Molecular dynamics simulations of detonations

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1 Introduction

Molecular models using a media composed of colliding hard disks (2D) or hard spheres (3D) serve as good approximations for gases and liquids. A dilute system of colliding hard particles can be used to represent ideal gases, for which the kinetic theory is well established [1]. The simple hard sphere model can be extended to model reactive collisions. Non-equilibrium molecular dynamic simulations can thus be used to address problems of reactive hydrodynamics. Since no assumptions are made about local thermodynamic equilibria, Boltzmann's molecular chaos, neglect of higher order transport effects, or any other non-equilibrium effect, such simulations can serve as a true direct numerical simulation offering a first-hand account of the physical phenomenon investigated. It can also serve to review any assumption made in continuum theories.

Computationally, hard particle models are attractive to study because of the very low computational price, compared with more realistic inter-particle force potentials. Since the pioneering work of Alder and Wainright [2], the dynamics of hard particles can be solved by solely solving for the time of collisions among different pair 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 a personal computer.

Not surprisingly, the first molecular dynamic investigations of non-equilibrium reactive phenomena, such as ignition [3] and detonation wave propagation [4] were conducted using the EDMD method. The present paper uses the same simple reactive dynamics assumed in these earlier papers to study piston initiated reaction waves.

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. We then present calculations of reactive waves initiated by the motion of a piston, and study the structure of these waves, by i) averaging over the particles motion in order to recover hydrodynamic descriptions, and ii) investigating the structure of the waves at the particle levels by following the particle reactive dynamics and any potential anomalous non-equilibrium effect. For simplicity, and in order to help us in visualizing the particle dynamics, we restrict our attention to a hard disk system evolving only in 2 space dimensions.

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2 Model Description

To adapt the EDMD method to study reactive collisions, we assume the following model. We assume an irreversible reaction of the form

$$A+B \rightarrow 2P$$

in which only collisions among the reactants A and B can yield two product species P. In the reactive collision, we simply transform each existing molecule A and B into "reacted" molecules P and P. Fig. 1 shows a schematic of the process. We are assuming that the collision is inelastic, and liberates a given amount of chemical energy *Q*, which will be given to the particles in order to increase their kinetic energies. Reactive collisions are also only permitted if the collision between particles A and B is sufficiently strong. The amplitude of the collision is measured by the relative velocity between A and B at the moment of collision along the line of action, see Fig.1. This means that the relative normal velocities must be greater than a threshold velocity, u_{max}, such that:

$$\left|u_{A\,(N)} - u_{B\,(N)}\right| > u_{max} \qquad 1)$$

This velocity is proportional to the activation energy of the system, E_A, which is the energy necessary for a reaction to occur. Where,

$$E_A \stackrel{\text{def}}{=} \frac{1}{2}u_{max}^2 \qquad 2)$$

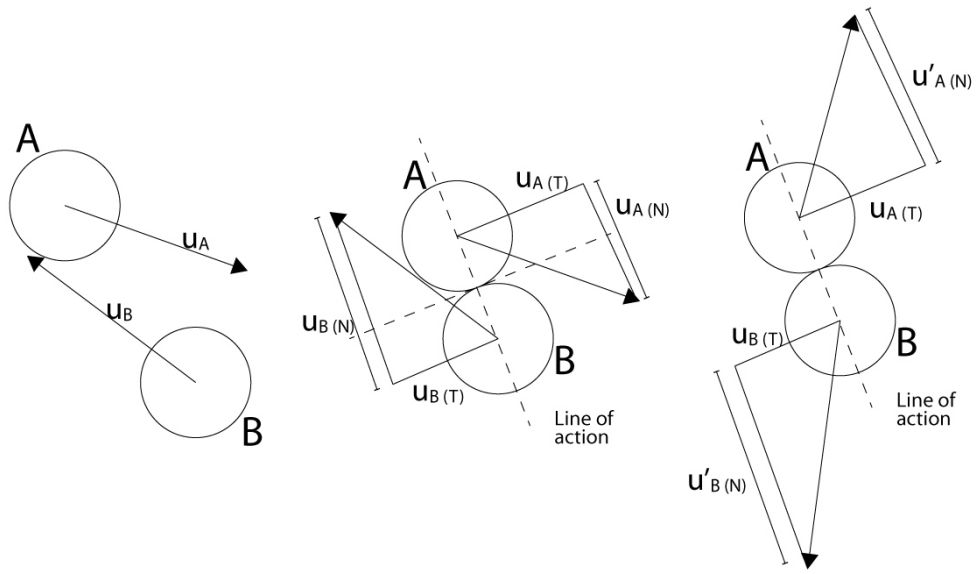

Figure 1: Kinematics of collision between particles A and B before impact(left), during impact(center) and immediately after collision(right)

The model can be formulated by separating the velocity of each particle into a normal component along the line of action, and a tangential component. The changes in velocity to the particles during impact occur along the line of action, while the tangential components will remain unchanged. The normal components of velocity before and after the collision of two particles of equal mass can be isolated through the conservation of linear momentum and energy, 3) and 4).

$$u_A + u_B = u_A^{'} + u_B^{'} \quad 3)$$

$$\frac{1}{2}u_A^2 + \frac{1}{2}u_B^2 + 2\lambda Q = \frac{1}{2}u_A^{'2} + \frac{1}{2}u_B^{'2} \quad 4)$$

The term λ represents whether a reaction will occur ($\lambda=1$), or will collide elastically ($\lambda=0$), which will be determined within the algorithm for the conditions presented in 1) and 2).

The normal velocity after the collision can be solved for with the following equation for both particles:

$$u_A^{'}, u_B^{'} = \frac{1}{2}(u_A + u_B \pm \sqrt{8\lambda Q + {u_A}^2 - 2u_A u_B + {u_B}^2}) \quad 5)$$

The velocity after the collision can be represented with 6) to compensate for the direction that the particles are going before the collision.

$$u_A^{'} = \frac{1}{2}\left(u_A\left(1 - \sqrt{1 + \frac{8\lambda Q}{(u_A - u_B)^2}}\right) + u_B\left(1 + \sqrt{1 + \frac{8\lambda Q}{(u_A - u_B)^2}}\right)\right)$$

$$u_B^{'} = \frac{1}{2}\left(u_A\left(1 + \sqrt{1 + \frac{8\lambda Q}{(u_A - u_B)^2}}\right) + u_B\left(1 - \sqrt{1 + \frac{8\lambda Q}{(u_A - u_B)^2}}\right)\right) \quad 6)$$

Model implementation

The collision rules for reactive and non-reactive encounters were then implemented in the EDMD algorithm. The model studied also involves a moving piston, used to initiate the reaction wave. To account for the moving wall, the algorithm described by Poschel and Schwager[5] was modified to account for a moving wall. Collisions with all walls were assumed elastic.

Initial and boundary conditions

In the present study a system of 40,000 particles was used within a fixed domain of dimensions L_x by L_y. The particles are initially positioned randomly with an equal speed and random direction. The length scale is non-dimensionalized by the particle radius, R, while the velocity is with the initial velocity of the particles, u_1, thus determining the time scale, t, as well. The energy terms per unit mass use the initial kinetic energy of the system, e_1.
The mean free path, α, of the system can be determined from 7) for a hard disk medium with N particles.

$$\alpha = \frac{L_x L_y}{4\sqrt{2}NR} \quad 7)$$

Table 1 summarizes the conditions surrounding the simulation in this study.

Table 1: Initial dimensionless conditions and parameters investigated via EDMD

Initial Conditions and Parameters	Dimensionless Value
L_x x L_y	6726 x 1868
α	55.5
u_p^2/e_1	8
Q/e_1	25
E_A/e_1	16

Given these parameters the Chapman-Jouguet solution can be calculated for this medium, determining the minimum speed for a detonation to occur:

$$M_{CJ}^2 = 1 + \frac{(\gamma^2 - 1)}{\gamma}\left(\frac{Q}{e_1}\right) + \sqrt{\left(\frac{(\gamma^2 - 1)}{\gamma}\left(\frac{Q}{e_1}\right) + 1\right)^2 - 1} \qquad 8)$$

Where the isentropic exponent, γ, is dependent on the degrees of freedom of the system, f.

$$\gamma = \frac{2 + f}{f} \qquad 9)$$

For this particular 2-D mixture, there are only two degrees of freedom, and with $Q/e_1 = 25$ the Chapman-Jouguet solution for the Mach number due to detonation, using 8), is $M_{CJ} = 8.77$.

3 Results and Discussion

The described model was run with the specified parameters, where the results presented are an ensemble average over ten simulations. A snapshot of the colliding disks is taken at equal steps of the piston propagating over time. In addition to the particle locations being recorded, properties of the medium are taken in vertical strips equal to a quarter of the mean free path. These properties include the number density of particles and the mean velocities within the strip. Figure 2 shows the results for the average density jump across the reaction and shock waves collected in this matter.

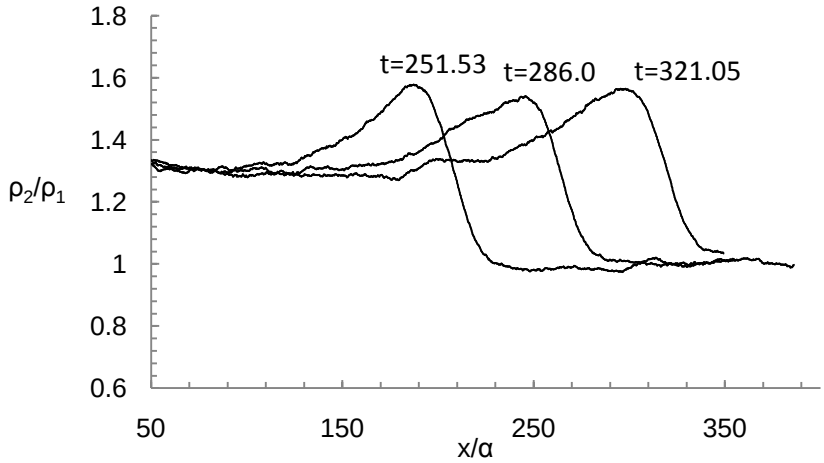

Figure 2: The average density profile related to the distance from the piston for Q/e_1=25 at three different time steps

Figure 3 shows snapshots of the instantaneous visual output which shows the location of the disks as well as the piston position. The reacted particles are black while the unreacted particles are grey. The three different snapshots show the reaction propagating through the hard disk medium. We observe that the shock and reaction waves overlap, with no distinct front. In addition to this, there are stems of the reaction which run ahead of the compression wave. The compression wave catches up to these fingers of reactions, although they are continuously formed and overcome by the compression wave.

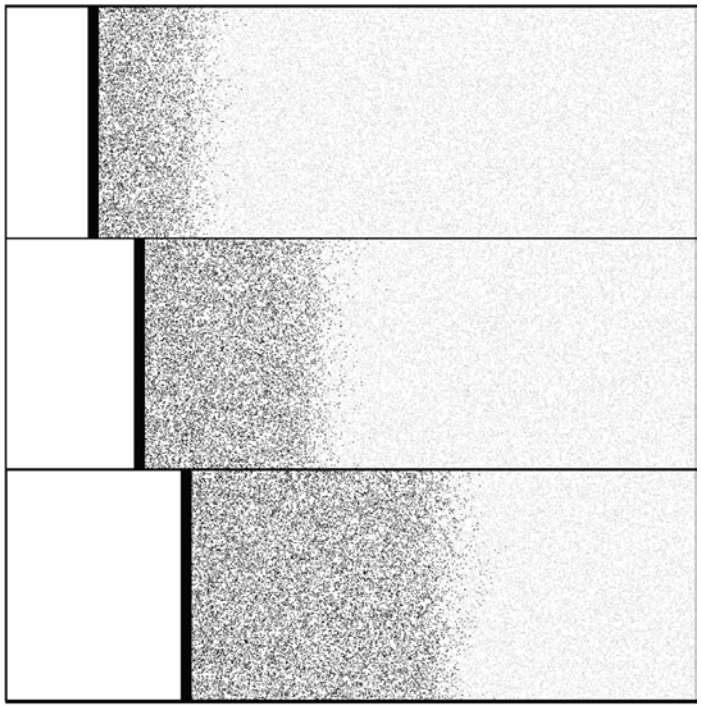

Figure 3: Snapshots of the reaction and shock wave progressing through the reactive hard disk medium, with Q/e_1=25 and u_p^2/e_1 =8(Note: The size of the disks was amplified four times to better see their locations)

Given the density profile, as presented in Figure 2, we can determine the Mach number of the reaction progressing through the hard disk medium. Figure 4 shows the evolution of this Mach number as the piston propagates through the medium.

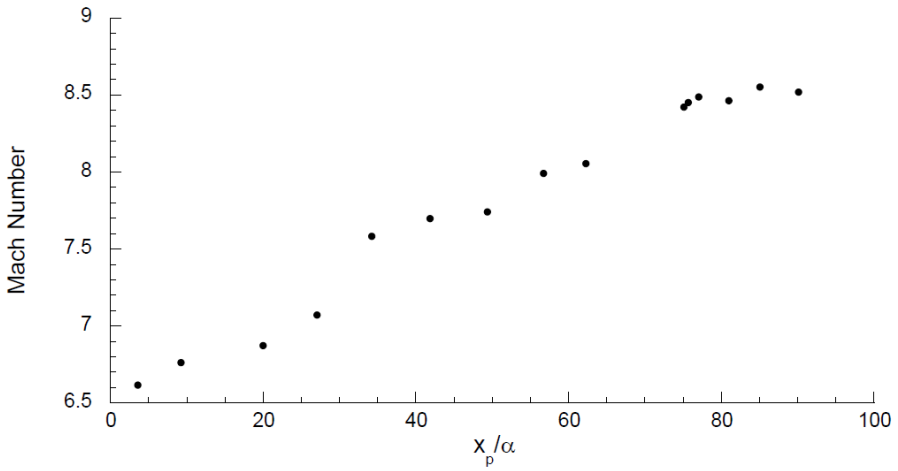

Figure 4: Evolution of the Mach number of the reaction and shock front propagating through the medium, compared to the piston location, with Q/e_1=25 and u_p^2/e_1 =8

The Mach number for this reactive medium, as obtained in Figure 4, looks to stabilize at a value of approximately 8.5. Comparing this value to the CJ Mach number, which was found early, we can see that the Mach number through the EDMD method is almost equal to that determined earlier.

Table 2: Mach number from EDMD method for a reactive medium with Q/ e_1=25 compared CJ Mach number

	Mach Number
EDMD Method	8.50
Chapman-Jouguet Solution	8.77

These results indicate a super-diffusive ZND detonation wave. The reactions that run ahead of the compression wave may be the cause of this diffusive structure.

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 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.

4 Conclusion

In this study we formulated a simple reactive dynamics molecular model and used it to study the reaction zone structure of detonations. The results obtained show a detonation wave propagating near the CJ velocity. 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. Future study will derive the kinetic theory for this system in order to quantify the effects that were observed.

References

[1] S. Chapman and T. G. Cowling, The mathematical theory of non-uniform gases; an account of the kinetic theory of viscosity, thermal conduction and diffusion in gases, 3rd ed. (Cambridge University Press, Cambridge, 1970).

[2] B. J. Alder and T. E. Wainwright, “Studies in molecular dynamics.1. General method,” Journal of Chemical Physics 31, 459–466, (1959).

[3]Chou, D.-P. and Yip, S, **“**Molecular dynamics simulation of thermal ignition in a reacting hard sphere fluid,” Combustion and Flame 58, 239-253 (1984).

[4]T. Kawakatsu, T. Matsuda, and A. Ueda, “A molecular dynamics study of an exothermically reacting system - a detonation phenomenon,” Journal of the Physical Society of Japan 57, 1191–1198 (1988).

[5] T. Poschel and T. Schwager, Computational granular dynamics: models and algorithms (Springer-Verlag, Berlin New York, 2005) p. 322.