Real-GasCorrection to Shock Wave Jump Relations in Diatomic Nitrogen

A. Markhotok

Physics Department
Old Dominion University
Norfolk, VA 23529

Abstract
Shock wave jump relations in real gas are determined analytically and numerically, in the range of gas parameters common for discharges. Non-dissociating gas on both sides of discontinuity with excited translational, rotational, vibrational, and electronic degrees of freedom is considered. The model relations are applied to \( \text{N}_2 \) gas at \( T=3000 \) K for which 11% density increase and 17% temperature and 7% pressure decrease, compared to the levels predicted by R-H relations, were found. The relations are largely built on experimental data thus avoiding the complexity of careful accounting for real gas effects and still offering satisfactory precision levels. The results can be found useful in a range of applications involving shocks interacting with substantially heated media including shock-flame interaction, shock wave assisted combustion, detonation, thermal energy deposition in the flow, and in astrophysics where shock waves generated in stellar interior are involved.

Key words: Shock waves, Real-gas Effects, Electrical Discharges.
E-mail of corresponding author: amarhotk@phys.washington.edu

I. INTRODUCTION

In many applications involving shock waves interacting with gaseous media, Rankine–Hugoniot (R–H) relations are the main equations on which the models are based. The R-H relations determine gas parameter jump across the shock and, in its classical form, assume the ideal-gas conditions on both sides of the discontinuity. In their formal derivation, the shock wave is approximated with a singular, infinitely thin surface of infinitesimal rise time that mathematically represents a very narrow region across which sharp changes of final amplitude in the gas properties occur. Since dissipation is neglected in the derivation, any information on its mechanisms is not included in the equations and thus the specific entropy in the flow on both sides of the discontinuity must be constant. On the other hand, the compression in a shock wave is an irreversible process leading to an increase in entropy. To avoid discrepancy, the shock is allowed to have a microscopic structure and it is supposed that the entropy increase across the shock occurs within its layer of a finite width. The type of the dissipation process determines the width that is adjusted in such a way that the specific entropy increase across the shock corresponds exactly to the parameter jump across the shock satisfying the R-H relations. In case of two-body collisions typical for moderate gas conditions, the shock thickness is on the order of
the molecules mean-free-path in the gas, however in some cases the shock layer can be up to tens of times wider.

In the problems involving shock waves interacting with substantially heated media, such as shock-flame interaction, thermal energy deposition in a hypersonic flow via electrical, RF or optical discharges, or in astrophysics for shocks generated on stellar surfaces, the validity of the ideal gas approximations, and consequently the applicability of the R-H relations, must be questioned.

The non-ideal gas effects are known to be quite strong, as for example in $O_2$ and $N_2$ where at very low pressures dissociation is significant. The density jump across a shock in those gases, for example, can exceed the maximum ideal diatomic value of 6 by several times reaching a value of 25, see reference [1]. If an experiment is creating substantially non-perfect gas conditions and its results are used for model validations, the criterion of ideality has to be applied and tested. Thus accounting for non-perfect gas effects is important and any numerical data for a particular gas and heating conditions, or a general procedure that can be used to account for the effects, is much desired by researchers.

The research on this subject has been done for various problems of gas dynamics, for example [2-7]. In this work, the real-gas jump conditions will be determined for a range of temperatures common for gas discharges. Then the relations will be applied to a specific gas (diatomic nitrogen) and the results are presented in the form of graphs, comparatively to that predicted for an ideal gas.

II. SHOCK WAVE JUMP CONDITIONS IN REAL GAS

This paragraph will be focused on determining the shock jump conditions that account for real-gas effects. In the derivations below, it will be first assumed that the system is in the thermodynamic ($TD$) equilibrium and, at the pressure and temperature levels considered here, no molecular dissociation in the gas is present. The time it takes for $TD$ equilibrium to be established depends on rates at which transfer of energy between the degrees of freedom occurs. The times for translational and rotational degrees are very short, but for vibrational and dissociation degrees they can be several orders of magnitudes longer. The $CO_2$ gas is known, for example, for having a vibrational relaxation time relatively shorter than the dissociation relaxation time, so the vibrational equilibrium is established well before the dissociation comes
into play. Thus the approach used here can be valid for the cases when the flow duration/interaction times are shorter than the dissociation time or for certain gases (for ex. \( \text{N}_2, \text{CO} \)) whose dissociation energies are high enough so this degree of freedom is not significantly excited.

When a shock wave propagates through a gas, due to compression the gas parameters across the shock experience jump and the pressure, temperature and density change significantly increase with the shock intensity. In monatomic gases, the ideal gas relations work until approximately 8000 \( K \) and at some lower temperatures in diatomic gases, when only translational and rotational degrees of freedom are excited. At higher temperatures, when the heat capacity of the gas increases due to excitation of vibrations, the temperature jump values \( T_2/T_1 \) begin to lag behind its ideal-gas value. This lag experiences steep increases with the onset of dissociation, and then electronic excitation and ionization as the temperature goes up. The real-gas density ratio \( \rho_2/\rho_1 \) in a shock wave considerably overtakes the ideal-gas levels and this tendency increases with the shock intensity, while the pressure jump usually becomes elevated rather slightly.

In one of the existing models accurately accounting for real-gas effects its relations rely on the values of the shock speed that are measured experimentally [1]. In many applications though, it is important to have analytical expressions as functions of shock strength (Mach number) and such an attempt will be done in this work.

Derivation of real-gas jump relations can be started with the same system of equations used for the ideal-gas flow through a discontinuity

\[
\begin{align*}
\rho_1 u_1 &= \rho_2 u_2 \quad (1) \\
p_1 + \rho_1 u_1^2 &= p_2 + \rho_2 u_2^2 \quad (2) \\
H_1 + \frac{1}{2} u_1^2 &= H_2 + \frac{1}{2} u_2^2 \quad (3)
\end{align*}
\]

The equations (1-3) are expressions of the three fundamental laws of conservation (mass, momentum, and energy) and thus are still valid for real gas. Here indices 1 and 2 correspond to the flow in front and behind the shock correspondingly, \( H \) is the specific enthalpy, \( u_2 = \text{V}_{sw} - v_2, \quad u_1 = \text{V}_{sw} - v_1 \) are the flow speeds across the shock in the reference frame moving with the shock wave, \( v_1 \) is the flow speed in front of the shock relative to laboratory reference frame, and \( \text{V}_{sw} \) is the shock speed relative to the gas. Using the first two equations in the system, the energy conservation equation (3) can be brought to the form

\[
H_2 - H_1 = \frac{u_2^2}{2} \left[ 1 - \left( \frac{\rho_1}{\rho_2} \right)^2 \right] \quad (4)
\]
Since the heat capacities $C_p$ and $C_v$ are not constant in real gases but are functions of temperature and pressure, the enthalpy cannot be written in its classical ideal-gas form and the system (1-3) cannot be solved explicitly. Thus, the real-gas solution here is reduced to finding a way to express the enthalpy in terms of real-gas parameters and the shock wave strength.

The complexity of careful accounting for various real-gas processes in the left-hand part of the expression (4) can be avoided if experimental data obtained for specific gases is used. Such data on real-gas enthalpy for various gases is available in literature, for ex. [1]. The numerical data for the enthalpy can be fit, for example, with a polynomial function of temperature

$$H(T) = \sum_{n=0}^{\infty} \alpha_n T^n$$

(5)

in which, because of the enthalpy difference in (4), only the second ($\alpha_1$) and higher order fit coefficients $\alpha_n$ are important. When applied to diatomic nitrogen, the fit (5) turns out to be quite linear. So if the higher order coefficients $\alpha_n$ are neglected, the enthalpy $\Delta H \approx \alpha_1 (T_2 - T_1)$. Then the eq. (4) transforms into

$$\frac{T_2}{T_1} = 1 + \frac{u_1^2}{2 \times 10^7 \alpha_1 T_1} \left[ 1 - \left( \frac{\rho_1}{\rho_2} \right)^2 \right]$$

(6)

where “J” is the mechanical equivalent of heat, $u_1$ is in cm/s, and the enthalpy is in Cal. For the compressions achievable in shock waves, the ideal-gas state equation

$$\frac{p_2}{p_1} = \left( \frac{\rho_2}{\rho_1} \right) \left( \frac{T_2}{T_1} \right) \left( \frac{\mu_1}{\mu_2} \right)$$

(7)

can be still valid\(^1\). Here $\mu_1$ and $\mu_2$ are the gas molar weights and $d = \mu_2 / \mu_1$ is the dissociation. Using this equation together with the system (1-3) yields

$$\frac{p_2}{p_1} = 1 + \frac{\mu_1 u_1^2}{RT_1} \left[ 1 - \frac{\rho_1}{\rho_2} \right]$$

(8)

and combining (6), (7) and (8) we obtain

$$1 + \frac{\mu_1 u_1^2}{RT_1} \left[ 1 - \frac{\rho_1}{\rho_2} \right] = \frac{\rho_2 \mu_2}{\rho_1 \mu_2} \left\{ 1 + \frac{u_1^2}{2 \times 10^7 \alpha_1 T_1} \left[ 1 - \left( \frac{\rho_1}{\rho_2} \right)^2 \right] \right\}$$

(9)

The speed $u_1$ in the eq. (9), which is equal to the shock speed relative to the gas (at $v_1 = 0$), can be expressed through the speed of sound $a_1$ and the shock Mach number $M_1$, $u_1 = M_1 a_1$, so the equation (9) can be solved for the density ratio versus $M_1$. In determining the speed of sound, the real gas effects must be accounted for as well. This will be done in the next paragraph, in the form of correction factor $\sigma$ used with the ideal-gas relation as $a_1^2 = \sigma (\gamma / R / \mu)$. For diatomic nitrogen, the dissociation levels remain insignificant even at $T=5000$ K and thus the ratio $d = \mu_2 / \mu_1$ in eq. (9) can be neglected. Then, with known solution for the density ratio obtained from the eq. (9), the full set of jump relations (eqs. 7, 8, 9) replacing the ideal gas Rankine-Hugoniot relations can be obtained.
Since the experimental data on enthalpy for a particular gas is available only in a definite range of temperatures, the solution validity (7-9) is limited by this range. In case the data is outside of a desired temperature interval, similar results for diatomic gases can be obtained with the following alternative solution. The enthalpy of a real gas consisting of diatomic molecules in equilibrium state at a temperature $T$ can be written as

$$H_T = \frac{3}{2} RT + \frac{2}{2} RT + \frac{N h v}{(e^{h v/k T} - 1)} + RT + \frac{h v}{2}$$  \hspace{1cm} (10)$$

where the first three terms correspond to the excited translational, rotational and vibrational degrees of freedom respectively, the last one is the zero point energy term, and no dissociation or electronic excitation is taken into account [1]. Here $\bar{N} = N/\mu$ is the number of molecules per unit mass of gas, $R$ is the universal gas constant per unit of mass of gas, and $v$ is in cycles/second. If no dissociation ($N_2 = N_1$),

$$H_2 - H_1 = \frac{7}{2} R (T_2 - T_1) + N h v \left[ \frac{1}{(e^{h v/k T_2} - 1)} - \frac{1}{(e^{h v/k T_1} - 1)} \right]$$  \hspace{1cm} (11)$$

The vibrational energy term represents the summation over $N$ quantized molecular oscillators having permissible energy levels corresponding to frequencies $\nu_n = n \nu$, with the fraction of molecules in any level being proportional to $\exp(-h v/k T)$. This applies to the case of a diatomic molecule in its electronic ground state vibrating with a characteristic frequency $\nu$ measured in cycles per second. The zero point energy term $h v/2$ does not enter the relation (11) since it does not depend on temperature. For nitrogen, at the temperature of $T = 3000$ K and the characteristic frequency $\nu = 0.826 \cdot 10^{13}$ s$^{-1}$, the ratio $h v/k T \ll 1$ so the exponential term can be approximated [8] with the first three terms in the expansion $e^{h v/k T} \cong 1 + h v/k T + \frac{1}{2} \left( \frac{h v}{k T} \right)^2 + \cdots$. Then, using the same approach as in the solution above with the eq. (4) and (10), the following relation can be obtained

$$u_1^2 \left[ 1 - \left( \frac{p_1}{p_2} \right)^2 \right] = \frac{7}{2} R T_1 \left( \frac{T_2}{T_1} - 1 \right) + R T_1 \left[ \frac{T_2}{T_1} \left( \frac{h v}{k T_2} \right)^2 \right] - \frac{1}{1 + \frac{h v}{k T_1}}$$  \hspace{1cm} (12)$$

If solved together with the relation (6), this yields a dimensionless equation that can be solved for the temperature ratio $T_{21} = T_2/T_1$

$$\frac{T_{12} d}{b_5 - b_1 T_{12} - b_2 T_{12}^2} = 1 + b_6 \left[ 1 - \sqrt{b_5 - b_1 T_{12} - b_2 T_{12}^2} \right]$$  \hspace{1cm} (13)$$
The solution to the equation (13) is

\[ \frac{T_{12}d}{s} = 1 + b_6[1 - s] \quad (14) \]

where \( s = \sqrt{b_5 - b_1T_{12} - \frac{b_2T_{12}^2}{b_3 + T_{12}}} \), \( d \) is dissociation, and the coefficients \( b_1 = \frac{7/2}{\gamma M_1^2 \sigma^2} \), \( b_2 = \frac{1}{\gamma M_1^2 \sigma^2} \), \( b_3 = \frac{hv}{2kT_1} \), \( b_4 = \frac{17/2}{1 + b_3} \), \( b_5 = 1 + \frac{9/2 + (1 + \frac{hv}{2kT_1})^{-1}}{\gamma M_1^2 \sigma^2} \), \( b_6 = \gamma M_1^2 \sigma^2 \) are the functions of the complex dimensionless parameters \( \gamma M_1^2 \sigma^2 \) and \( hv/2kT_1 \). Here \( \gamma \) is the real-gas adiabatic coefficient and \( \sigma \) is the correction factor to the speed of sound (discussed in next paragraph). The solution for \( T_{21} \), together with (6-8) represent the alternative real-gas system of \( R-H \) relations that can be used to determine the temperature, density and pressure jumps across the shock.

III. SPEED OF SOUND IN REAL GASES

To estimate real-gas effects on the speed of sound, the approach [9] using a correction to its ideal gas value can be utilized. The real-gas equation will keep the same form as the Laplace equation \( a^2 = \gamma_i RT/\mu \) used for ideal gas but corrected with three factors

\[ a^2 = (\gamma_i RT/\mu)(1 + K_c)(1 + K_v)(1 + K_r) \quad (15) \]

Here the \( i \) - subscript refers to the ideal gas where only translational and rotational degrees of freedom are excited, the compression factor \( z = P/\rho RT \) is independent of pressure, there are no losses during the sound wave propagation, and the parameter \( \sigma = (1 + K_v)(1 + K_v)(1 + K_r) \). The coefficient \( K_c \) is the specific heat correction accounting for the temperature, \( K_v \) is the virial correction taking into account intermolecular interactions and is the function of temperature and pressure. And the relaxation correction \( K_r \) accounts for relaxation processes leading to acoustical dispersion and is a function of temperature, pressure and frequency. All the three corrections are independent of each other and thus will be calculated separately.

III A. Specific Heat Correction

One of the ways to estimate the specific heat correction \( K_c \) can be the use of a fit function to experimental data that is available, for example, in reference [9]

\[ K_c = \frac{\gamma_c}{\gamma_i} - 1 = \frac{1}{\gamma_i} (1 + a_{c0} + a_{c1}T + a_{c2}T^2 + a_{c3}T^3 + a_{c4}T^{-1}) - 1 \quad (16) \]
The applicability of the equation (16) is dependent on the range of temperatures within which the data is available. For example, for diatomic nitrogen the temperature range in the above reference is relatively narrow, between 80 and 775 K. If higher temperatures are of interest, an alternative procedure using relations from the same reference [9] can be used. Each type of the various excited modes in the gas are considered there separately assuming that the heat capacity $C_{vc}$ is additive. The Decoupled Rridged-Rotor Harmonic oscillator (DRH) model that can be used in this case is based on the assumption that there is no Coriolis interaction between the modes, no modes of motion associated with molecular distortions are excited and no low-\(T\) quantum effects. The model precision is on the order 0.5\% for temperatures up to 1500 K and the number increases with further temperature increase. The square well potential model can be also applied to the problem though its precision was shown to be much less than for the DRH model, with up to +/- 20\% error.

The following mode contributions to the specific heat are considered, in the typical order of their excitation as the gas temperature increases. The translational specific heat $C_{v0} = \frac{3}{2} R$, if no other modes are present, results in the contribution to the correction coefficient

$$K_c = \frac{\gamma_c - 1}{\gamma_c} = 1 + \frac{R}{C_{vc}} \tag{17}$$

The rotational specific heat (for linear molecules)

$$\frac{C_{vcrot}}{R} = 1 + \frac{1}{45} \left( \frac{\theta_{rot}}{T} \right)^2 + \cdots \tag{18}$$

and for nonlinear molecules

$$\frac{C_{vcrot}}{R} = \frac{3}{2} + \frac{1}{45} \left( \frac{\theta_{rot}}{T} \right)^2 + \cdots \tag{19}$$

where the values of characteristic temperature $\theta_{rot}$ in the quantum correction (second) term are available [9]. For the air gas components such as $N_2$, $NO$, and $O_2$, for example, the characteristic temperature values are very low and are 2.81 K, 2.45 K, and 2.08 K respectively, making the correction, even at room temperature, negligible.

The vibrational specific heat for a diatomic molecule can be estimated using the harmonic oscillator mode

$$\frac{C_{vc,vib}}{R} = \left( \frac{\theta_{vib}}{T} \right)^2 \frac{\exp\left(\frac{\theta_{vib}}{T}\right)}{\left[1 - \exp\left(\frac{\theta_{vib}}{T}\right)\right]^2} \tag{20}$$

and the characteristic temperatures $\theta_{vib}$ that can be also found in [9].

For the conditions developed in shocks, the typical contribution of electronic excitation to the specific heat
is usually very insignificant due to its high (relatively to the previous modes) excitation energies, except in some specific gases. For example, in $N_2$ molecule, its singlet ground $X_1 \Sigma^+_g$ and first excited $^1\Pi_g$ states are separated by 69290 cm$^{-1}$ that is corresponding to $\theta_{el} = 69,290$ K. With both degeneracies $g_0 = g_1 = 1$, the correction, at room temperature, yields just the value $2.4 \cdot 10^{-143}$ that can be safely neglected. However, in the $NO$ molecule, the ground level is doubly degenerate: the spin-orbit coupling splits the ground level ($^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states) with the separation of only 174.2 K that atypically strongly contributes to the specific heat [9].

Using the specific heat additivity, the contribution of all modes

$$\frac{C_{\text{uc,el}}}{R} = g_0 g_1 \left( \frac{\theta_{el}}{T} \right)^2 \frac{\exp\left(\frac{\theta_{el}}{T}\right)}{g_0 + g_1 \exp\left(\frac{\theta_{el}}{T}\right)}$$

(21)

can be used in (17) to finally obtain the correction $K_c$.

III B. Virial Correction

The virial correction factor $K_v$ accounts for intermolecular interactions. For compressions typical in shocks its value is rather negligible, however in some media with specific molecular structure and characterized by low temperatures and high pressures, it should be considered. The virial correction can be determined using the expansion of the equation of state with pressure $P$ used as the expansion variable

$$\frac{PV}{RT} = 1 + B_p P + C_p P^2 + \cdots$$

(23)

Here $V$ is the molar volume and $B_p = B/RT$ and $C_p = (C - B^2)/(RT)^2$ are the second and third pressure virial coefficients related to the corresponding volumetric coefficients $B$ and $C$. Then the virial correction, if limited with the first two terms,

$$K_v = FP + GP^2$$

where $F = \frac{K}{RT}$, $G = (L - BK)/(RT)^2$ and the acoustical virial coefficients $B$, $K$ and $L$ will be determined below as follows. The coefficient $B$ can be obtained by fitting experimental data, as described in reference [9].

$$B = a_v - b_v \exp \left( \frac{c_v}{T} \right)$$

(24)

The coefficient $K$ can be expressed via the following fit

$$K = a_{v0} + \left( a_{v1} + \frac{a_{v2}}{T} + \frac{a_{v3}}{T^2} \right) \exp \left( \frac{c_v}{T} \right)$$

(25)
and the numerical coefficients in (25) are related to those in (24) as
\[ a_{\nu 0} = 2 a_{\nu}, \quad a_{\nu 1} = -2 b_{\nu}, \quad a_{\nu 2} = \frac{2(y_0 - 1)C_{\nu}b_{\nu}}{y_0}, \quad a_{\nu 3} = \frac{(y_0 - 1)^2(C_{\nu})^2b_{\nu}}{y_0}. \]
The coefficient \( L \) can be determined in a similar way, using a fit to the data for the third virial coefficient. Due to bulkiness of the final expressions, they are not presented here but instead can found in [9].

Molecular association that is also related to the virial coefficients is impacted through the molar mass, specific heat \( C_{vc} \), and the compressibility factor. Molecular collisions can produce stably bound long-lived or metastably bound short-lived molecular formations that should be considered depending on whether the system is in TD equilibrium or not. For linear molecules, the association of two monomers result in the loss of 3 translational and 3 rotational degrees of freedom that are replaced by 6 dimer-specific vibrational, ”weak” modes. If the mode’s characteristic temperatures are relatively low, they contribute \( 6R \) to the specific heat, so the total specific heat \( C_{\nu, \text{d}} = x_1 3R + x_2 (3R + 6R) = (3 + 6x_2)R \) and the specific heat ratio \( \gamma_{\nu} = (4 + 6x_2)/(3 + 6x_2) \), see reference [9]. Here \( x_1 \) and \( x_2 \) are mole fractions for monomers and dimers correspondingly, and \( x_1 + x_2 = 1 \).

### III C. Relaxation Correction \( K_r \)

Sound wave energy dissipates via collisions during which a portion of energy is transferred to the translational degrees of freedom followed with its transfer to the inner molecular degrees of freedom. During the relaxation period gas parameters change until a new TD equilibrium establishes. Because it may take up to billions collisions to activate each of the transitions and, accounting for finite de-excitation times, the time delay between excitation and response causes the sound wave dispersion followed with change in the speed of sound and absorption. If impurities are present in the gas, the dispersion effect can be stronger.

The sound speed \( a \) and the absorption \( \mu_1 \) can be expressed in terms of relaxation strength \( \varepsilon \) and relaxation times [9], the dispersion time \( \tau_d \), frequency \( \omega \), and absorption time \( \tau_a \), as
\[
\begin{align*}
    a^2 &= a_{c\nu}^2 \left[ 1 + \frac{\varepsilon}{1 - \varepsilon} \frac{(\omega \tau_d)^2}{1 + (\omega \tau_d)^2} \right] \quad (26) \\
    \mu_1 &= \frac{\omega \tau_d}{\sqrt{1 - \varepsilon} \left( 1 + (\omega \tau_d)^2 \right)} \quad (27)
\end{align*}
\]
Here index \( i \) will be referred to an ideal gas and \( c - \) to a lossless real gas that accounts for two previously discussed corrections, \( a_{c\nu}^2 = a_{i}^2 \left( 1 + K_c \right) \left( 1 + K_{\nu} \right) \), and times \( \tau_d \) and \( \tau_a \) are related as \( \tau_d = \tau_a \sqrt{1 - \varepsilon} \). Then the relaxation correction
\[
K_r = \frac{\varepsilon}{1 - \varepsilon} \frac{(\omega \tau_d)^2}{1 + (\omega \tau_d)^2} \quad (28)
\]
The relaxation intensity $\varepsilon$ for a specific $i$-th reaction can be obtained via the corresponding specific heat capacity $C_i$ and using its additivity property

$$\varepsilon = \frac{R \sum_i C_i}{(C_p - \sum_i C_i)(C_p - R)} \tag{29}$$

If an $i$-th vibrational degree of freedom is excited, its isothermal heat capacity can be determined as

$$C_i = q_i R \left( \frac{\theta_{vib}^{(i)}}{T} \right)^2 \frac{\exp\left( -\frac{\theta_{vib}^{(i)}}{T} \right)}{\left[ 1 - \exp\left( -\frac{\theta_{vib}^{(i)}}{T} \right) \right]^2} \tag{30}$$

where $R$ is the universal gas constant, $g_i$ is the vibrational energy level degeneracy, and the vibrational temperature values $\theta_{vib}$ are found experimentally and listed for various gases in [9].

The relaxation time $\tau_{VT}$ can be calculated using the following fit to experimental data

$$\log(\tau_{VT}P) = a_r(1) + a_r(2)T^{-1/2} + a_r(3)T^{-1} \tag{31}$$

where $T$ is the temperature in K, $P$ is pressure in atm, time is in $\mu$s, and the numerical coefficients $a_r(i)$ are given in [9]. Then the dispersion time can be derived using the values of time $\tau_{VT}$, specific reaction heat capacity $C_i$ and that of an ideal gas $C_V^0$

$$\tau_d = \tau_{VT} \left( 1 - \frac{C_i}{C_V^0} \right) \tag{32}$$

The range of sound wave frequencies $\omega$ is specific to the way it is created. However, the correction $K_r$ in the equation (28) can be readily determined for two limiting cases. When the complex $\omega \tau_d \ll 1$, the correction simplifies to

$$K_r = \varepsilon \left( \omega \tau_d \right)^2 \tag{33}$$

and this condition corresponds to the frequencies

$$\omega_k \ll \left[ \tau_{VT} \left( 1 - \frac{C_i}{C_V^0} \right) \right]^{-1} \tag{34}$$

If $\omega \tau_d \gg 1$, the correction $K_r = \frac{\varepsilon}{1 - \varepsilon}$ is the function of the relaxation strength only, and applies to the frequencies $\omega \gg \omega_k$.

IV. CORRECTION TO THE SPEED OF SOUND IN $N_2$

As a numerical example, the real-gas correction to the speed of sound will be determined here for diatomic nitrogen. This specific gas was chosen due to its dominant contribution in the air and the gas temperature taken as $T_2=3000$ K is common for the applications involving shock waves interacting with plasma produced in discharges. For these specific parameters, the approach using eq. (16) cannot
be used because the numerical coefficients $a_{ci}$ in eq. (16) are available only in the range of temperatures between 80 $K$ and 775 $K$. Then the alternative procedure with equations (17-32) will be utilized. In the calculations below, all experimental data including the values of characteristic temperatures will be taken from reference [9] unless otherwise noted.

To determine the value of specific heat correction $K_c$, the contribution of the following degrees of freedom in the gas will be taken into account. In the nitrogen gas, the translational degree of freedom term $C_v/T = 3/2$. The value of rotational specific temperature in the quantum correction (second) term $\theta_{rot} = 2.08 K$, that is very low. This makes the correction to the rotational specific heat in eq. (18), $C_{vc,rot}/R = 1 + 2.0 \cdot 10^{-8}$ negligible. However the characteristic vibrational temperature in this gas, $\theta_{vib} = 3352.0 K$ is comparable to the gas temperature $T_2$ and the correction to the specific heat term in eq. (20), $C_{vc,vib}/R = 0.902$ is significant. For electronic transitions, the characteristic temperature $\theta_e = 99,692 K$ is relatively high and in the ground state ($g_0 = g_1 = 1$) the contribution $C_{vc,el}/R = 4.14 \cdot 10^{-7}$ can be neglected. As temperature increases, its value is still low reaching $4.5538 \cdot 10^{-3}$ at $T = 10,000 K$.

The contribution of all modes into the total specific heat can be determined using the additive property of heat capacities, $C_{vc,Total}/R = 3.402$, so $K_c = 0.0758$ and $\gamma_c = 1 + R C_{vc,T} = 1.293$. Applying the procedure within a range of temperatures 300 -10,000 $K$, the correction $K_c$ vs temperature curves can be obtained. The results presented in Fig. 1 can be used as an extension into higher temperatures of similar graphs obtained in reference [9].

![Fig. 1. Specific heat correction $K_c$ and corresponding specific heat ratio $\gamma_c$ vs gas temperature, for $N_2$ gas.](image)

For the virial correction, a very small value $K_v = 0.374 \cdot 10^{-8}$ can be obtained using the equations (23-25), and thus, in considered circumstances, its contribution to the sound speed is insignificant.
The value of relaxation correction $K_r$ at the specified temperature can be determined using equations (26-32). In diatomic nitrogen, when only one vibrational degree of freedom is excited, its isothermal heat capacity $C_i = 7.5016 \text{ J/(molK)}$ can be determined from eq. (30) at $\theta_{\text{vib}} = 3352.0 \text{ K}$. Then the relaxation intensity $\varepsilon = 0.04558$ is obtained from the eq. (29). Using numerical coefficients $a_1 = -3.6481$, $a_2 = 71.6300$ and $a_3 = 0$ in the equation (31), the time $\tau_{VT} = 20.827 \mu\text{ks}$. Then, from the values of $\tau_{VT}$, specific heat capacity $C_i$, and that of an ideal gas $C_{vi}$ in the eqn. (32) the “relaxation” time $\tau_d = 16.56 \mu\text{ks}$.

The sound wave frequency $\omega$ that is entering the expression (28) can be determined from experimental data. Particularly, when a shock wave interacts with a plasma volume created in an optical discharge, the frequency can be estimated from pressure rise time in the gas explosion. In one of such experiments\textsuperscript{10}, the typical time for the pressure to increase to maximum was around $t_0 = 50 \mu\text{ks}$ corresponding to the frequency $\omega = 12.56 \times 10^4 \text{ rad/s}$. Then the correction $K_r = 0.0388$, and thus, with all the three corrections $K_c$, $K_v$, and $K_r$ known, the speed of sound correction can be determined as $\sigma = 0.9472$.

V. SHOCK JUMP RELATIONS IN REAL GAS

With the value of the speed of sound correction determined, the real gas jump relations can be computed using the system of equations (6-9). The curves in Fig. 2 are the jump relations versus Mach number, in non-dissociating ($d = 1$) real gas ($N_2$) obtained at the temperature $T = 3000 \text{ K}$, presented comparatively to the ideal gas case. The results represent real-gas equivalent (solid lines) of the jump relations in ideal gases (dashed line). On the graphs, the green line corresponds to the speed of sound corrected results ($\sigma = 0.9472$). The black solid line corresponding to uncorrected speed of sound results ($\sigma = 1$) facilitates the size of the effect.
The results show noticeable departure of the jump relations from its ideal gas values. For this particular gas and temperature, around 11% increase in the density jump, 17% decrease in the temperature, and 10% decrease in pressure relative to the ideal gas values are determined.

VI. CONCLUSION

In this work, a procedure allowing determination of shock wave jump relations in real gas was developed here. Non-dissociating gas on both sides of discontinuity with excited translational, rotational, vibrational and electronic degrees of freedom was considered. The advantage of the procedure used here is that its relations are mainly based on experimental data thus avoiding the complexity accounting for all possible effects in real gas, yet still offering a satisfactory precision level. The data used in the calculations, such as enthalpy, specific heat capacity, specific relaxation times, and characteristic temperatures for rotational, vibrational and electronic excitation degrees of freedom is conveniently available in literature, for a large number of various gases. Because the data is usually given for particular gases within definite ranges of gas temperature, the model validity is mostly limited by availability of the experimental data and the temperature range. If the desired data is outside of the range, an alternative, analytical procedure can be used.

As a numerical example, the jump relations were applied to a specific gas (diatomic nitrogen) at temperature typical for gas discharges, $T=3000 \, K$. Compared to the levels predicted by the ideal gas equations, noticeable increase in the density, considerable lag in the temperature and a slighter increase in the pressure, were determined. The 5% level correction to the speed of sound in diatomic nitrogen at $T=3000 \, K$ was also determined and, in general, the estimate is dependent on the stage and the way the shock wave is created. The results for jump relations correction are found to be strongly sensitive to the speed of sound correction. In general, the size of the effect and the curve trends found here are quite typical for most real gases. As intermediate results, the specific heat correction $K_c$ and corresponding specific heat ratio $\gamma_c$ for an extended range of gas temperatures in the $N_2$ gas were obtained.

The results can be found useful in a wide range of applications involving shocks interacting with substantially heated media and include shock-flame interaction, detonation, shock wave assisted
combustion, thermal energy deposition in the flow for hypersonic flight and spacecraft design, and in astrophysics for understanding the dynamics of shock waves generated in stellar interior.

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