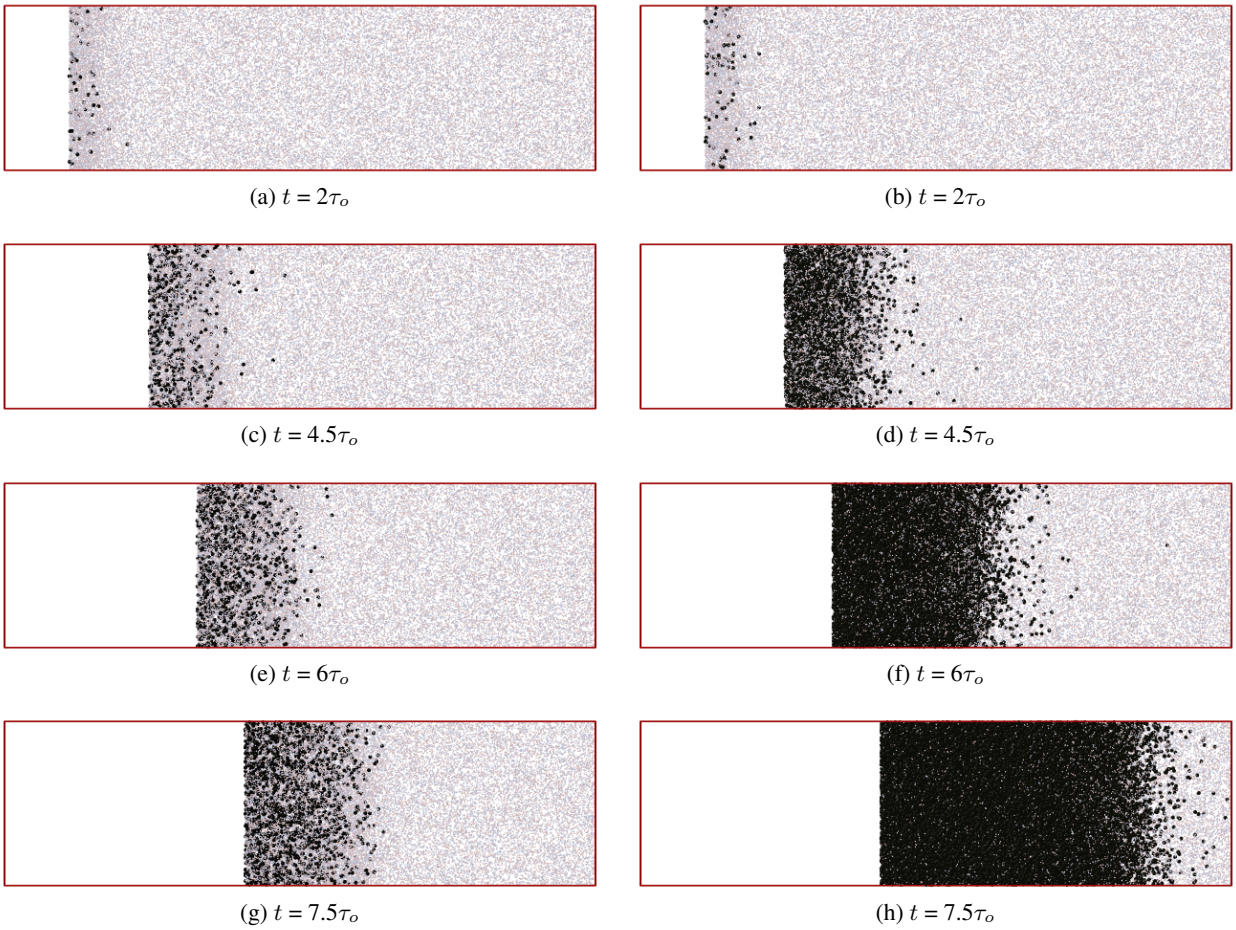
where Y_A and Y_B are the mass fractions of reactants A and B, respectively. η is the volume fraction, ρ is the density and R is the gas constant.

5 Results and Discussion

The results presented in this paper are the ensemble average of ten simulations. In each simulations, the density, temperature and the velocity are obtained by coarse-grained averages. For example, at a particular

time of the simulation, the domain has been divided into strips of 0.5λ. In each strip, the density was directly obtained by counting the number of particles. And the temperature of the system is calculated by taking average of the kinetic energies of each particle comprised in the strip and subtracting the mean kinetic energy in the macroscopic motion:

$$T = \frac{\frac{1}{2}\langle U - \langle U_x \rangle \rangle^2}{k/m} \tag{11}$$



(a) $t = 2\tau_o$ (b) $t = 2\tau_o$

(c) $t = 4.5\tau_o$ (d) $t = 4.5\tau_o$

(e) $t = 6\tau_o$ (f) $t = 6\tau_o$

(g) $t = 7.5\tau_o$ (h) $t = 7.5\tau_o$

Figure 2: Snapshots of the reaction and shock wave progressing through the reactive hard disk medium, with $Q/RT_1 = 8$ (left), $Q/RT_1 = 38$ (right) and $u_p^2/e_1 = 8$ (Note: The size of the disks was amplified twice to better see their locations)

Figure 2 shows the snapshots of the instantaneous output which shows the location of the particles as well as the piston position. The reacted particles are represented by black and the unreacted particles are in blue and red. Using the above parameters, the Chapman-Jouguet solution can be calculated from equation (12),

Table 2: Simulation results of ignition delay and shock Mach number for E_A/RT_1=19

Q/RT_1	Mach number		t_{ig}
	EDMD	Chapman-Jouguet	
8	3.73	3.59	6.78
38	7.43	7.54	4.59

which determines the minimum speed for a detonation to occur.

$$M_{CJ}^2 = 1 + \frac{\gamma^2 - 1}{\gamma}\left(\frac{2Q}{3RT_1}\right) + \sqrt{\left(1 + \frac{\gamma^2 - 1}{\gamma}\left(\frac{2Q}{3RT_1}\right)\right)^2 - 1} \tag{12}$$

where, γ is the isentropic exponent that depends on the number of degrees of freedom, f, of the system, given by,

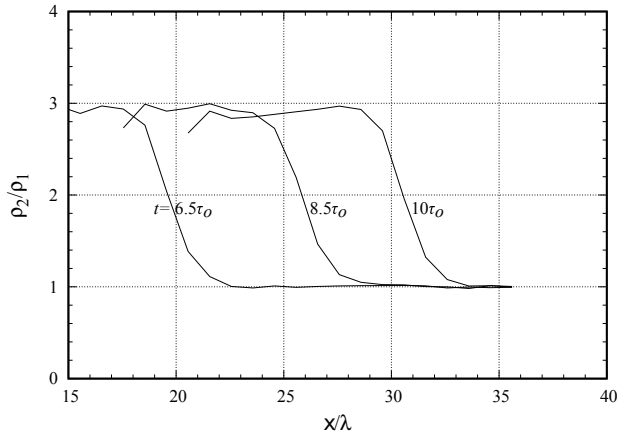
$$\gamma = \frac{2 + f}{f} \tag{13}$$

The results for all the values of Q/RT_1 initiate detonation waves propagating with the velocity approximately equal to Chapman-Jouguet velocity as shown in the Table 2. It is also evident from the figure that the reaction waves and shock waves overlap each other, with no distinct front. Added to that, one can see stems of finger like reactions which run ahead of the compression wave. Although the compression wave catches up to these fingers of reactions, they are continuously formed and overcome by the compression wave. These results indicate a super-diffusive detonation wave. And we suspect that these reactions that run ahead of the compression wave may be the reason for diffusive structure.

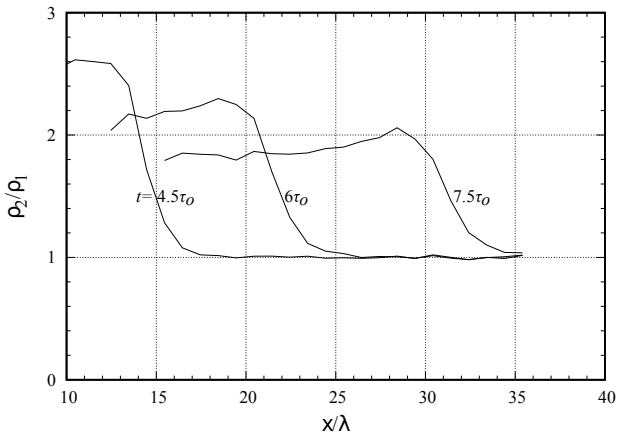
Fig. 3 (left and right), shows the average density, temperature and velocity across the reaction and shock waves obtained at different times for low and high heat release case, respectivley. For low heat release case, the trend stabilizes once the shock speed reaches the detonation speed. However, interesting is the high heat release case, where the average properties keeps fluctuating because of the instabilities arising in the reaction structure.

Ignition delay time is defined as the time at which the system releases maximum amount of energy. The ignition delay is calculated for each heat releases considered and is also tabulated in Table 2. We found that the ignition delay for low heat release case is larger than the high heat release case. This is in accordance with the results obtained by Sirmas et al. [9], where they studied the constant volume ignition process using hard disks(2D).

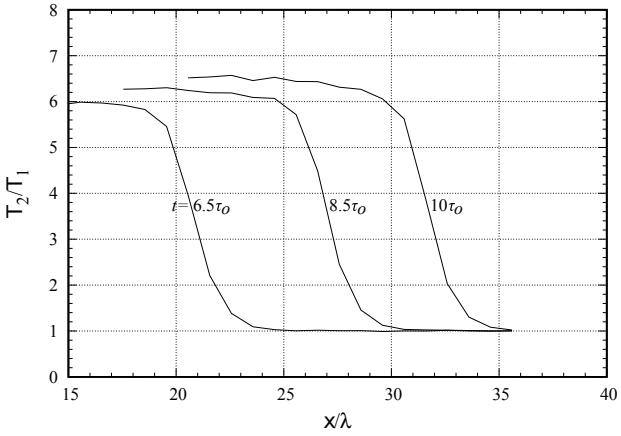
The quantitative description is underway to fully quantify these effects. Since the kinetic theory of dilute hard particles is well understood, the continuum Navier-Stokes equations can be readily derived, including the magnitude of the transport terms. Likewise, the kinetic rates of a system of binary particles undergoing an energy activated reaction are also well understood. A rigorous continuum model can be derived and its dynamics will be compared with the result of molecular dynamic simulations. The comparison with the present MD simulations can shed further light on the structure of the reaction wave. In this manner, any non-equilibrium effect discarded in the derivation of the continuum description can be isolated and studied.



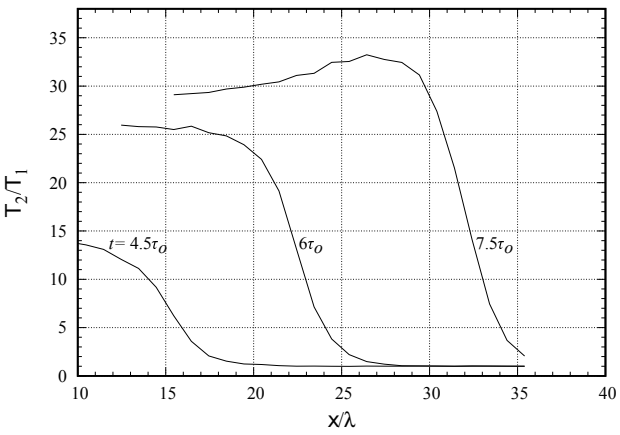
(a) Average density profile for $Q/RT_1 = 8$



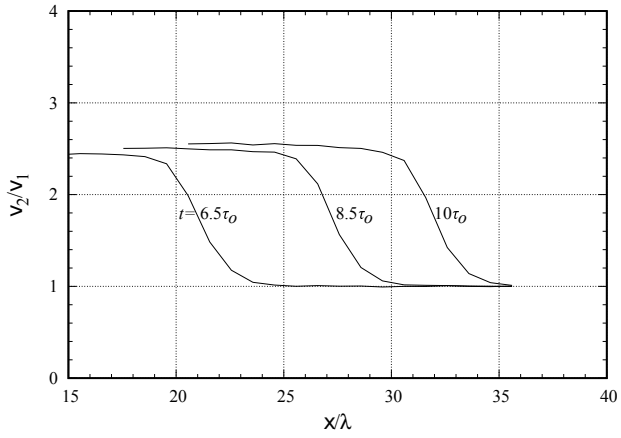
(b) Average density profile for $Q/RT_1 = 38$



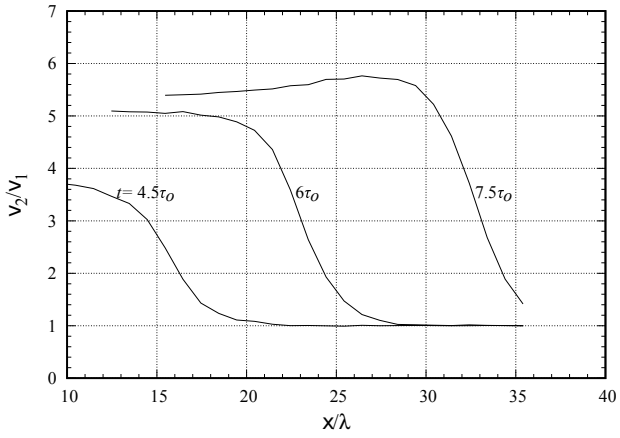
(c) Average Temperature profile for $Q/RT_1 = 8$



(d) Average Temperature profile for $Q/RT_1 = 38$



(e) Average velocity profile for $Q/RT_1 = 8$



(f) Average velocity profile for $Q/RT_1 = 38$

Figure 3: Average properties of the system for $Q/RT_1 = 8$ (left), $Q/RT_1 = 38$ (right) at different timesteps

6 Conclusion

In this study we formulated a simple reactive dynamics molecular model and used it to study the reaction zone structure of detonations. The diffusive structure appears to be from the non-equilibrium effects and reactive fingers accelerating the reaction rates, making the shock transition overlap with the reaction zone. Our MD model thus permits us to determine how the assumptions of the distinct shock and reaction zone structures in hydrodynamic models of detonations impact the detonation wave dynamic predictability (initiation and failure). Further comparison and quantification of the MD results with the continuum results is underway and will be communicated at the conference.

Acknowledgments

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