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# Predictive Modeling of Thermophysical Properties of Shocked Solid Diamond

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# PREDICTIVE MODELING OF THERMOPHYSICAL PROPERTIES OF SHOCKED SOLID DIAMOND

By

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# Abstract

Shocks are high pressure waves that propagate in a material above the local speed of sound and induce severe pressure, density, and temperature changes, thus it is critical to be able to predict these effects. The shock Hugoniot Equations of State (EoS) allow for the calculation of Hugoniot pressure and volume in a shocked material, but require a linear relationship between shock velocity and particle velocity, both experimentally determined variables. A computational approach is required to evaluate shock propagation in materials and calculate the Hugoniot temperature. Currently a combination of Density Functional Theory (DFT) and Quantum Molecular Dynamics (QMD) is the most widely used method capable of predicting the EoS of materials. While useful, it requires large amounts of computational power and time. Diamond is a simply structured form of carbon, an abundant element found in most materials. The EoS of diamond calculated from the DFT-QMD approach were parameterized and implemented as the REODP computer code. REODP can evaluate the pre-shock state of solid diamond phase much faster than it can be done using the DFT-QMD method. The shock Hugoniot EoS implemented into REODP successfully replicated data compiled by the DFT-QMD code and experimental data to a high degree of accuracy. The Hugoniot temperature was calculated as the difference in the straight line Rayleigh energy and the Hugoniot energy determined from the integral of curve fits. REODP predicts the thermophysical properties of shocked solid diamond at a given initial temperature, volume, and shock velocity.

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# Introduction

A shockwave is a high pressure wave that propagates above the local speed of sound and induces severe pressure, density, and temperature changes to a medium. The interaction of shock waves with different materials is a subject that is common to many fields of science today, but not a field that is extensively modeled. The abrupt change to a medium's thermophysical properties as a shockwave passes through makes it critical to understand how a material will change when exposed to a shockwave. Shockwaves can be encountered from plate tectonics to large blasts like nuclear explosions or cruise missiles.

The shock Rankine-Hugoniot jump conditions, or simply the shock Hugoniot Equations of State (EoS) allow for the calculation of thermophysical properties in shocked material, but require a linear relationship between shock velocity and particle velocity, two experimentally determined variables. This means that the shock Hugoniot EoS are only readily usable for single element mediums and only for Hugoniot pressure and density. Currently there are two means of determining the Hugoniot: numerical prediction and experimental results.

Density Functional Theory (DFT) Quantum Molecular Dynamics (QMD) has been a popular numerical method necessary to solve advanced physics, chemistry, and engineering problems where no Equation of State (EoS) is explicitly involved. Software used in both types of simulation methods often take days or even weeks to generate solutions, which is costly in both time and money. Additionally, the more complex a material is in structure and composition, the more complex and time consuming the calculations are to solve the thermophysical properties while introducing more error.

Experimentally, there are shock Hugoniot data for only the most simple of elements or materials. Most often these data are generated by shooting a powerful laser beam into a material to generate a shockwave. This takes time and a lot of resources, and is only practical for solid materials. As there are literally infinite ways to combine elements into compounds and materials, it is impossible to gather shock Hugoniot data for every case, thus limiting the capability to predict the shock effects on everything but the most simple of elements and compounds in a narrow range of pressure and temperature.

Calculating Hugoniot temperature is a separate function from the Hugoniot EoS, which focuses on internal energy, pressure and volume. There have been many methods devised to calculate the Hugoniot temperature, with work starting with the Mie-Gruneisen EoS. Methods have included using the isotherm of the shock loading, the Gruneisen parameter, and the Rayleigh line. This field is often associated with explosion modeling and plate tectonics, so there is not a lot of literature and data associated with shocking a material beyond experimental measurements of post-shock temperature.

This thesis will focus on the modeling of pre- and post-shock conditions using the shock Hugoniot EoS in solid diamond. The Hugoniot EoS link the pre- and post-shock thermodynamic properties of a material and are critical to understanding shock wave interaction with their medium. Solid diamond, a form of crystalline carbon, is an element found in some form in most materials, for which DFT-QMD solutions exist and there are numerous experimental results. Benedict et al [1] determined a general EoS for five different phases of diamond in both solid and liquid form based on Helmholtz free energy and fitted with QMD-DFT and PIMC data. Benedict's work was further extrapolated into a computational REODP (Radiative Emissivity and Opacity of Dense Plasmas) computer program that incorporates Benedict's EoS and data that can calculate the pre-shock state of a solid diamond much quicker than both DFT-QMD [2]. Combining the ability of REODP to calculate pre-shock conditions and the Hugoniot Shock EoS to predict post-shock conditions to create an effective, yet computationally easy model will allow for an easier way to understand the effects of shock waves and how they can be mitigated or used appropriately.

# Chapter 1: Shock Wave Physics and Shock Hugoniot EoS

## *1.1: Shock Frame of Reference*

The shock Hugoniot state occurs when a material undergoes transformation as a shock wave passes through it. A shockwave is a high pressure wave that as it travels through a medium, it imparts energy that increases temperature and density of the material. To analyze the effects of a shockwave as it passes through a medium moving at the shock velocity, a moving frame of reference is employed to simplify the analysis, as shown in **Fig 1**:

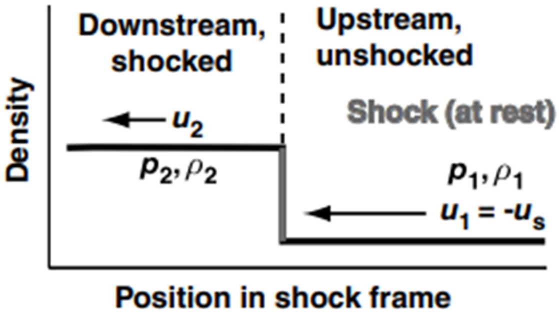

**Fig 1**: Shockwave Frame of Reference [3]

In this shock frame of reference, the shock wave is held still. The upstream medium, State 1, is now approaching the shockwave at the shock wave's original velocity, $u_s$, in the opposite direction as $u_1$. To balance the energy loss of moving "through" the shock wave, the medium leaves the shock wave as State 2 at $u_2$. The difference between $u_1$ and $u_2$ is treated as the particle velocity, $u_p$.

### *1.2: Shock Hugoniot EoS*

The energy balance across the shockwave can be quantified from the shock Hugoniot equations of state. These equations are derived from the conservation equations for mass, momentum, and energy in their Eularian form as demonstrated by Drake [3]:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho u) \tag{1}$$

$$\frac{\partial}{\partial t}(\rho u) = -\nabla \cdot (\rho u u) - \nabla p \tag{2}$$

$$\frac{\partial}{\partial t}(\frac{\rho u^2}{2} + \rho e) = -\nabla \cdot (\rho u(e + \frac{u^2}{2}) + p u) \tag{3}$$

As the medium travels from State 1 to State 2 in the shock frame of reference, there is an associated flux of the parameters in each state due to the shock across a distance, represented by the right side of any of the equations above. As this distance, $\Delta x$, approaches zero, the material derivative $\partial/\partial t$ becomes zero, in other words an instantaneous conversion between State 1 and State 2 across an infinitesimally thin shock. The flux of each state can be considered equal in this static frame of reference and becomes the difference in State 1 and State 2 properties for each of the conservation equations, hence the reason for the shock frame of reference [3]. Further assuming a one dimensional shock (a normal shock) the conservation equations are equal between State 1 and State 2 as shown below:

$$\rho_1 u_1 = \rho_2 u_2 \tag{4}$$

$$\rho_1 u_1^2 + p_1 = \rho_2 u_2^2 + p_2 \tag{5}$$

$$\rho_1 u_1 (e_1 + \frac{u_1^2}{2}) + p_1 u_1 = \rho_2 u_2 (e_2 + \frac{u_2^2}{2}) + p_2 u_2 \tag{6}$$

with the State 1 conditions known other than velocity, there are five unknown variables, $u_1, u_2, \rho_2, p_2, e_2$, with three equations. Given that the particle velocity is the difference between

$u_1$ and $u_2$, Equation 4 can be rewritten in terms of shock and particle velocity. Equation 4 can be substituted in Equations 5 and 6, and the shock Hugoniot EoS can be rewritten as:

$$p_2 = p_1 + \rho_1 u_s u_p \tag{7}$$

$$e_2 = e_1 + \frac{1}{2}(p_2 - p_1)(v_1 - v_2) \tag{8}$$

This still leaves four unknowns, $u_s, u_p, p_2, e_2$. Experimentally, the shock velocity and particle velocity are able to be measured. Through various experiments, shock velocity has taken to be linearly related to particle velocity for all materials:

$$u_s = bu_p + c_o \tag{9}$$

where $b$ and $c_0$ are the coefficient and constant from the curve fit of $u_s$ to $u_p$, respectively. $b$ is treated as the bulk sound modulus of the medium. As particle velocity is an artificial variable, particle velocity can be substituted out in Equation 7 with the relationship in Equation 9. This linear relationship allows for the Hugoniot EoS to be solved given only initial pressure, volume, and shock velocity. What this does not solve is the Hugoniot temperature, which will be discussed in Chapter 2.

### *1.3: Existing Literature and Data Sources*

The interest in shockwave physics has existed since the 19th century with work from William Rankine and Pierre Hugoniot forming the basis of its study and lending their names to the shock Rankine-Hugoniot condition, shorthanded to the Hugoniot EoS. Initial interest in the field was due to shockwaves from conventional explosions, with Hugoniot being an artillery officer in the French Army and later a professor of ballistics at France's premier military academy. Hugoniot's equations were based on work from Poise, further modified by Stokes and Rayleigh to the common form of the Hugoniot EoS, Equations 4-6 [4]. Interest in the field became predominant in the 1950s with the advent of nuclear technology and the acceptance of plate tectonics in the 1960s. A decent history and literature overview is provided by Salas [4].

In 1955, Walsh and Christian [5] derived a method to calculate the Hugoniot temperature with the inclusion of the Mie-Gruneisen EoS with the shock Hugoniot conditions:

$$c_v \frac{dT_h}{dv} + \left(\frac{\partial p}{\partial T}\right)_v T_h = \frac{1}{2}\frac{dp_h}{dv}(v_o - v) + \frac{1}{2}(p_h - p_o) \tag{10}$$

where the $(\partial p/\partial T)_v$ becomes a function of the Gruneisen parameter. This equation was further developed by Raikes and Ahrens [6] and will be discussed in the next section.

In the field of explosion physics, another derivation to solve Hugoniot temperature is to use the isothermal pressure and temperature of the post-shock state as detailed by Takazawa et al [7]:

$$P_s = \frac{3}{2}K_o[\frac{V_o}{V}^{7/3} - \frac{V_o}{V}^{5/3}]1 + \frac{3}{4}(K_o' - 4)[\frac{V_o}{V}^{2/3} - 1] \tag{11}$$

$$T_s = T_o exp\left(-\int_{v_o}^{v} \frac{\gamma}{V} dV\right) \tag{12}$$

where both $P_s$ and $T_s$ are the isothermal pressure and temperatures, respectively. This leads to a modified version of the Hugoniot pressure and temperature:

$$P_h = P_s + \tfrac{\gamma}{V}\left[\left(\int_{v_o}^{v} P_s dV\right) - E_{tr}\right]\left[1 - \frac{\gamma}{2V}(V_{oo} - V)\right]^{-1} \tag{13}$$

where $E_{tr}$ is the transformation energy between the low pressure pre-shock state to the high pressure post-shock state, and $V_{oo}$ and $V$ are the specific volumes at the pre- and post-shock state, respectively.

$$T_h = T_s + \frac{V}{\gamma c_v}(P_h - P_s) \tag{14}$$

This derivation of the Hugoniot temperature is also used by Nagayama et al [8], and Ahrens in "High Pressure Shock Compression of Solids" [9].

Benedict et al [1] EoS is based on Helmholtz free energy that is composed of electronic, ionic, and cold energy. A similar EoS was derived by Khishchenko et al [10] that utilizes thermal energy of atoms instead of ionic energy in the calculation of Helmholtz free energy.

The available post-shock Hugoniot data are extensive for Hugoniot pressure and volume with a database of shocked material properties and $u_s - u_p$ curve fits developed by the Los Alamos Scientific Laboratory [11], QMD generated post-shock thermophysical properties FPEOS database maintained by the University of California, Berkeley [12], Sandia National Laboratories PANDA computational code generated results [13]. Diamond specific data has been experimentally determined by Hicks et al [14] and computationally with Benedict et al [1] amongst others. Data for Hugoniot temperature for solid diamond is not as widely found as Hugoniot pressure and volume, which this thesis has found limited to Benedict's QMD-DFT generated data [1] and new data collected by the Johns Hopkins (JH) research group [15]. This is more than likely due to the fact that the calculation for Hugoniot temperature does not have a EoS, with numerous methods of calculation, which will be discussed in the next chapter.

# Chapter 2: System Modeling

## *2.1: Pre-shock State Calculations*

The EoS derived by Benedict et al [1] for carbon is based on Helmholtz free energy, which is composed of cold energy calculated from the Vinet EoS, ionic excitation calculated from double Debye free energy, and electronic excitation energy calculated from a parametric EoS all fitted to data from QMD-DFT calculations and PIMC simulations. REODP incorporates Benedict's EoS, and with an initial temperature and volume, performs the calculations for pre-shock thermophysical properties. REODP [2] is currently programmed to be able to analyze simple cubic, simple hexagonal, BC8, and diamond solid phases of carbon as well as liquid phase of carbon. The initial inputs of volume or temperature require at least four values to perform calculations due to using a fourth order finite difference technique. Otherwise both isotherms and isochores can be calculated in the specified range of temperature and volume. In order to satisfy the Hugoniot EoS, shock velocity is the third dimension that is required to be entered initially, and can be programmed for a range of shocks or a single shock. Further information on the REODP code and its applications can be found in [2, 16-19].

## *2.2: Constants and $u_s - u_p$ Curve*

Shockwaves induce severe temperature, density, and pressures to the shocked medium, thus the specific heat of diamond at constant volume cannot be evaluated at room temperature. Diamond undergoing transformation induced by shockwaves can reach hundreds of GPa in pressure and thousands of Kelvin in temperature. Naumovets et al [20] utilized the Debye energy and the Dulong-Petit Law to predict diamond's molar constant volume specific heat capacity. Predicted results are close to experimental results in the range of 1600K to 3000K, and both the

Debye model and Dulong-Petit Law are integral to Benedict's model, thus this model was incorporated into the Hugoniot EoS for solid diamond.

The Johns Hopkins research group [15] have conducted a literature survey of shocked diamond experimental results and compiled an average $u_s - u_p$ curve as seen in **Fig. 2**:

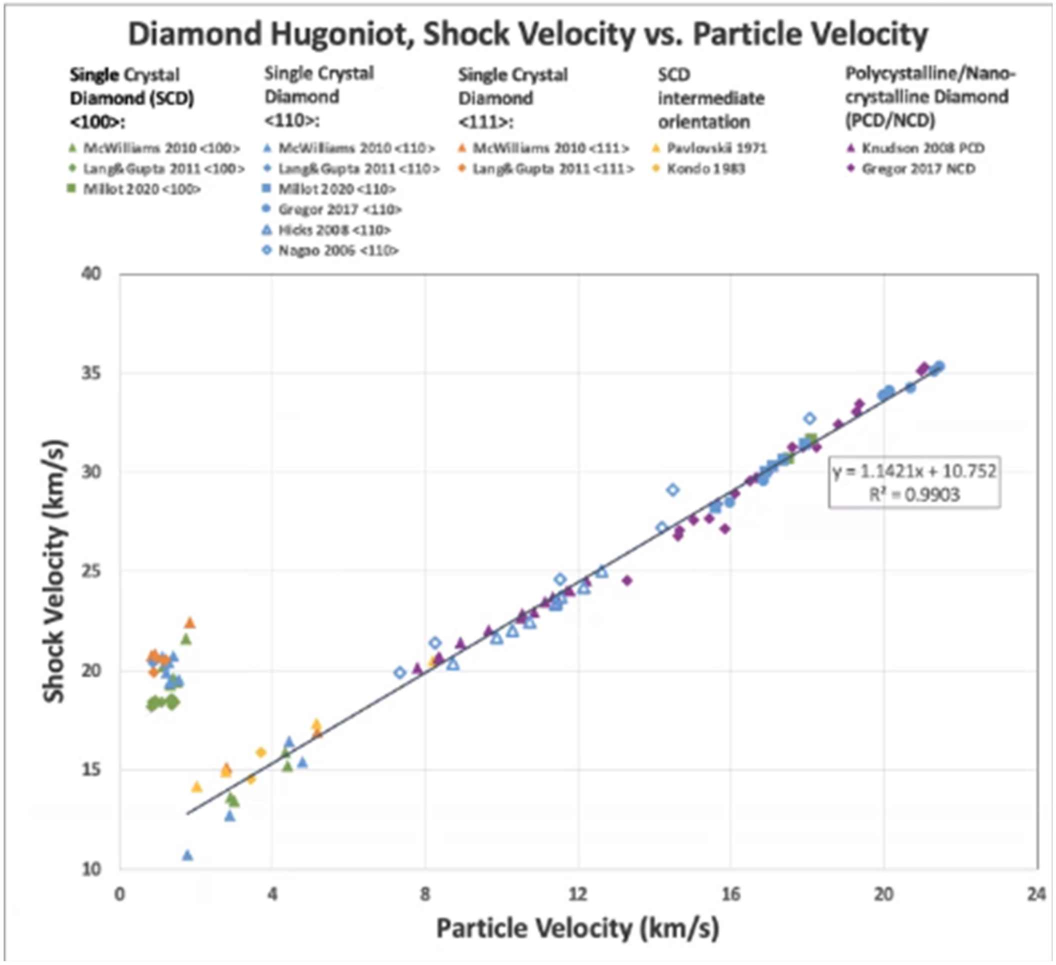

**Fig 2**: JH Research Group Compiled $u_s - u_p$ Curve [15]

The fitted curve has a $u_s$-intercept of 10.752, thus if a measured shock velocity is below 10.752 km/s, the curve fit will be unable to predict a particle velocity. Another $u_s - u_p$ curve was calculated at the LANL [11]:

$$u_s = 7.81 + 1.49 u_p \tag{15}$$

### *2.3: Hugoniot Pressure and Volume*

From a user defined shock velocity, particle velocity is calculated via Equation 9 based on the Johns Hopkins $u_s - u_p$ curve fit. Equations 7 and 8 are used to calculate temperature and volume, respectively. Pressure Volume (PV) curves are often used to express Hugoniot data since they require little computational power to create and the PV curve itself is called the Hugoniot of a material. To validate the Hugoniot module in REODP, both computational and experimental sources were used to match REODP's output, with the results discussed in the next chapter. The Hugoniot is replicated by REODP by initializing REODP with given initial volume and temperature stated by the numerical or experimental Hugoniot data source or if there are no initial conditions stated they were assumed to be the standard density of diamond and room temperature. In general most literature do not state the shock velocities used to obtain results, both experimentally or computationally, thus the shock velocity range has to be estimated and manually fitted to reproduce a given Hugoniot curve.

### *2.4: Hugoniot Temperature*

Hugoniot temperature calculations are not as clear cut as Hugoniot pressure and volume. Walsh and Christian derived a method to calculate the Hugoniot temperature with the inclusion of the Mie-Gruneisen EoS with the shock Hugoniot conditions [5], with a more common form of the equation developed by Raikes and Ahrens [6]:

$$T_h|_{v_h} = T_o exp(-\int_{v_o}^{v_h} b(v)dv) + exp(-\int_{v_o}^{v_h} b(v)dv) \int_{v_o}^{v_h} \frac{f(v)}{C_v} exp(-\int_{v_o}^{v} b(v)dv)dv \tag{16}$$

where

$$b = \frac{\gamma}{v} \tag{17}$$

$$\gamma = \gamma_o \left( \frac{v}{v_o} \right)^n \tag{18}$$

$$f(v) = \frac{dp}{dv} \frac{v_o - v}{2} + \frac{p}{2} \tag{19}$$

$\gamma$ is the Gruneisen parameter, with the relationship between it and volume usually taken as linear, thus $n$ is equal to one in Equation . $f(v)$ is the rate of change between Hugoniot pressure and volume times the average volume plus the average Hugoniot pressure (initial pressure is usually not factored in since it is orders of magnitude lower than the shocked pressure) which can be taken as simply the Hugoniot pressure.

Taking the $dp/dv$ as the slope of a linear curve fit of the Hugoniot and analytically solving the integrals in Equations 16, the Hugoniot pressure and volume calculated by REODP were unable to replicate the TP curve from Benedict [1] as seen in **Fig 3**:

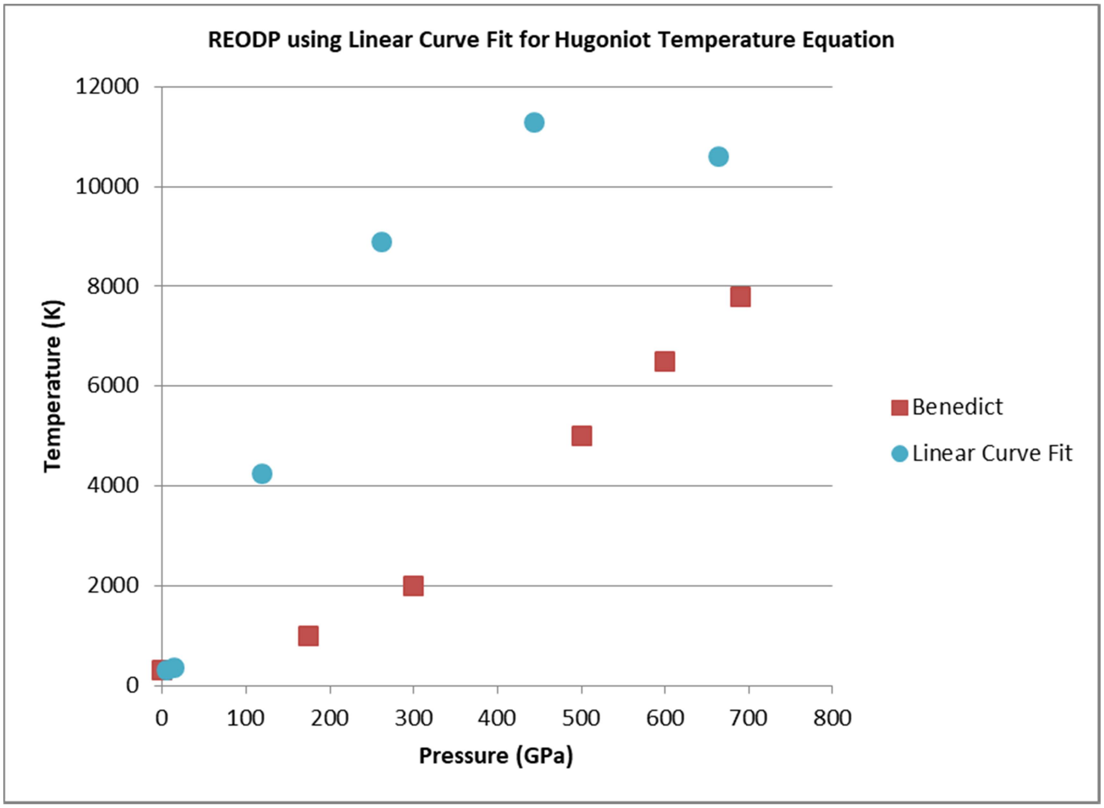

**Fig 3**: REODP results using Linear Curve Fit vs Benedict EoS Predictions [1]

Initially the error was attributed to using linear curve fits in Equation 19, so cubic curve fits provided by plotting the data in MATLAB were used. This provided extremely inaccurate curve fits that had no physical meaning.

Similar results were experienced when using the isothermal derivation, Equations 13 and 14 from Takazawa [7]. A similar methodology was employed by Lyzenga who used the same equation as Raikes and Ahrens, but based on Gruneisen's work, and determined that the energy released during the shock that influences the Hugoniot temperature is the difference between the Hugoniot and the isothermal post-shock state [21]. The isothermal pressure $P_s$ that was calculated using Hugoniot pressure calculated by REODP with Equation 7 was greater than the

Hugoniot pressure itself, thus resulting in a negative temperature using Equation 14 for both Takazawa and Lyzenga's methods of Hugoniot temperature calculation.

The method that has proven to work is using the difference in energy between the Rayleigh line and the Hugoniot outlined by a lecture from Sharp [22]. The Rayleigh line, the straight path between any post-shock state with the pre-shock state, is the thermodynamic loading of the medium by the shock, as seen in **Fig 4**:

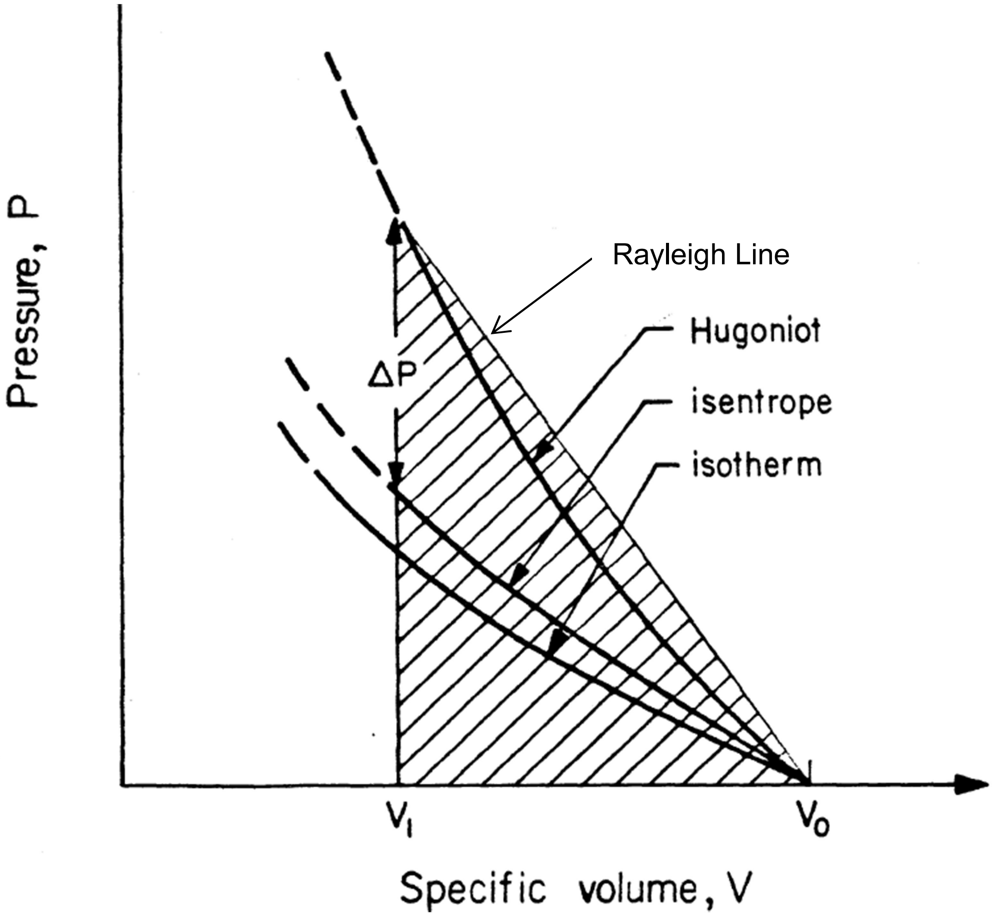

**Fig 4**: Graphical Representation of the Rayleigh Line, Hugoniot, Isentrope, and Isotherm [21]

The Hugoniot represents all the possible post-shock states. While there are many possible Hugoniot states between a post-shock state and pre-shock state as represented by the Hugoniot itself, these do not influence each other [9]. The Rayleigh line is the only loading path that a shock creates between a pre- and post-shock state, thus each post-shock state has its own unique Rayleigh line. The difference in Rayleigh energy and the Hugoniot energy is the available energy that raises the post-shock temperature of the medium. The change in temperature can be found by:

$$\Delta E = c_v \Delta T \tag{20}$$

To solve for the energy under the Hugoniot, functions must be curve fitted to the data points and integrated. For both the first and second post-shock points, a quadratic function is used as the fit. The quadratic between the first post-shock state and pre-shock state is determined by solving the quadratic in its vertex form:

$$y = a(x-h)^2 + k \tag{21}$$

where $h$ and $k$ are the x and y points at the vertex. In this case, the vertex is the initial pre-shock state, thus $h$ is $v_o$ and $k$ is $p_o$. Given $v_1$ and $p_1$, the coefficient $a$ can be calculated. A linear function cannot be used because the loading path, shown in **Fig 4**, is not linear either even though there are only two points. The quadratic between the second post-shock state and the pre-shock state is formed through polynomial regression.

The function between the third post-shock state and the pre-shock state is a cubic function derived from Newton Divided Difference method. Using MATLAB, curve fits for further points of data were best matched with cubic functions, generating the smallest $R^2$ error. Four points are required to generate cubic functions with Newton Divided Difference, which are always the $nth$ post-shock state, the pre-shock state, and the two intermediary points.

The fourth post-shock point to the $nth$ point all have more than two intermediary points, thus interpolation was used to create two new intermediary points. Due to the iterative nature of these calculations, previous curve fit methods can be used. For the fourth post-shock state point this simply means that the interpolation is a quadratic fit since there are three intermediary points. For the fifth post-shock state, this uses a cubic fit for four intermediary points. For the sixth post-shock point to the $nth$, this uses the $nth - 1$ curve fit, which is always a cubic curve fit based on the data that composes of the intermediary points of the $nth$ point. The two new intermediary points are the interval average of the pre-shock state and the $nth$ point, with the averages being ⅓ and ⅔ given there are four points for a cubic curve fit.

Once a function has been calculated given the specific method, they are then integrated with a one-dimensional Gaussian quadrature on the appropriate interval of volume to determine the Hugoniot energy. Given that energy concerned is only from the initial pressure which is non-zero, a correction factor must be included in the temperature calculation. This correction factor is simply the initial pressure times the interval of volume from the initial volume to whatever post-shock volume is in interest. Using a two-dimensional Gaussian quadrature would be able to account for this. Temperature is calculated using Equation 20.

### *2.5: Post-shock Calculations and Data Management*

Utilizing the same REODP functions that calculate enthalpy, entropy, etc for the pre-shock state, REODP calculates the same quantities given the new post-shock parameters from the Hugoniot pressure, volume and temperature. Both pre-shock and post-shock cold, ionic, electronic, and total energy are written to their own data files. Both initial and Hugoniot pressure, volume, density, compression ratio, and temperature are written to a separate text file.

# Chapter 3: Results

## *3.1: Pressure Density Data Fit*

Benedict predicted a pressure-density curve with a range of density from 3.45 to 9 $g/cm^3$ and pressure from 5 to 4000 GPa from an initial temperature of 295K and volume of 5.7034 $A^3/atom$. Benedict's values were estimated from visual inspection of Figure 16 in ref [1]. The fitted range for shock velocity was 0-40 km/s. **Fig 5** shows the comparison between Benedict's predicted pressure-density and REODP curves:

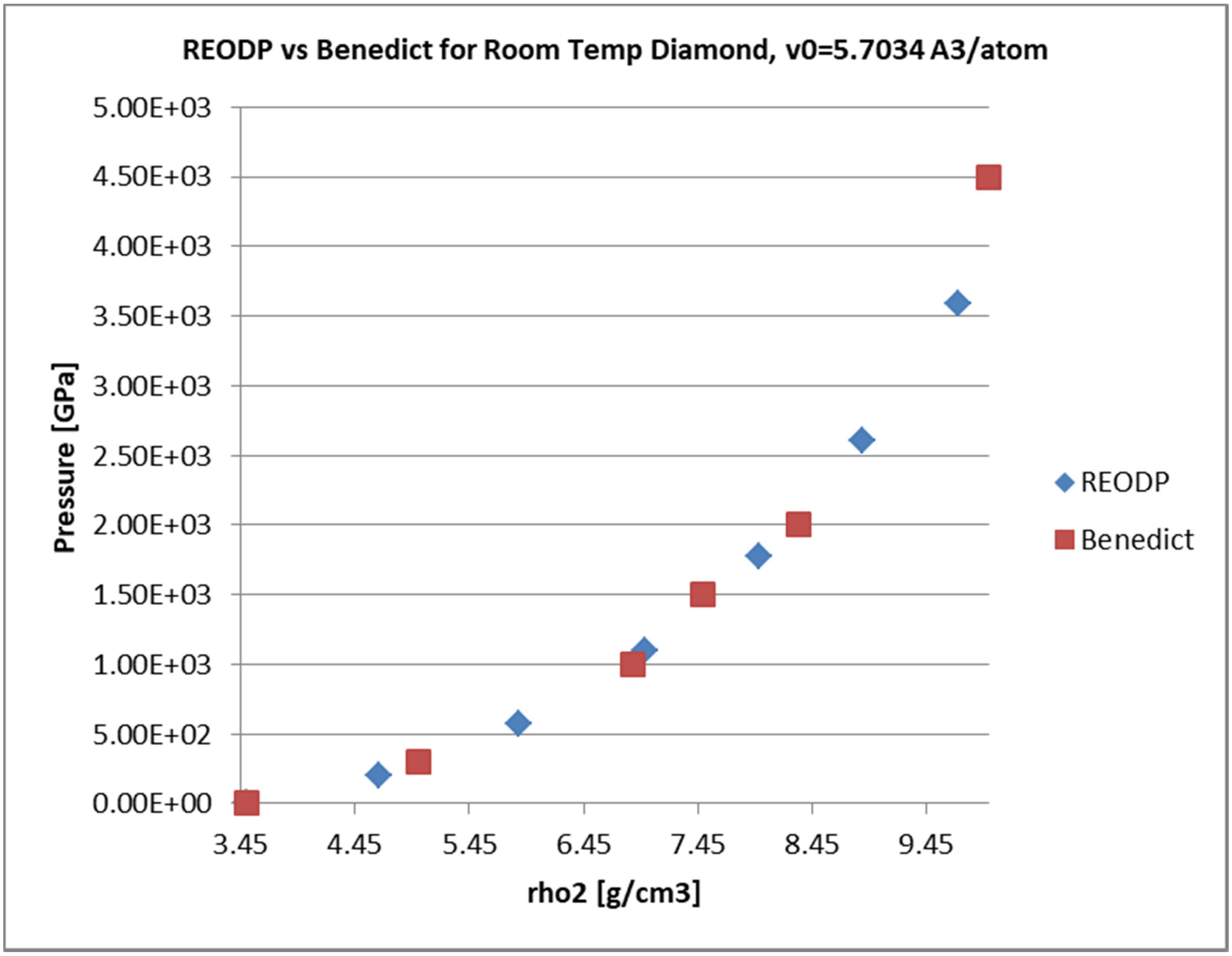

**Fig 5**: REODP results vs Benedict EoS Prediction [1]

Both results are plotted as Hugoniot density vs Hugoniot pressure. Hugoniot density was calculated from the Hugoniot volume by using the average molecular weight of carbon of 12.011 $g/cm^3$ and Avagadro's number. As one would expect, the REODP agrees with the Benedict EoS, given that REODP implements the Benedict EoS and only adds the Hugoniot EoS. The next comparison with the QMD generated FPEOS database for carbon [12] is shown in **Fig 6**:

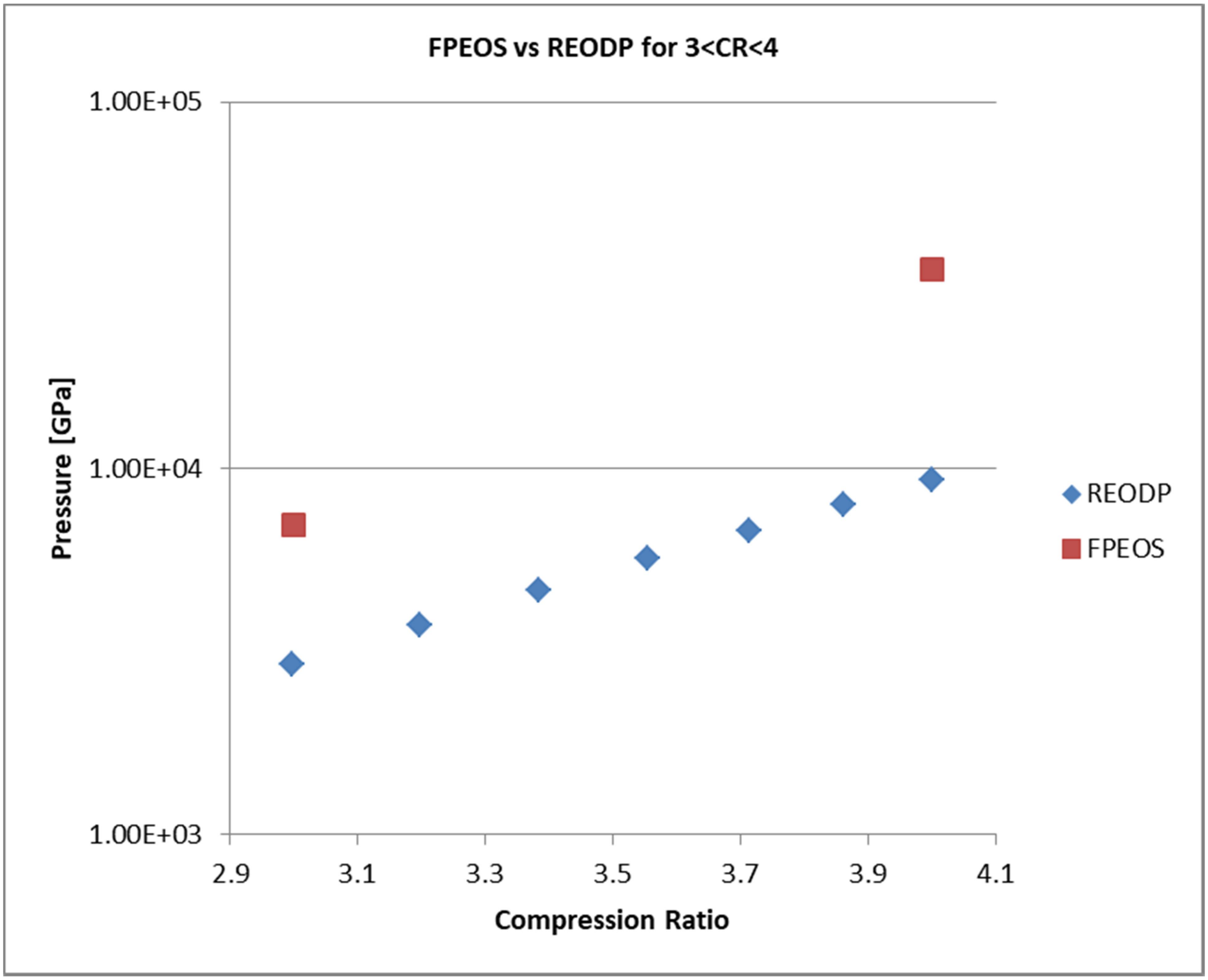

**Fig 6**: REODP Results vs FPEOS QMD-DFT Carbon Prediction [12]

The FPEOS data is for plain carbon and not diamond, and plots Hugoniot pressure vs the compression ratio of Hugoniot volume and pre-shock volume. REODP was initialized with a volume of 5.672131 $A^3/atom$ at 5000K, with shock velocity manually indexed to match the FPEOS data. The FPEOS data only has two points in the solid region of carbon. This results does support the effectiveness of REODP as a predictive tool as the calculated slope generally follows the same slope as the FPEOS carbon data, which is to be expected given that both results utilize a carbon derivative, and that a pre-shock temperature of 5000K is close to the melting region of diamond, for which REODP is not built to evaluate in. The next comparison was with the Sandia PANDA code in **Fig 7**:

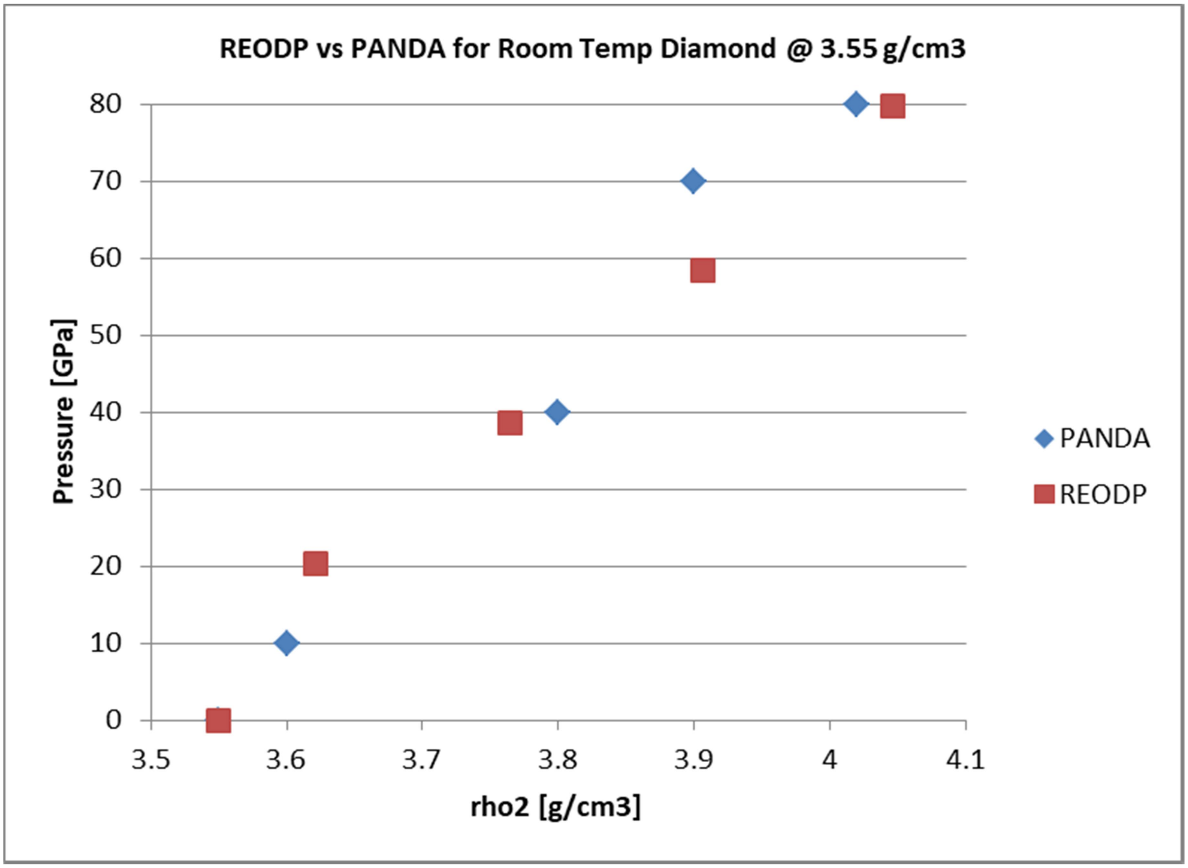

**Fig 7**: REODP Results vs Sandia PANDA Code Predictions [13]

The values for the PANDA code were estimated from visual inspection of Figure 1 of the Sandia report into multiphase equations of state [13]. Temperature was initialized at 295K, and volume taken from an initial density of 3.55 $g/cm^3$. As can be seen from inspection of **Fig 7**, the REODP calculations agree with the Sandia PANDA predictions. The next comparison was with the experimental results of Hicks et al [14] in **Fig 8**:

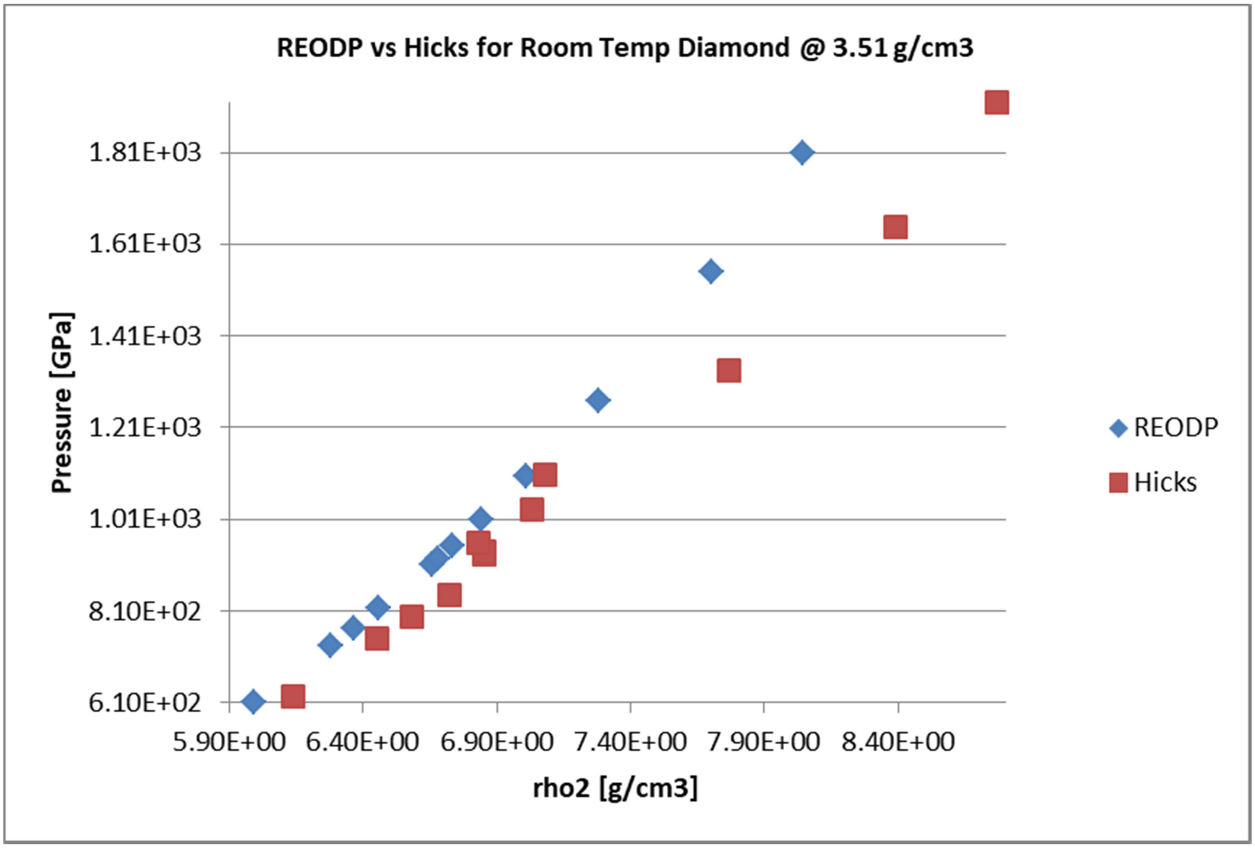

**Fig 8**: REODP Results vs Hicks et al Experimental Data [14]

REODP was initialized with a density of 3.51 $g/cm^3$ and a temperature of 295K. The REODP results match Hicks data closely, as the Hicks data is part of the compiled $u_s - u_p$

curve fit utilized in REODP. Hick's data suggests a lower $u_s$-intercept that what was used in REODP, but the slope matched closely.

### *3.2: Temperature Pressure Data Fit*

The pool of available data for TP curves is less than PV curves, but REODP will be compared to both computational results and experimental data. The first comparison was with QMD-DFT predicted curve from Benedict [1] as shown in **Fig 9**:

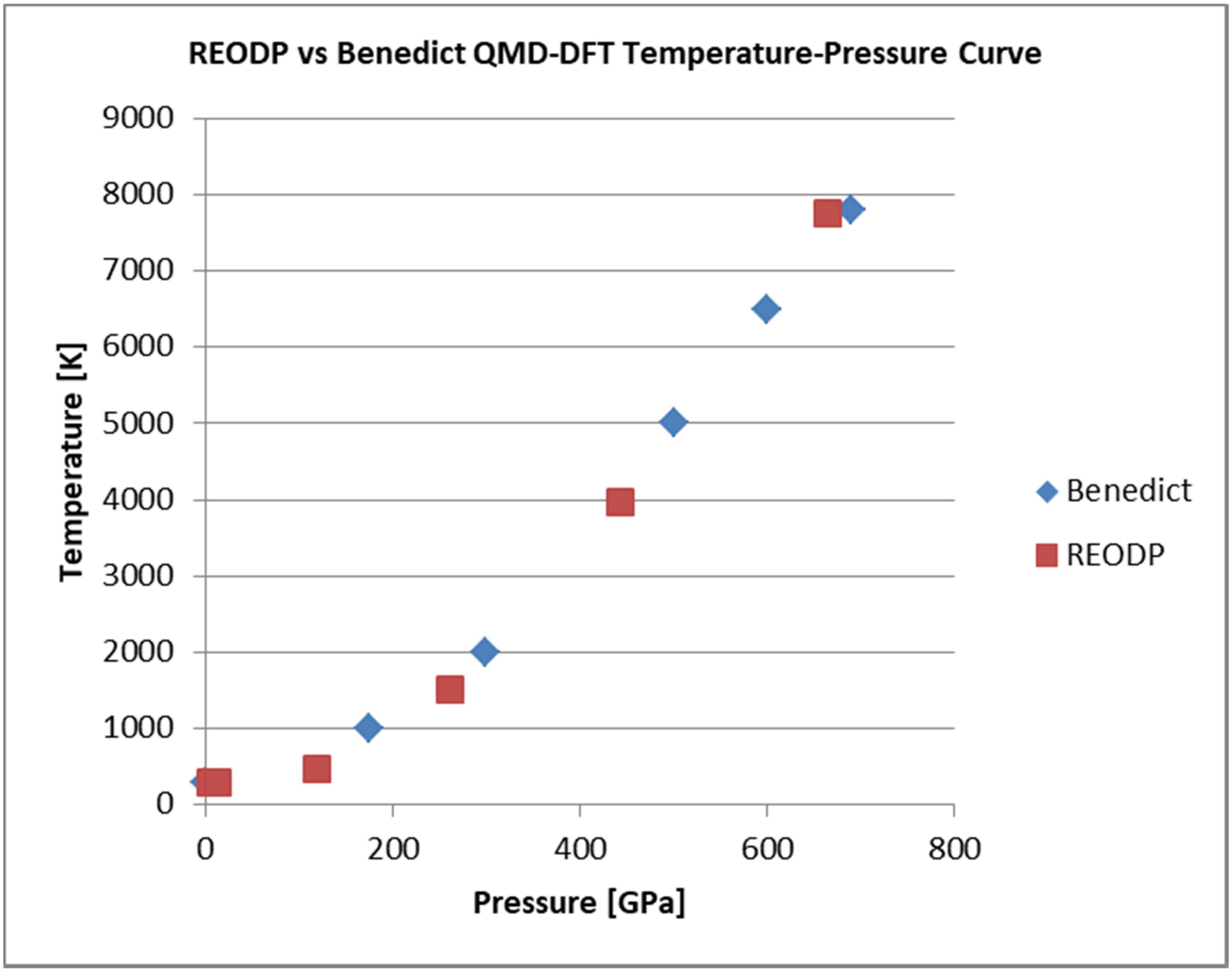

**Fig 9**: REODP Results vs Benedict Prediction [1]

The results from REODP agree with the Benedict prediction. The next comparison was with experimental data gathered by the JH research group on **Fig 10**:

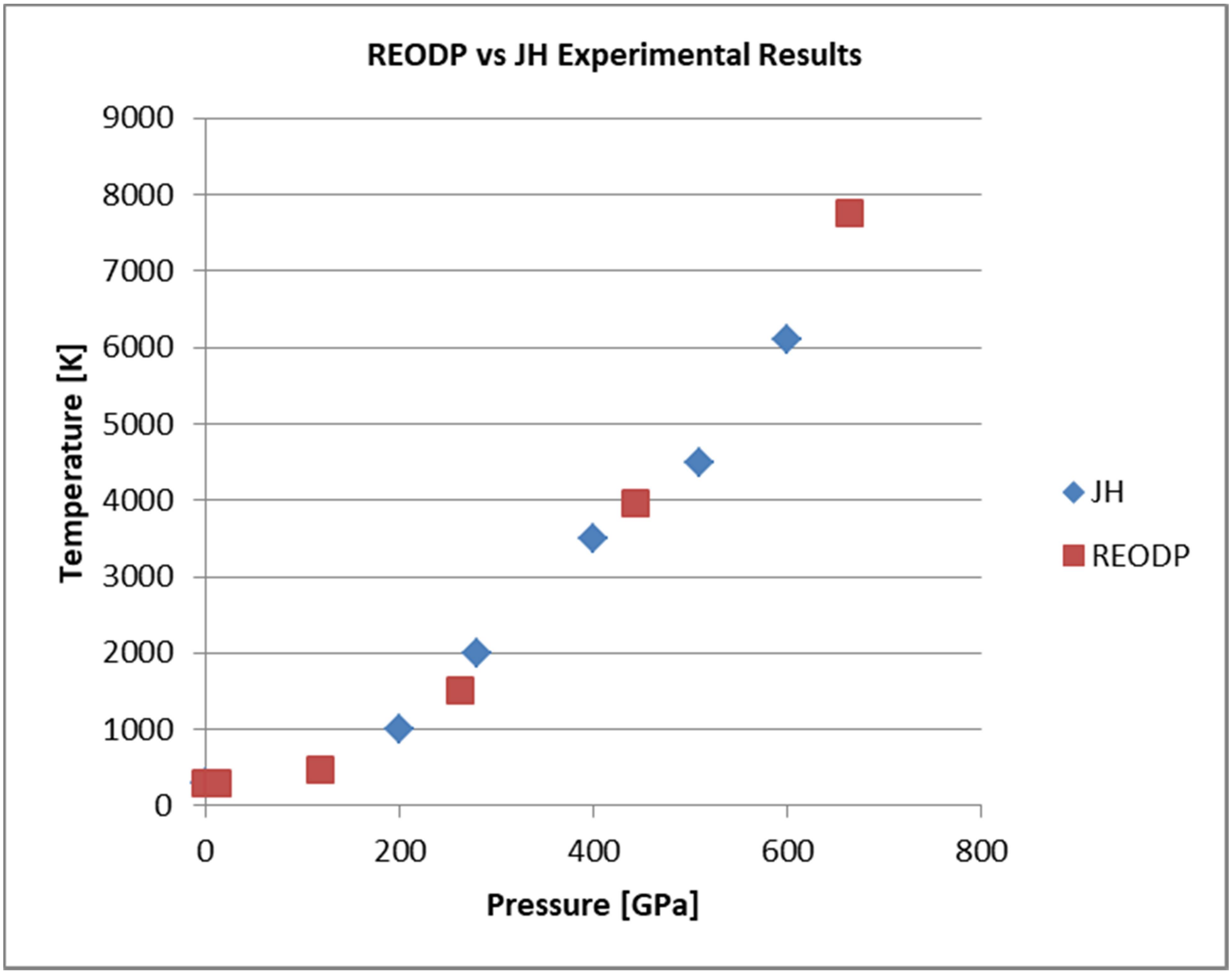

**Fig 10**: REODP Results vs Experimental data from JH Research Group [15]

# Conclusions

Utilizing a linear relationship between the shock velocity and particle velocity determined from experimental and numerical results allows for the Hugoniot EoS to solve for Hugoniot pressure and volume. There are many ways to calculate Hugoniot temperature including the Mie-Gruneisen EoS or using the isotherm of the shocked state. The method found the most accurate was the energy from the difference of the Rayleigh line and the Hugoniot calculated from the integral of curve fits between the pre- and post-shock states. REODP can predict the thermophysical properties of shocked solid diamond for both pre- and post-shock states with a given initial temperature, volume, and shock velocity.

The shock Hugoniot EoS implemented into REODP was able to successfully replicate data compiled by QMD-DFT codes, and experimental data to a high degree of accuracy based on visual observation of **Figs 5-10**. As REODP is partially a function of shock velocity, it is impossible to produce an exact dependent variable for both PV and TP curves since QMD-DFT and experimental results do not rely on shock velocity to produce data. This means any analytical error or difference calculation is based on the time and patience of the user to input shock velocities across a range and identify which shock produces a post-shock state that matches a given experimental or numerical data point. The outlier is **Fig 6**, which is due to the difference between the plain carbon properties used by FPEOS [12] versus solid diamond used in REODP. The data generated by Benedict [1] matches REODP results closely in **Figs 5** and **9**, which confirms the validity of the REODP code since Benedict's EoS is what REODP is based on. REOPD matches well with experimental data from Hicks [14] for the pressure-density curve shown in **Fig 8**. REODP results tend to be slightly higher than Hicks's data due to the larger slope of the $u_s - u_p$ curve used in the Hugoniot EoS calculated by Johns Hopkins [15]. REODP also replicates experimental TP data closely as shown in **Fig 10**. As there are not many sources of Hugoniot temperature data, it is encouraging to see that REODP can calculate both experimental and numerical Hugoniot temperature data closely.

As stated before, a shockwave induces severe pressure, temperature, and volume changes. Hugoniot pressure is in the hundreds of GPa, compression ratios in excess of four, temperature in the thousands of degrees Kelvin, and shock velocities measured in km/s. The results in **Figs 5-10** illustrate this. Cubic curve fits were used to match Hugoniot pressure to Hugoniot density with the expectation of the first two post-shock points. Generally, Hugoniot pressure can be described as a positive cubic function of Hugoniot density with a local minimum as room temperature solid diamond. Hugoniot volume is the opposite function as a negative cubic function. Temperature greatly increases with pressure, which again can be described as a positive cubic function with a local minimum at room temperature with respect to Hugoniot pressure. The curves of pressure-density and temperature-pressure mirror each other. The ionic energy and electronic energy both increase, as well as internal energy, enthalpy, and entropy. The only state variable to decrease when shock induced is volume, which makes physical sense as Hugoniot density increases. With the given linear relationship of the $u_s - u_p$ curve, shock velocity will always be faster than particle velocity, which again makes sense because particle velocity is an artificial variable to account for the energy leaving a shock frame of reference, as shown in **Fig 1**. Shown in both **Figs 9** and **10**, the shock only starts to influence solid diamond once it departs the $u_s$ intercept of Equation 15 from the $u_s - u_p$ curve. At a shock velocity of $u_s = 11.5km/s$, the temperature only increases to 299K and a pressure of 13 GPa, compared to the resting case calculated from pre-shock REODP where the temperature is 295K and the pressure 5.01 GPa. This indicates the required energy needed to experimentally create shocks in diamond, if the energy shocking diamond is less than the $u_s$ intercept, it will not generate a shock wave that alters solid diamond's thermophysical properties.

REODP as it is programmed right now with the additional modules for the Hugoniot EoS and Hugoniot temperature calculations is not the most efficient means in terms of computational power and storage required. A lot of calculations, especially for the curve fitting, are hard coded based on iteration and are not as flexible to user input as they could be. Another area of improvement would be to incorporate the shock velocity data into the read file REODP uses to initialize. Currently it is hard coded into the module that does the reading of the initial data file. This would make using REODP more user friendly and prevent the need to actually modify the program itself.

For the curve fitting of the sixth post-shock point and beyond, it would have been better to use global variables to store the intermediary points calculated, and using those points plus the $nth - 1$ point as the basis of a the $nth$ intermediary point curve fit. This would be slightly more accurate the method described in Section 2.4.

As discussed in the previous paragraph, REODP requires user estimation to match experimental or numerical data. This could be improved by programming REODP to be able to select values within a defined tolerance that match a given data set. Another way to bridge this knowledge gap would be an empirical relationship between laser energy and shock velocity. This could be used to estimate shock velocities from laser energies, which are often reported with experimental results. The closest relationship this thesis has found is a relationship between laser energy and ablation pressure of the material being struck with the laser beam.

Future work is currently being worked on by Dr. Gennady Miloshevsky. The ability to analyze diamond in the melt stage, along with the ability to predict post-shock states in liquid phase are currently being analyzed by Dr. Miloshevsky. An area that will require much further research to implement is phase transition, which even QMD-DFT solutions have trouble predicting. The eventual goal of REODP is to be able to predict the pre-and post-shock data for any given material in any state. Such predictive ability in a computational power friendly environment will aid research into the effects shockwaves have on materials, thus enabling the design of shock proof or shock resistant materials and devices.

# Author's Presentations

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