Modeling Gas Dynamic Effects in Shock-Tubes for Reaction Kinetics Measurements

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A low-order model was developed to simulate shock-tube systems in consideration of heat transfer and boundary layer effects. The model is derived from the reactive Navier-Stokes equations where losses are accounted for by additional sink terms in the momentum and energy equations. The model was demonstrated to replicate experiments and was shown to perform well against substantially more computationally expensive unsteady Reynolds-averaged Navier-Stokes models. Additionally, a kinetic rate measurement experiment was simulated using the model. From this, non-idealities due to the boundary layer were quantified to yield a 23% discrepancy in activation energy between the actual kinetic rate and that obtained from the simulation.

I. Introduction

Accurate chemical kinetic models are pivotal for characterizing the effects of new fuel compositions on existing propulsion systems and for developing future combustion technologies. Shock-tube facilities remain invaluable for providing detailed information about ignition delay times, extinction limits, and species time histories for the development and validation of reaction mechanisms. In its simplest form, a shock-tube consists of a constant diameter pipe, which is divided into a driver section and a driven section by a diaphragm. The driver section is pressurized with an inert gas, and the driven section contains the test gas mixture that is under experimental investigation. Following the rupture of the diaphragm, a normal shock develops which propagates into the driven section and is reflected at the end wall. Under ideal conditions, the test gas mixture in the region behind the reflected shock is stationary and uniform. While this condition is ideal for chemical kinetics investigations, practical shock-tube systems are affected by non-idealities. Over recent years, several sources responsible for non-ideal shock-tube behaviors have been identified, including

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boundary layer growth, reflected shock/boundary layer interactions, and inhomogeneous ignition phenomena. The direct consequence of these non-idealities are increasing uncertainties in measurements, resulting in potential errors in derived rate coefficients and ignition delay times.

Due to viscous and heat transfer effects along the shock-tube wall, the incident shock wave attenuates and propagates at a reduced velocity. These boundary layer effects cause a temporal temperature rise behind the reflected shock wave, which significantly affects the reaction kinetics. For practical applications, boundary layer effects can be partially mitigated by employing large shock-tube diameters, using driver inserts, and reducing the test time. However, if the operating range is extended to longer ignition delay times, these gas dynamic effects could increase in importance and may affect the experimental accuracy. Therefore, effects of the boundary layer on the conditions behind the reflected shock represent a limiting factor towards extending the shock-tube performance to longer test times.

Simple models such as CHEMSHOCK and the VTIM (volume as a function of time) reactor model have been developed to consider effects of the pressure rise of realistic shock-tube systems in homogeneous reactor models. They both work by incorporating pressure measurements from shock-tube experiments and isentropically correcting the temperature (CHEMSHOCK) or volume (VTIM). By incorporating pressure measurements into zero-dimensional simulations, these models have been found to improve the agreement with experimental data; however, they incorporate boundary layer effects in an a posteriori manner, and hence, their use is limited in the design of experiments.

The purpose of this work is to examine the ability of gas dynamic models to replicate the observed effects of the boundary layer in shock-tube experiments and to use them to study these effects on reaction kinetics measurements. For this, a one-dimensional model (STANSHOCK) was developed that captures the relevant physics within a shock-tube.

II. Mathematical model

STANSHOCK is derived by cross-sectional averaging the axisymmetric, reactive Navier-Stokes equations. These quasi-1D equations are given by

\[
\frac{\partial}{\partial t} (\rho_i a_{\rho_i}) + \frac{\partial}{\partial x} (\rho_i u a_{\rho_i} u) = \dot{\omega}_i a_{\omega_i}, \quad (1a)
\]

\[
\frac{\partial}{\partial t} (\rho u a_{\rho u}) + \frac{\partial}{\partial x} (\rho u^2 a_{\rho u} + p) = -\frac{4}{D} \tau, \quad (1b)
\]

\[
\frac{\partial}{\partial t} (\rho e a_{\rho e}) + \frac{\partial}{\partial x} (\rho u e a_{\rho e} + p u a_u) = -\sum_{i=1}^{N_m} e_i \dot{\omega}_i a_{e_i} - \frac{4}{D} q - \frac{4}{D} \mu, \quad (1c)
\]

where \(\dot{\omega}_i\) is the mass production rate for the \(i^{th}\) species, the shear stress at the wall is given by \(\tau\), the heat
loss to the wall is given by $q$, the viscous-work losses are given by $\mu$, and the diameter of the shock-tube is given by $D$. The variable area terms, $a_\chi$, are given by the following relation to first order:

$$a_\chi = 1 - \frac{4}{D} \int_0^{D/2} 1 - \frac{\chi_{BL}(r)}{\chi} dr ,$$

(2)

where $\chi$ is the free stream variable, and $\chi_{BL}$ is the radially-dependent variable within the boundary layer. Additional terms including mass diffusion, thermal conductivity, and viscosity in the axial direction are neglected. The shock-tube surface is considered non-catalytic, and no source term appears in the species and energy equations due to this assumption. Since the thickness of the boundary layer is small compared to the shock-tube diameter, the variable-area terms may be neglected assuming a fully-developed and quasi-steady flow with respect to the boundary layer. Additionally, the viscous-work due to the boundary layer is agglomerated in the heat transfer term for convenience to yield the following governing equations for Stanshock:

$$\frac{\partial}{\partial t} (\rho_i) + \frac{\partial}{\partial x} (\rho_i u) = \dot{\omega}_i ,$$

(3a)

$$\frac{\partial}{\partial t} (\rho u) + \frac{\partial}{\partial x} (\rho u^2 + p) = -\frac{4}{D} \tau ,$$

(3b)

$$\frac{\partial}{\partial t} (\rho e) + \frac{\partial}{\partial x} (\rho u e + p u) = - \sum_{i=1}^{N_{sp}} e_i \dot{\omega}_i - 4 \frac{q}{D} ,$$

(3c)

The shear stress at the wall is found through the classical Karman-Nikuradse skin-friction correlation:

$$\frac{1}{\sqrt{C_f/2}} = 2.46 \ln \left( \text{Re}_D \sqrt{C_f/2} \right) + 0.3 ,$$

(4)

where the skin-friction coefficient, $C_f$, is related to the wall shear stress by

$$C_f = \frac{\tau}{\frac{1}{2} \rho u^2} ,$$

(5)

and the Reynolds number is based on the diameter of the shock-tube and the local velocity

$$\text{Re}_D = \frac{\rho |u| D}{\mu} .$$

(6)

Note that the absolute value of axial velocity is taken to yield a positive Reynolds number. Also, the sign of $\tau$ is adjusted to ensure that it remains in opposition to the flow. The skin-friction coefficient is solved for implicitly via Newton’s method and is taken to be zero for $\text{Re}_D < 2300$.

The heat loss from the boundary layer is found by using the Stanton number correlation for turbulent
and fully-developed flows:  

$$\text{St} = \frac{C_f/2}{0.88 + 13.39(P_f^{2/3} - 0.78) \sqrt{C_f/2}},$$

(7)

where the Stanton number relates to the heat loss by

$$q = \rho u c_p (T - T_w) \text{St},$$

(8)

where $T_w$ is the wall temperature of the shock-tube.

The governing equations are solved using an adaptive mesh refinement (AMR) method, which is implemented in the object-oriented framework AMROC (Adaptive Mesh Refinement in Objective-oriented C++). The spatial derivatives are discretized using a second-order accurate finite-volume scheme, a forward Euler method is used for the temporal integration, and a Minmod limiter is used to capture shocks and contact discontinuities.

III. Model validation

Of primary interest in this study is the prediction of the temporal pressure rise behind the reflected shock as reported by Pang et al.\textsuperscript{15} The temporal pressure rise increases the reaction rate of the test mixture above that predicted by reactor models for shock-tubes. Additionally, a rise in pressure in the test section implies a corresponding rise in temperature, which further accelerates the reaction rate by increasing the value of the kinetic rate coefficient. For instance, assuming an isentropic relation between pressure and temperature in the test section, a 2% pressure rise will yield a 0.8% temperature rise in argon. Hence, the ability of Stanshock to capture this boundary layer effect was examined.

Two unsteady Reynolds-averaged Navier-Stokes (URANS) calculations were performed for comparison against Stanshock. The open-source CFD software OpenFOAM was used for both URANS calculations. The two-equation $k - \omega$\textsuperscript{16} and the one-equation Spalart-Allmaras\textsuperscript{17} turbulence closure models were chosen. Both calculations had a stretched grid of 2048 cells in the axial direction and 64 cells in the wall-normal direction. Isothermal boundary conditions at 304 K as well as no-slip boundary conditions were considered. The Stanshock calculation used the same resolution in the axial direction and the same wall temperature as the URANS cases; AMR was not used for this Stanshock calculation.

The calculations were initialized as a classical Riemann problem. This assumption does not take into effect the non-ideal rupture of the diaphragm, which can have a non-negligible effect on the attenuation of the shock wave.\textsuperscript{2} The dimensions of the domain were taken from Pang\textsuperscript{18} and are representative of the Stanford Kinetics Shock-Tube. The shock-tube has a total length of 14.89 m with the driven section having a length of 8.54 m. Also, the shock-tube has a diameter of 14.13 cm. The test gas was argon, and the
nominal temperature and pressure behind the reflected shock were 940 K and 3.5 atm, respectively.

Results showing the pressure as a function of time along the centerline and 1 cm away from the end wall are shown in Fig. 1. As shown in this figure, an increase in pressure with time occurs after the reflected shock wave passes the probe location.

A summary of the results is given in Table 1. The $k - \omega$ model is shown to have the best agreement with the experiment. The Spalart-Allmaras model tends to under-predict the pressure rise. The deviation of STANSHOCK from experiment is likely due to the selection of a general skin-friction and Stanton number correlation to describe the boundary layer losses; loss terms tailored to the gas dynamics of a shock-tube should yield a better correspondence to experiment. Additionally, the rupture of the diaphragm may create a transitional region that alters the pressure distribution that the reflected shock wave is traversing at long times. Also, heat loss to the wall in the test section is not modeled in STANSHOCK, which could account for some of the over-prediction in pressure. These slight effects will be investigated in future studies.

Overall, The results show STANSHOCK performing well in comparison to the URANS model. However, STANSHOCK requires approximately $1/100^{th}$ of the computational resources allowing for detailed parametric studies to be performed. The reduction in computational cost in STANSHOCK is primarily attributed to the reduced dimensionality of the model.

<table>
<thead>
<tr>
<th>Case</th>
<th>$d \ln p/dt$ (%/ms)</th>
<th>Normalized cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment$^{15}$</td>
<td>2.2</td>
<td>N/A</td>
</tr>
<tr>
<td>$k - \omega$</td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td>Spallart-Allmaras</td>
<td>0.3</td>
<td>0.85</td>
</tr>
<tr>
<td>STANSHOCK</td>
<td>2.9</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 1. Validation results showing the pressure rise in the test section and the computational cost normalized to that of the $k - \omega$ model.
As reported by Petersen,\textsuperscript{19} the attenuation of a shock wave was found to adhere to the following empirical relation:

\[
\alpha = 2.5p_1^{-0.14} \sqrt{M_s} ,
\]

where \(\alpha\) is the percent attenuation in the Mach number of the shock, \(M_s\), per meter, and \(p_1\) is the pressure of the driver gas. For the case under consideration, Eq. 9 predicts a shock attenuation of 0.9%/m. The attenuation of the shock wave can be found from post-processing the shock location from the CFD data. Since the value of the attenuation of the shock is small, it cannot be measured from a plot of the derivative of the shock location. Hence, only the position data is useful since a numerical derivative of the position incurs significant noise. The attenuation of the shock wave is supposed to adhere to the following exponential relationship:

\[
\beta M_s = \frac{dM_s}{dx_s} ,
\]

where \(\beta = -\alpha/100\). Since the Mach number is found with respect to the state in front of the propagating shock, the shock velocity, \(U_s\), varies while the speed of sound remains constant. The shock velocity is related to the measured shock position by the following relation:

\[
\frac{dx_s}{dt} = U_s .
\]

Solving Eq. 10, noting the equivalency of the ratio of Mach number to the ratio of the shock velocity, and substituting in Eq. 11, we have

\[
e^{\beta x_s} dx_s = U_{s,0} dt .
\]

Now, integrating and solving for \(x_s\), the final relations for the position of the shock wave is recovered:

\[
x_s = \frac{\ln(\beta U_{s,0} t + 1)}{\beta} .
\]

Note that as \(\beta\) goes to zero, the constant velocity relation is recovered. Using Eq. 13 and the data produced by the simulations, \(\beta\) is solved for via a least squares fit.

The comparison of the correlation to the simulation data is shown in Fig. 2. From Eq. 13, both Stanshock and \(k - \omega\) models yield an attenuation of approximately 0.6%. This is close to the value of 0.9% predicted by Eq. 9, and is well within the quoted experimental uncertainty of \(\pm 0.5\%\). However, Eq. 9 includes the attenuation due non-ideal diaphragm rupture, which increases the attenuation rate, leading to much of the discrepancy with the simulation. Hence, under these considerations, Stanshock was shown to perform rather well in comparison to the URANS model and Eq. 9.
Figure 2. Comparison of the shock attenuation with the prediction of Petersen's experimental relation. \( x_s \) corresponds to the shock location and \( U_{S0} \) corresponds to the initial speed of the shock derived from normal shock relations. Shaded region represents Petersen’s quoted uncertainty of the shock attenuation rate.

IV. Simulation of experiment

From the previous section, STANSHOCK was demonstrated to replicate key experimental observations including the temporal pressure rise in the test section and the attenuation of the incident shock wave. With confidence that STANSHOCK can reproduce the gas dynamics of a shock-tube, a simulated experiment was performed to quantify boundary layer effects on the measurement of a kinetic rate.

The simulated experiment considers the thermal decomposition of hydrogen peroxide via the following reactions:

\[
\begin{align*}
20 \text{H}_2\text{O}_2 + \text{M} & \rightleftharpoons 2\text{OH} + \text{M} \quad (14a) \\
\text{OH} + \text{H}_2\text{O}_2 & \rightleftharpoons \text{HO}_2 + \text{H}_2\text{O} \quad (14b) \\
\text{OH} + \text{HO}_2 & \rightleftharpoons \text{O}_2 + \text{H}_2\text{O} \quad (14c)
\end{align*}
\]

It was found by Hong that the initiation reaction given by Eq. 14a governs the formation of \( \text{H}_2\text{O} \). Hence, in a highly diluted mixture of 860 ppm \( \text{H}_2\text{O}_2 \)/663 ppm \( \text{H}_2\text{O} \)/332 ppm \( \text{O}_2 \)/Ar, the forward reaction rate of Eq. 14a can be determined at a given test temperature from the molar concentration of water in a shock-tube experiment with negligible influence of the reactions given by Eqs. 14b and 14c.

STANSHOCK was used to simulate the hydrogen peroxide pyrolysis experiment at temperatures between
$T_5 = 950$-1200 K. The STANSHOCK calculations use the $H_2/O_2$ mechanism of Hong et al. From the STANSHOCK calculations, the time-histories of the water concentration were gathered and the forward rate coefficient of Eq. 14a was adjusted in the Hong et al. mechanism such that

$$k_{\text{eff.}} = \arg\min_{k>0} (\|\epsilon(k)\|_2),$$

where $k_{\text{eff.}}$ is the effective forward rate coefficient of Eq. 14a due to the presence of the boundary layer, and $\epsilon$ is an error function given by

$$\epsilon = X_{H_2O, \text{SS}} - X_{H_2O, \text{UV}}(k).$$

$X_{H_2O, \text{SS}}$ is the mole fraction of water given by STANSHOCK, while $X_{H_2O, \text{UV}}$ is the mole fraction given by an adiabatic and isochoric reactor (UV). The governing equations for a UV reactor are given by

$$\frac{d\rho_i}{dt} = \dot{\omega}_i, \quad (17a)$$
$$\rho c_v \frac{dT}{dt} = -\sum_{i=1}^{N_{sp}} e_i \dot{\omega}_i. \quad (17b)$$

The initial conditions for the UV reactor are taken from the conditions in STANSHOCK after the reflected shock wave passes a probe located 1 cm from the end wall.

Chemical kinetics experiments often model boundary layer effects by incorporating pressure traces and assuming isentropic compression of the test gas. Assuming isentropic compression, the governing equations of an adiabatic reactor are given by

$$\frac{d\rho_i}{dt} = \dot{\omega}_i, \quad (18a)$$
$$\rho c_v \frac{dT}{dt} = -\sum_{i=1}^{N_{sp}} e_i \dot{\omega}_i + \frac{1}{\gamma} \frac{dp}{dt}. \quad (18b)$$

Note that Eq. 18 only differs from Eq. 17 by the isentropic pressure work term in the energy equation. The viability of isentropic modeling was examined using the pressure trace taken from STANSHOCK.

A comparison of the molar fractions of water are shown in Fig. 3. UV-modeling with the actual kinetic rate is shown to under-predict the rate of water formation in STANSHOCK. In an actual experiment, this would translate into a tuned kinetic rate that is higher than the actual rate. This is due to the approximately 1.4–2.1%/ms increase in temperature found in the STANSHOCK simulations. From Fig. 3, it is quite manifest that UV-modeling does a poor job at representing a shock-tube under the prescribed conditions; however, an integrated metric such as ignition delay would not be nearly as clear. No significant deviation between STANSHOCK and the isentropic model is apparent in Fig. 3.
Figure 3. Comparison of the water mole fractions to that given by STANSHOCK. Both of the effective rates are least square fits to the STANSHOCK trace using UV and isentropic models. The initial conditions are at a temperature of 1080 K and a pressure of 1.9 atm.

Figure 4 illustrates the error in using UV reactors to model shock-tubes in the presence of boundary layer effects. In the most extreme case at the lowest temperature, UV-modeling in the presence of boundary layer effects is shown to over-predict the rate coefficient by a factor of 2.1. However, the highest temperature case only differs by 8%. The effective rate coefficient of the UV model shows a 23% decrease in the activation energy when compared to the actual kinetic rate. However, isentropic modeling was found to accurately reproduce the actual rate coefficient; this indicates that isentropic modeling is a viable method for this particular experiment. Hence, this simulated experiment demonstrates that STANSHOCK modeling could be used to help determine the validity of reactor modeling for chemical kinetic studies.

V. Conclusions

STANSHOCK was developed to simulate boundary layer effects in shock-tube experiments in a computationally efficient manner. The model was shown to replicate the effects of the boundary layer in regimes where the shock-tube is prone to neither shock bifurcation nor weak ignition; however, these higher dimensional effects were examined in previous studies.\(^{22,23,24}\) Using STANSHOCK, a simulated experiment was performed, demonstrating that large discrepancies will arise in UV reactor modeling of shock-tubes in regimes with significant boundary layer effects (i.e. low temperatures). However, STANSHOCK also showed that isentropic reactor modeling with a known pressure trace is an effective method for dealing with boundary layer effects.
for the configuration under examination. Although, isentropic reactor modeling is limited since it relies on the availability of a time-resolved pressure measurement. STANSHOCK was shown to be an effective tool in evaluating boundary layer effects in shock-tube studies. Additionally, STANSHOCK can be used to determine whether detonation waves are likely to form and can simulate tailored experiments.

In addition to isentropic reactor modeling, experimentalists use devices that reflect the expansion waves in the driver section of the shock-tube to counteract the non-ideal gas dynamics due to the boundary layer.\textsuperscript{25} It is the subject of future studies to incorporate such effects into the modeling of shock-tube kinetic experiments.

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