Non-Equilibrium Translational Effects and the Limits of Weak Detonations in Shock-to-Detonation Transition

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1   Introduction

Detonation waves in gases are typically modeled using the Euler hydrodynamic framework, where kinetics are assumed to be governed by local thermal equilibrium, and shocks are treated as jump discontinuities. These shock waves are captured or tracked numerically, without explicitly accounting for their internal structure. In the present study, we revisit this assumption of thermal equilibrium and neglect of shock structure by investigating the role of thermal non-equilibrium and its coupling with reactive kinetics during the shock-to-detonation transition. The process—where a shock wave accelerates into a detonation as a result of energy released by shock-triggered reactions—is central to detonation physics and illustrates the interplay between flow dynamics and chemical activity. When reactions are modeled using a single-step Arrhenius reaction, the coupling of ignition, gas dynamics, and transition to detonation is well understood [1,2]. Here, we explore the shock-to-detonation transition through molecular dynamics simulations of a binary reacting system. We show that the reactive processes couple with the non-equilibrium structure of the shock, leading to a faster reaction wave amplification in a non-equilibrium version of Zel'dovich's spontaneous wave concept.

The problem of shock-to-detonation transition is also central to understanding the internal structure of gas-phase detonations. The detonation wave consists of transverse shock waves that propagate through a gas undergoing decomposition, with variations in lead shock strength influencing the overall dynamics [3]. While the lead shock is spatially decoupled from the region of exothermicity by a well-defined induction zone, the interaction between transverse shocks and reactive chemistry remains less understood. This study investigates this interaction within a 1D model, where exothermicity is controlled by a few key reactions [4]. Experiments have shown that pockets of gas react faster than predicted by traditional continuum descriptions [5], with some attributing this to turbulence [6]. Interestingly, Wood's 1D viscous detonation study predicts weak detonations that propagate faster than the classical Chapman-Jouguet (CJ) value, especially under high diffusivity conditions [7]. Such weak detonations have been confirmed in numerical simulations by Gamezo et al. [8] and other studies [9–11].

In addition to gas-phase detonations, similar non-equilibrium effects have been identified in condensed-phase systems, where shock-induced exothermicity is modulated by factors such as strain rate. In these environments, non-equilibrium conditions can significantly amplify both energy release and chemical reactivity. Gilman [12] proposed that mechanochemical processes—where high strain rates can trigger or accelerate reactions—may play a central role. Supporting this view, Armstrong et al. [13] provided experimental evidence of chemical reactions occurring within 100 ps of shock passage, underscoring the rapid response enabled by non-equilibrium dynamics. Although these observations originate from condensed phases, they bear strong resemblance to the non-equilibrium behavior seen in gas-phase detonations, particularly in the coupling between shock waves and reactive kinetics.

Building on these insights, our study focuses on the role of such non-equilibrium effects in detonation re-initiation. Notably, we observe that the reinitiated detonation propagates at a velocity exceeding

Table 1: Parameters considered for molecular dynamics simulations

Initial conditions and parameters	Dimensionless values
$(L_x \times L_y \times L_z)/\lambda$	$255.91 \times 10.325 \times 1.0235$
d/λ	0.08
η	0.01
No. of particles	100000
$u_p/\sqrt{e_0}$	2.26
E/RT_s	5
E/RT_0	20
Q/RT	20 and 40

the classical CJ speed—a hallmark of weak detonations. This deviation suggests that enhanced energy release mechanisms under non-equilibrium conditions may stabilize a detonation mode distinct from the conventional CJ structure, offering a new perspective on detonation dynamics in simplified reactive systems.

As in our previous studies, we focus on a binary reaction model, with reactive molecules modeled as hard spheres to facilitate both continuum and molecular-level analysis. The molecular dynamics results are compared to continuum solutions, including Euler (inviscid flow) and Navier-Stokes equations (with gradient transport terms for a hard sphere gas), under various kinetic assumptions. Through this approach, we aim to uncover insights into the weak detonation regime and critically review Wood's pioneering work on weak detonations and their relevance to the present understanding of detonation dynamics.

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 [14]. 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.

3   Molecular Dynamics Description

The progression of particle positions and velocities is determined by the Event Driven Molecular Dynamics algorithm [16, 17]. The dynamics of hard sphere models can be obtained analytically. 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/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.
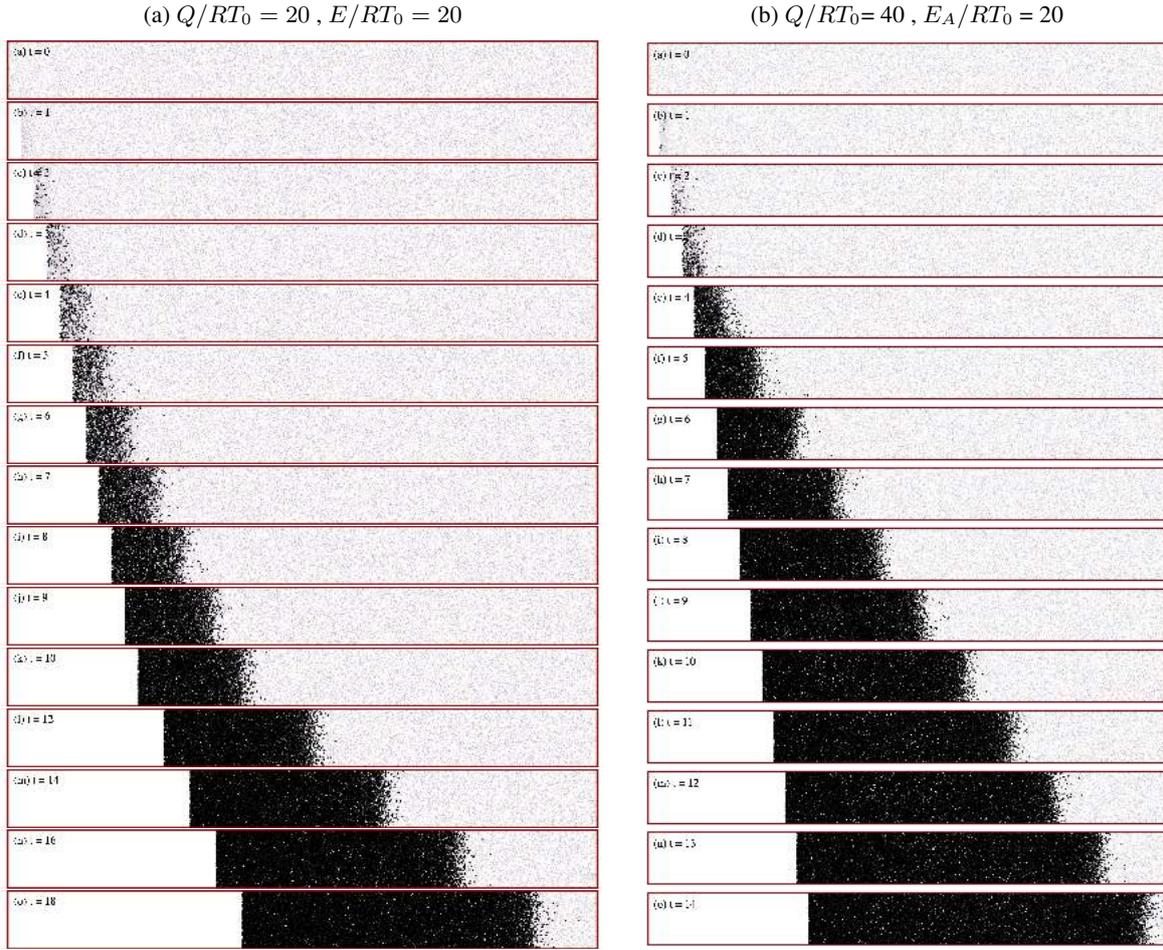
(a) $Q/RT_0 = 20$, $E/RT_0 = 20$ (b) $Q/RT_0 = 40$, $E_A/RT_0 = 20$

Figure 1: Time series snapshot of a sliced three-dimensional box for lower (left) and higher (right) heat release cases.

4   Continuum level description from kinetic theory

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

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} = 0 \tag{2}$$

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

$$\frac{\partial(\rho e_{tot})}{\partial t} + \frac{\partial\big(\rho\big(e_{tot} + p\big)u\big)}{\partial x} = k\frac{\partial}{\partial t}\left(\frac{\partial T}{\partial x}\right) + \frac{4}{3}\mu\frac{\partial}{\partial x}\left(u\frac{\partial u}{\partial x}\right) + Q\omega_C \tag{4}$$

$$\frac{\partial(\rho Y_C)}{\partial t} + \frac{\partial(\rho u Y_C)}{\partial x} = \frac{\partial}{\partial x}\left(\rho D\frac{\partial Y_C}{\partial x}\right) - \omega_C \tag{5}$$

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, k, 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 [14]:

$$\omega_C = 48 \frac{\eta}{\sqrt{\pi}d} \rho Y_A Y_B \sqrt{RT} \exp\left(-\frac{E}{RT}\right) \tag{6}$$

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. [18]. The solver employs a second-order accurate exact Godunov scheme for the convective terms. The modeling framework and numerical methods employed in this study follow those detailed in [19].
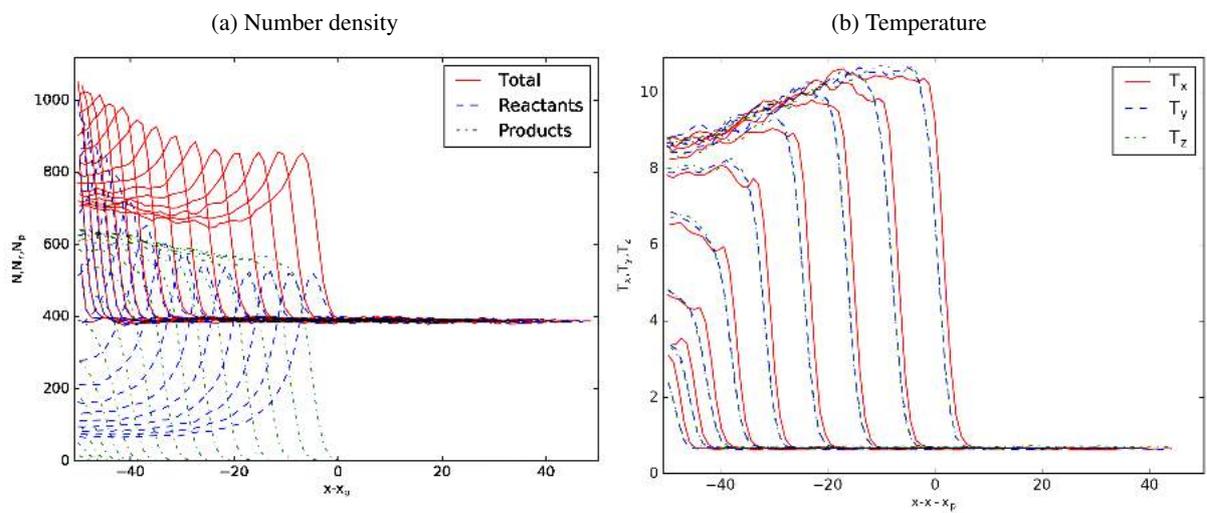
5   Results

Figure 2: Time evolution of (a) species profile with reactants (dashed blue line), products (dash-dotted green line) and total species (red line) and (b) temperature profile in the piston frame of reference for $Q/RT_0 = 20$, $E/RT_0 = 20$ and $E/RT_s = 5$
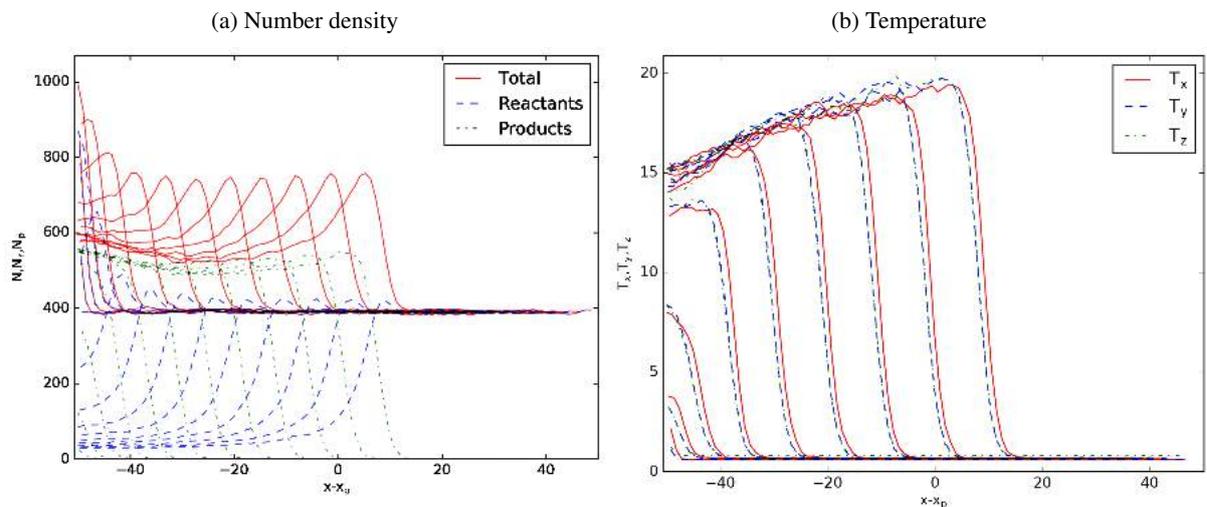
Figure 3: Description same as Fig. 2 for $Q/RT_0 = 40$, $E/RT_0 = 20$ and $E/RT_s = 5$

(a) $E/RT_0 = 20$ and $Q/RT_0 = 20$ (b) $E/RT_0 = 20$ and $Q/RT_0 = 40$
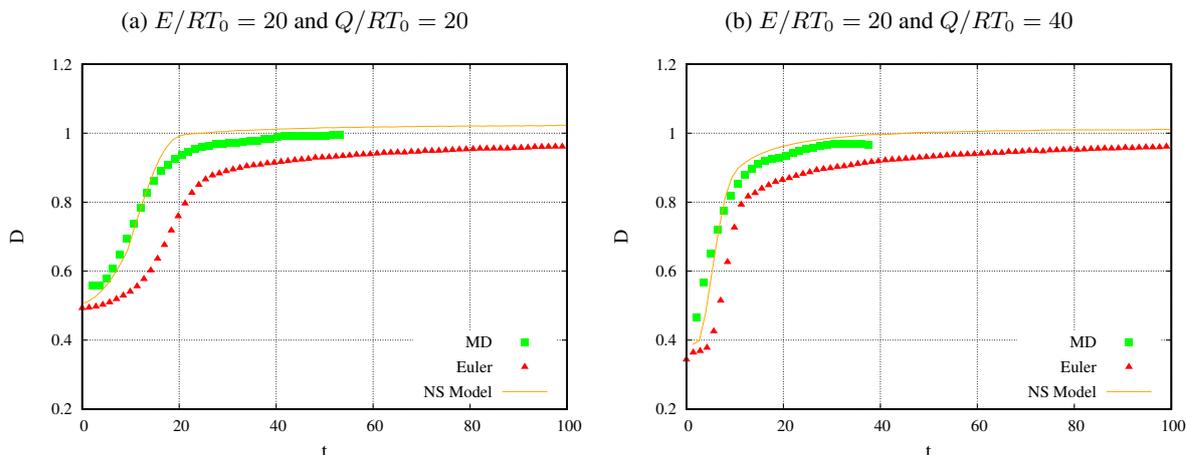
Figure 4: Comparison of detonation initiation process from MD with continuum models for $E/RT_s = 5$.

The first case considered is $Q/RT_0 = 20$. At time zero, the piston is accelerated from left into the quiescent 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, $Q/RT_0 = 40$ (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.

7 Discussion

The results from the MD simulations were compared with those obtained from inviscid and viscous reactive compressible Navier-Stokes simulations, using the solver mentioned above. For the viscous calculations, transport coefficients for hard-sphere molecules were derived from kinetic theory and applied as non-dimensional parameters, specifically with a Prandtl number of 2/3 and a Lewis number of 1.25. Fig. 4 illustrates the initiation of detonation from simulations using Euler, Navier-Stokes, and Molecular Dynamics methods. The latter two methods show good correlation in both cases, while the Euler calculations predict the onset of detonation 50% later, highlighting the importance of diffusion effects in the initiation process. This is further demonstrated by the finger-like structures observed ahead of the compression wave in MD simulations, a characteristic feature of diffusive detonation behavior.

Given the significant computational overhead, MD simulations were not conducted for extended periods. However, as shown in Fig. 4, MD results closely follow the Navier-Stokes predictions, with the wave speed computed from Navier-Stokes traveling approximately 2% above the CJ detonation speed in both cases. This aligns with the observations of Wood et al. [7], who noted that detonation waves propagate

faster than the CJ speed for large values of the rate parameter in a one-step reaction. To explore this phenomenon further, we compared the rate parameter obtained in this study with those reported in Wood's work.

From equation (6), the pre-exponential factor in our study is determined to be 3.38. In Wood's work [7], pre-exponential factors for low and high heat release cases were reported as 15 and 4, respectively, in non-dimensionalized units. Our results suggest that the pre-exponential factor falls within a similar range to Wood's reported values, indicating that the detonation in our simulations likely resides in the weak detonation regime.

While the molecular model used in this study excludes internal degrees of freedom such as rotation and vibration, this simplification directs all energy into translational motion, resulting in higher post-shock temperatures and enhanced ignition sensitivity. This deviation from real gas behavior may inhibit convergence with continuum (Navier-Stokes) solutions under the present parameters, but it provides a focused examination of the coupling between shock structure and chemical reactivity in highly non-equilibrium regimes. Moving forward, future studies will investigate parameter regimes where convergence with continuum descriptions is restored, which will provide a more complete understanding of the transition from molecular-scale dynamics to classical hydrodynamic behavior. Additionally, we plan to explore the detonation structure in greater detail, particularly focusing on the role of non-equilibrium effects in weak detonations and the limits of their applicability. These aspects will be further discussed at the upcoming conference.

7   Conclusion

This study employed molecular dynamics simulations to examine the influence of translational non-equilibrium on the shock-to-detonation transition in a reactive medium. The simulations revealed that non-equilibrium chemistry leads to a faster development of the reaction wave, with notable phenomena such as reactive fingers and the super-diffusion of hot particles ahead of the reaction front. Once detonation was established, the results showed that the reaction zone and shock wave overlap, contradicting the conventional view of a clear separation between the two. Furthermore, the detonation exhibited features consistent with the weak detonation regime, including propagation speeds exceeding the Chapman-Jouguet (CJ) value. This aligns with Wood's earlier theoretical work on weak detonations in high-diffusivity conditions, providing further validation for his predictions. The findings were also confirmed through Navier-Stokes simulations, which supported the existence of solutions for traveling waves under these conditions, offering new insights into the behavior of detonations in the weak detonation regime.

Acknowledgments

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