The influence of non-equilibrium translational effects on reactive dynamics during shock to detonation transition using molecular dynamics

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Abstract

The current study examines the impact of non-equilibrium effects associated with the coupling of reactive dynamics and translational non-equilibrium in the problem of shock to detonation transition in gases. Using hard-sphere molecular dynamics of a single Arrhenius reaction, we show that the process of shock induced ignition and transition to detonation involves non-equilibrium reactions partly overlapping with the shock structure. Strong translational non-equilibrium is observed, with product particles forming reactive fingers extending into the reactants. The shock amplification rate and transition to detonation is found approximately 2 times faster than predicted by conventional Euler hydrodynamic models. A Navier-Stokes model with the hard sphere transport properties is found to capture well the acceleration process, in spite of the evidence for strong non-equilibrium. The findings have significance in the modeling of gaseous detonations with fast reactions, where pressure wave dynamics and reactivity in the detonation structure are likely to be much strongly coupled than predicted by Euler models. Experimental evidence for such diffusively-assisted waves is discussed in the context of transverse wave structure of gaseous detonations.

1 Introduction

Detonation waves in gases are traditionally modeled using the Euler hydrodynamic description with kinetics provided by assuming local thermal equilibrium. Shocks are treated as jump discontinuities. The shocks are numerically tracked or captured in numerical simulations without an explicit account of their inner structure. In the present study, we revisit this fundamental assumption of thermal equilibrium and neglect of shock structure by addressing the role of thermal non-equilibrium and coupling with reactive kinetics in the problem of shock to detonation transition. This problem consists of studying the acceleration of a shock wave to a detonation due to the shock induced energy release. This is generic to detonation problems, as it encapsulates the coupling between gas-dynamics and reactivity. When the reactions are modeled by a single step Arrhenius reaction, the ignition, gas-dynamic coupling and transition to detonation is very well understood [1, 2]. In the present study, we revisit this problem using molecular dynamics of a single binary chemical reaction. We show that the reactions couple with the non-equilibrium structure of the shock. This gives rise to substantially faster reaction wave amplification in a non-equilibrium version of Zel'dovich's spontaneous wave concept.

The problem of shock to detonation transition is directly relevant to the inner structure of gas phase detonations. This structure is three-dimensional and consists of transverse shock waves propagating through gases at various stages of their decomposition, modulated by variations in the lead shock strength [3]. While the lead shock is spatially decoupled from the region of exothermicity by a well-defined induction zone, the situation is much less clear for transverse shocks. The resulting transverse shock - chemistry coupling is what we wish to investigate in the model 1D problem posed, where exothermicity is controlled by only a few key exothermic reactions [4]. Experiments have demonstrated that pockets of gas react faster than anticipated from basic continuum descriptions [5], although these have been attributed to turbulence in the past [6].

In condensed media, there is also an ongoing debate whether shock induced exothermicity may depend on non-equilibrium properties of the shock, such as its strain rate. Gilman [7] suggests that mechanochemistry may play an important role. Some evidence for such strain-rate dependent initiation of chemistry stems from the experiments of Armstrong et al. [8]. Their shock-initiation of hydrogen peroxide using laser-driven shocks found reactions occurring within 100 ps immediately behind the lead shock. Molecular dynamics simulations confirmed these ultra-fast response, suggesting the possibility of strain-rate dependent initiation.

In gases, non-equilibrium effects in the reactive dynamics themselves have been demonstated in our recent study [4]. We demonstrated the role of "molecular hotspots", first suggested by Prigogine et al. [9], in accelerating the exothermicity. Reactive collisions giving rise to excess translational energy facilitate neighboring reactive collisions. In the present work, we study how this exothermicity is further enhanced in the presence of strong pressure waves.

Like in our previous investigation, we focus on a single binary reaction model. The reactive molecules are taken as hard spheres, to facilitate modeling of their dynamics at both the continuum and molecular level. The molecular dynamics simulations are compared to continuum solutions of Euler (inviscid flow) and Navier-Stokes (including gradient transport terms for a hard sphere gas) with various assumptions on the kinetics.

2   Model Description

The problem being addressed is the shock to detonation transition, which occurs when a piston suddenly moves into a system of reactive hard spheres. The model under examination is a binary irreversible exothermic reaction, expressed as follows:

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

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 [10]. 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. Further information about the model descriptions can be found in [11].

3 Molecular Dynamics Description

The progression of particle positions and velocities is determined by the Event Driven Molecular Dynamics algorithm [12,13]. The dynamics of hard sphere models can be obtained analytically. For clarity, the comprehensive details of the molecular dynamics description can be found in the our previous paper [4]. 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 $\eta = 0.01$, respectively. With this scaling the homogeneous ignition description is independent of η, allowing Q/RT_0 and E_A/RT_0 to uniquely define the system's evolution. The parameters used in this study can be found in Table 1. The piston speed is chosen so that the post-shock activation energy is 5, which is of practical interest.

Table 1: Parameters considered for molecular dynamics simulations

Initial conditions and parameters	Dimensionless values
$(L_x \times L_y \times L_z)/\lambda$	$102.35 \times 10.325 \times 1.0235$
d/λ	0.08
η	0.01
No. of particles	40000
$u_p/\sqrt{e_0}$	2.26
E_A/RT_s	5
E_A/RT_0	20
Q/RT	20 and 40

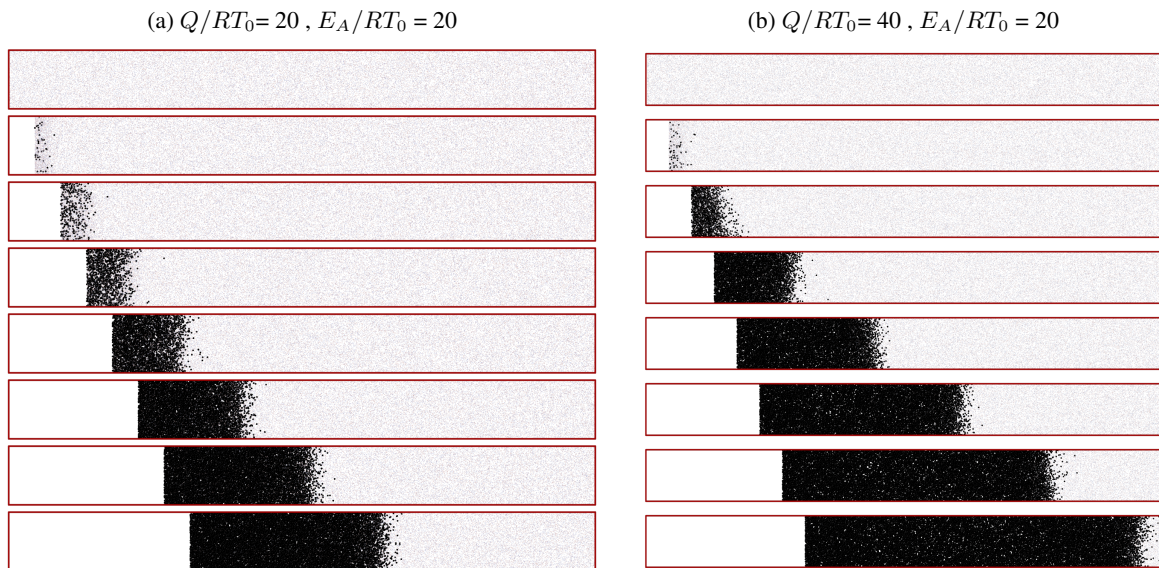(a) $Q/RT_0 = 20$, $E_A/RT_0 = 20$ (b) $Q/RT_0 = 40$, $E_A/RT_0 = 20$

Figure 1: A snapshot of a three-dimensional box over time for lower (left) and higher (right) heat release cases, with slices taken from t=0 to t=14 at an interval of 2.

4 Continuum level description from kinetic theory

The reactive Navier-Stokes equations in compressible form are presented below.

$$\frac{\mathrm{d}(\rho u)}{\mathrm{d}x} = 0 \tag{2}$$

$$\frac{\mathrm{d}(\rho u^2 + p)}{\mathrm{d}x} = \frac{4}{3}\mu\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}u}{\mathrm{d}x}\right) \tag{3}$$

$$\frac{\mathrm{d}\left(\rho\left(C_p T + \frac{u^2}{2}\right)u\right)}{\mathrm{d}x} = \lambda\frac{\mathrm{d}^2 T}{\mathrm{d}x^2} + \frac{4}{3}\mu\frac{\mathrm{d}}{\mathrm{d}x}\left(u\frac{\mathrm{d}u}{\mathrm{d}x}\right) - \omega_\mathrm{C}Q \tag{4}$$

$$\frac{\mathrm{d}(\rho u Y_\mathrm{C})}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\rho D\frac{\mathrm{d}Y_\mathrm{C}}{\mathrm{d}x}\right) + \omega_\mathrm{C} \tag{5}$$

where Y_C and ω_C are the mass fraction and the production rate of product C, respectively. By neglecting the transport coefficients like dynamic viscosity, μ, thermal conductivity, λ, and species diffusion, D, the compressible motion of a reactive medium governed by the Euler equations are obtained. Given the initial conditions, the integration of these equations provide the evolution of the system's temperature and concentrations.

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

$$\omega_\mathrm{C} = 48\frac{\eta}{\sqrt{\pi}d}\rho Y_\mathrm{A}Y_\mathrm{B}\sqrt{RT}\exp\left(-\frac{E_\mathrm{A}}{RT}\right) \tag{6}$$

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. The unsteady calculations in this study utilizes a finite-volume computational package named mg developed by Falle et al. [14]. The solver employs a second-order accurate exact Godunov scheme for the convective terms.
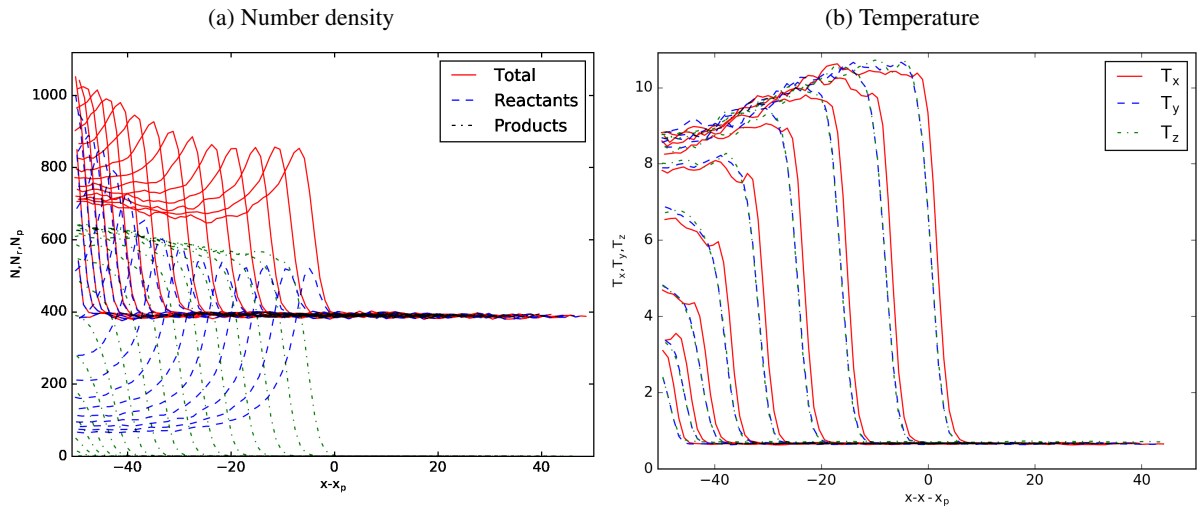
5 Results and Discussion
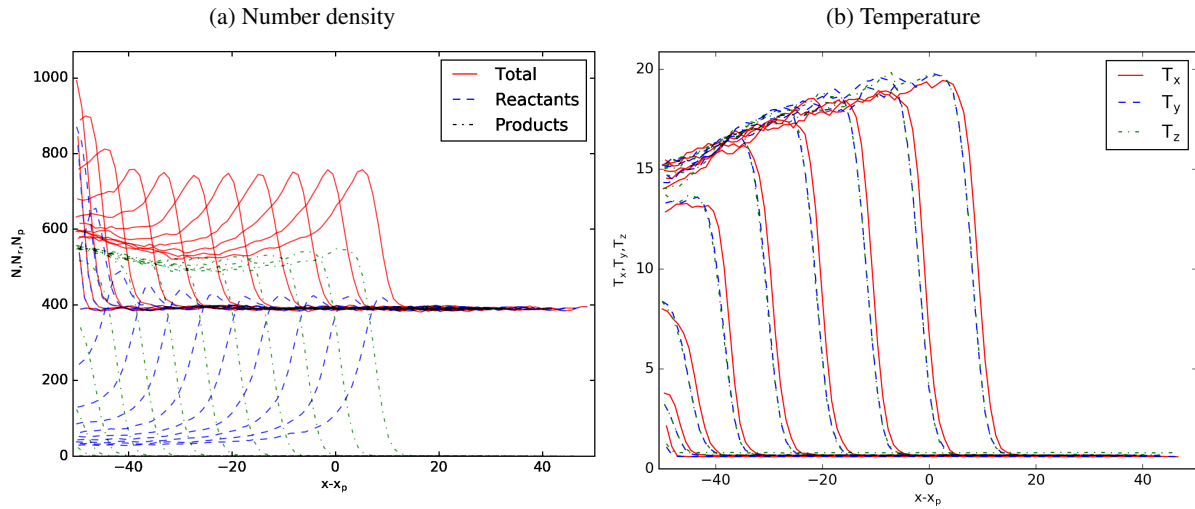

Figure 2: $E/RT_0 = 20$ $Q/RT_0 = 20$

(a) Number density

(b) Temperature

Figure 3: $E/RT_0 = 40$ $Q/RT_0 = 20$

(a) $E/RT_0 = 20$ $Q/RT_0 = 20$
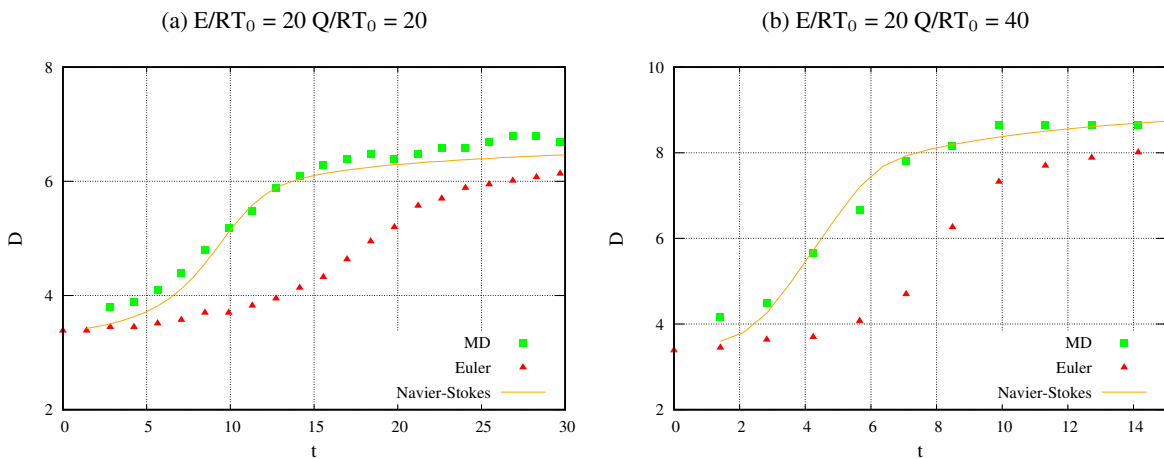
(b) $E/RT_0 = 20$ $Q/RT_0 = 40$

Figure 4

The first case considered is $Q/RT_0 = 20$. At time zero, the piston is accelerated from left into the qui-escent reactive medium. This in turn generates the shock and transits to detonation. Fig.1(a) shows a time series of sliced three dimensional box with reactant and product species. Once after detonation is established, one can notice stems of finger like reactions which runs ahead of the compression wave. These are continuously formed and overcome by the compression wave. It is suspected that these reactions may be the reason for the diffusive structure. Figs. 2(a) and 2(b) shows the species density and temperature profile, respectively, with the distance in the x in piston frame of reference for lower heat release case. To further support the above argument, from the species density profile (Fig. 2(a)) it is evident that there is no distinct reaction zone and the reaction starts immediately after the reactants (dashed blue line) enter the shock which is marked by the immediate formation of product species profile (dash-dotted green line) and also indicated by the rise in temperature profile in Fig. 2(b). The second case is for higher heat release where, Q/RT0 = 40 (see Fig. 1(b)). In this case, the transition occurs faster than the previous one . This is because the non-equilibrium effect is more pronounced with higher values of heat release. Hence, for higher heat release, more finger-like structures can be seen running ahead of

the compression wave which acts like a hotspot to further accelerate the ignition process. This is well identified in the temperature and species profile in Figs. 3(a) and 3(b), respectively. The trend remains the same for both the cases, except that the transition happens faster for higher heat release.

The results from the MD simulations were compared with those obtained from the inviscid and viscous reactive compressible Navier-Stokes simulations, using the solver mentioned above. For viscous calculations, the transport coefficients are obtained for hard-sphere molecules from kinetic theory and used in the simulation as non-dimensional parameters, which is Prandl number of 2/3 and Lewis number of 1.25. Fig. 4 illustrates the initiation of detonation from simulations using Euler, Navier-Stokes, and Molecular Dynamics methods. It can be seen that the latter two methods show a good correlation in the two cases examined. Conversely, the Euler calculations predict the onset of detonation to occur 50% later in both cases. This highlights the significance of diffusion effects on the detonation initiation process, as evidenced by the finger-like structure ahead of the compression wave in MD simulations, which is a hallmark of the diffusive nature of the detonation structure.

6   Conclusion

Molecular dynamics simulations were performed to investigate the impact of translational non-equilibrium on the shock-to-detonation transition in a reactive medium, as well as its coupling with compressible phenomena. The results showed several important features: as expected, non-equilibrium chemistry gave rise to faster reaction wave development. A connection was observed between the non-equilibrium chemistry and the reaction wave propagation, which was facilitated by compression waves. This was manifest in the form of reactive fingers, the super-diffusion of hot particles ahead of the reaction wave, and the interaction between the reaction wave and shock wave. Once the detonation was established, its structure was revealed to be the result of an overlap between the reaction zone and the shock wave. This contradicts the traditional understanding of a clear separation between the shock wave and reaction zone. The overlapping of shock and reaction zone was explored in the Navier Stokes limit for fast reactions by studying the general solutions for travelling waves in the Navier Stokes limit, validating previous theoretical work on conditions for existence of solutions with fully transient Navier-Stokes simulations in 1D.

Acknowledgments

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