

Density Functional Theory (DFT) simulations of porous tantalum pentoxide

K R Cochrane, T J Vogler, M P Desjarlais and T R Mattsson

Sandia National Laboratories, MS 1189, P.O. Box 5800, Albuquerque NM, 87185

E-mail: kcocra@sandia.gov

Abstract. Density Functional Theory (DFT) based molecular dynamics has been established as a method capable of yielding high fidelity results for many materials at a wide range of pressures and temperatures and has recently been applied to complex polymers such as polyethylene, compounds such as ethane or CO₂, and oxides such as MgO. We use this method to obtain a Grüneisen Γ and thereby build a Mie-Grüneisen equation of state (EOS) and a Rice-Walsh EOS for tantalum pentoxide (Ta₂O₅ or tantala) and compare to experimental data. The experimental data have initial densities (ρ_{00}) of approximately 1.13, 3, and 7.4 g/cm³, reduced from a crystalline of 8.36 g/cm³. We found that Γ becomes constant at higher temperatures and pressure, but is a function of both density and temperature at lower densities and temperatures. Finally, the Mie-Grüneisen EOS is adequate for modeling the slightly distended Hugoniot with an initial density of 7.4 g/cm³, however it is inadequate for the more porous Hugoniot, while the Rice-Walsh EOS combined with a $P - \lambda$ crush model approximates the experimental data quite well.

1. Introduction

Porosity adds significant complexity to the behavior of materials and can be used to tailor materials for specific properties. For example, porous aerogel has similar release properties to deuterium while being much easier to handle [1, 2]. One of the primary ways we have to explore material properties is through shock response. Shock experiments on porous materials allows us to explore more of equation of state (EOS) space because we can adjust or change the initial density and follow a new Hugoniot locus of points. These tailored benefits can add significant challenges to modeling. In this study, we use quantum molecular dynamics (QMD) to calculate tantalum pentoxide (Ta₂O₅ or tantala) material state variables. We then use those variables to calculate Γ in order to create a Mie-Grüneisen EOS (equation (3)) and a Rice-Walsh EOS [3]. The resulting EOSs are then compared to data taken by Vogler et. al [4].

The Mie-Grüneisen analytical EOS [5] uses the relationship between the shock velocity (U_s) and the particle velocity (u_p), as well as the sound speed to approximate material properties such as the shock Hugoniot. P_H is the linear U_s/u_p representation of the pressure along the Hugoniot as a function of density and P_{MG} is the Mie-Grüneisen EOS pressure based on that Hugoniot.

$$P_H = \frac{\rho_0 C_0^2 \chi}{(1 - \frac{\partial U_s}{\partial u_p} \chi)^2} \quad (1)$$

$$\chi = 1 - \frac{\rho_0}{\rho} \quad (2)$$



$$P_{MG} = P_H[1 - \frac{\Gamma_0}{2}\chi] + \rho_0\Gamma_0 E \quad (3)$$

where ρ_0 is the initial crystalline density, C_0 is the initial sound speed, E is specific internal energy, and Γ_0 is the initial value of the Grüneisen parameter. It should be noted that Γ_0 and C_0 are often assumed to be constants, which is not true of many materials. In this study, we assume C_0 is constant and Γ is a function of both density and temperature.

2. Simulations

We used the Density Functional Theory (DFT) code VASP (Vienna Ab Initio Simulation Package) [6, 7], where the Kohn-Sham equations [8, 9] are solved in a plane-wave basis set. Projector augmented wave potentials [10, 11] are used with local density approximation (LDA) as parameterized by Perdew and Zunger [12] as the exchange and correlation functional.

An approximate tantala crystal unit cell is a 14 atom rhombohedron [13] extended in all directions to a 112 atom supercell. We performed a convergence study using the cold curve as the metric and chose the LDA potential [14] for reasons discussed by Ramprasad [13]. We also used an 11 electron tantalum PAW potential and a 6 electron oxygen PAW potential. Our cutoff energy was 600 eV and we used the mean value point (1/4, 1/4, 1/4) for the kpoint as discussed in [15]. Most of our simulations consisted of a time step of approximately 1 fs, but did decrease to 0.4 fs as temperature increased to several eV. The simulations were allowed to equilibrate until the standard deviations of both the mean pressure and energy were less than 1%. We used block averaging [16] when computing the standard deviation of our pressure and energy means.

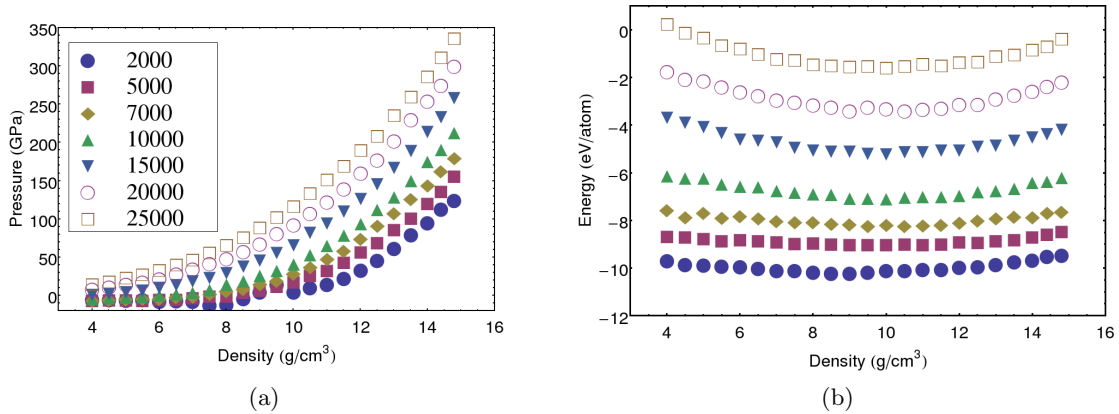


Figure 1. VASP simulations of Ta₂O₅ using a 112 atom supercell. Figure (a) is pressure as a function of density and figure (b) is energy as a function of density. Each symbol type represents a different isotherm (2000, 5000, 7000, 10000, 15000, 20000, and 25000 Kelvin). An obvious phase shift (melting) can be seen between 8.5 and 10 g/cm³ for the 2000 Kelvin isotherm.

Figure 1 shows the pressure and internal energy calculated from VASP. For ease of calculating derivative values along a constant volume, we constructed a rectilinear ρ, T grid. This grid is fine enough that the resulting pressure and energy curves can be used as a tabular EOS. We then calculated the Grüneisen Γ ,

$$\Gamma = V \frac{\partial P / \partial T}{\partial E / \partial T} \bigg|_V \quad (4)$$

using a simple finite difference method ($P[\rho, T_1] - P[\rho, T_2]$) where V is the specific volume, P is the pressure, E is specific energy, and T is the temperature. These results are shown in figure 2. For completeness, we calculated Γ for each of the adjacent isotherms and found that at lower

density Γ is a function of both density and temperature, but at higher compressions, it is only a function of temperature. At several eV, Γ becomes constant at higher pressures. It should be noted that Γ along an isotherm is not always smooth. One reason for this is we may be attempting to calculate equation (4) across a phase boundary. For example, the two spurious blue circles in figure 2(a) coincide with tantalum melting for densities between from 8.5 g/cm³ and 10 g/cm³ at 2000 Kelvin illustrating the complex behavior around phase transitions.

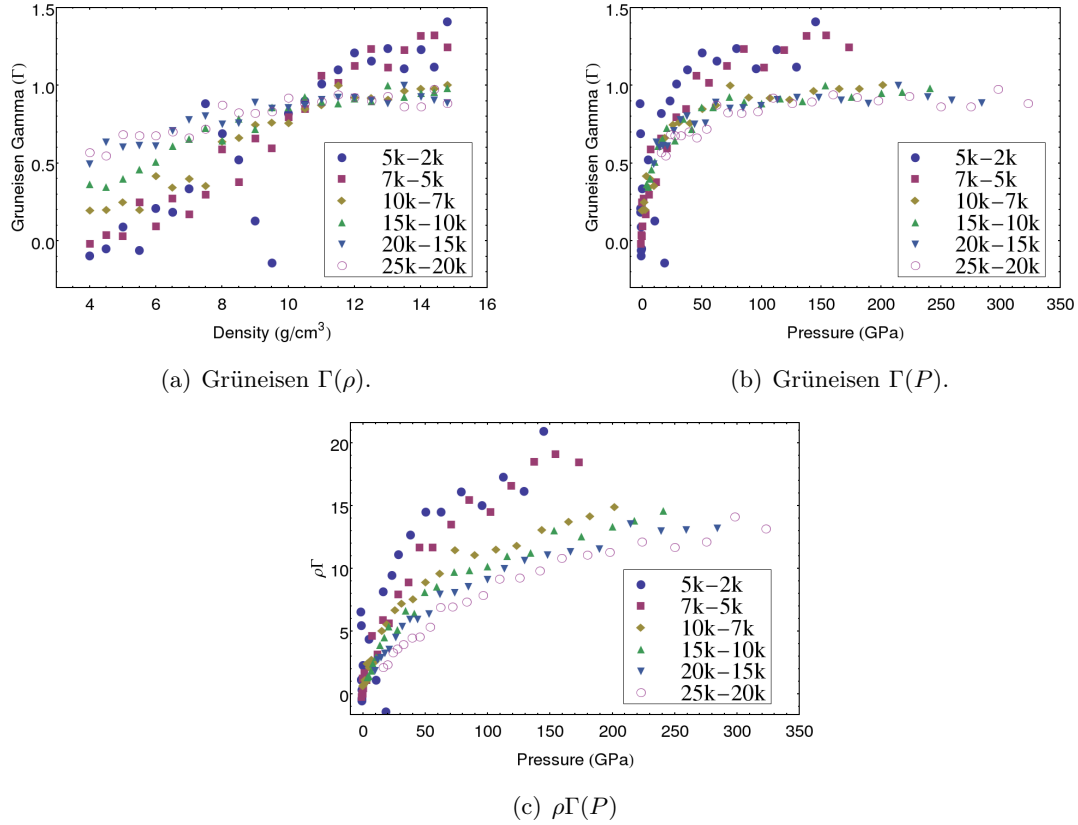


Figure 2. Γ as a function of density (figure (a)) and pressure (figures (b) and (c)). In figures (b) and (c), pressure is the centered value $\frac{1}{2}(P[\rho, T_1] + P[\rho, T_2])$. The Grüneisen Γ is calculated from equation (4).

Next, we used the experimental U_s/u_p data from the highest initial density experiment (approximately 7.4 g/cm³) to calculate the sound speed by extrapolating a linear fit to the U_s/u_p data for $u_p = 0$ and found it is 2.5 km/s. We also calculated the $\frac{\partial U_s}{\partial u_p}$ from experimental values and found while not constant, it did not vary widely and so we assumed a constant of 1.4. To approximate the porous Hugoniot we applied the porosity correction term in equation (5) [17] to all three initial densities (figure 3). $P_{H,P}$ is the pressure for the porous Hugoniot.

$$P_{H,P} = \frac{P_{MG} \left(1 + \frac{\Gamma}{2} \left(1 - \frac{\rho}{\rho_0} \right) \right)}{1 + \frac{\Gamma}{2} \left(1 - \frac{\rho}{\rho_{00}} \right)} \quad (5)$$

We tested the sensitivity of the principal Hugoniot to Γ and found that between 8.2 and 11 g/cm³, the pressure as a function of density was similar for $0.5 \leq \Gamma \leq 1.2$. After 11 g/cm³ or about 30 GPa, the pressure for the variety of Γ values diverged. Therefore, we set Γ to a

function of density such that it increased from 0.5 at reference density to 1.2 at 12 g/cm³ and then back to 0.9 as density continued to increase.

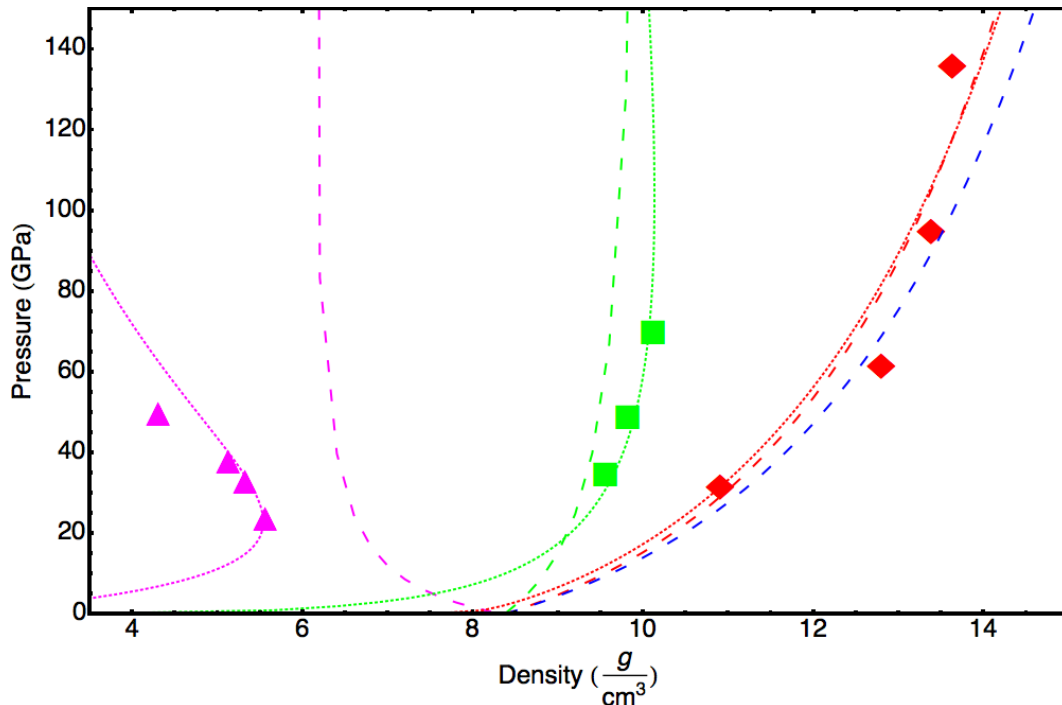


Figure 3. Mie-Grüneisen EOS and Rice-Walsh EOS. The blue dashed line is the Mie-Grüneisen EOS as calculated from the reference density of 8.36 g/cm³ with the off Hugoniot energy term set to zero. The red, green, and magenta dashed lines are the Hugoniot curves from the same reference density but modified with equation (5) with $\rho_{00}=7.4$, 3.0, and 1.13 g/cm³ respectively. The red, green, and magenta dotted lines are from the Fenton implementation of the Rice-Walsh EOS. The diamonds, squares, and triangles are the experimental data by Vogler et. al [4] with initial densities of approximately 7.4 ± 0.12 , 3.0 ± 0.2 , and 1.13 ± 0.01 g/cm³.

3. Results

The Mie-Grüneisen EOS with a porous density of $\rho_{00}=7.4$ g/cm³ shows good agreement with experimental data (figure 3). Using $\rho_{00}=3$ g/cm³, the agreement is only moderately good and the initial density does not start at the porous density. The 1.13 g/cm³ line has very poor agreement and also starts from an incorrect initial density. We found that adjusting the various parameters such as the sound speed and ρ_{00} did not significantly improve the fits to the higher porosity data leading us to assume that the Mie-Grüneisen EOS as a stand alone model may not be a suitable EOS for significantly porous tantalum.

We also used the Rice-Walsh EOS framework, as implemented by Fenton et al. [3], using parameters determined from the VASP simulations presented here along with experimental data. This EOS is combined with a $P - \lambda$ crush model that describes the material behavior below 5 GPa for $\rho_{00}=3$ g/cm³ and $\rho_{00}=7.4$ g/cm³ and to 15 GPa for $\rho_{00}=1.13$ g/cm³. The model computes the principal or reference Hugoniot and then scales it in ρ for a given pressure based on a combination of the Rice-Walsh EOS and the $P - \lambda$ crush model. Void space is assumed to be filled with air, which was present during the experiments, and so all model parameters are scaled as a blend of tantalum and air based on initial porosity. We set the Grüneisen Γ for tantalum

as a function of pressure. At zero pressure, Γ is 0.5, increasing to 1.2 as pressure increases to about 50 GPa. We then decrease Γ to 0.9 as the pressure continues to increase. After 150 GPa, Γ is constant at 0.9. As can be seen in figure 3, the dotted lines representing this EOS agree very well with the experimental data.

4. Conclusions

We used VASP to calculate a Grüneisen Γ in an attempt to create a useful broad ranged Mie-Grüneisen EOS. At lower density and temperature, Γ is a function of both. However, as density increases, Γ becomes a weak function of temperature and constant with density. At higher pressures, Γ is also constant with pressure. The corrections to the Mie-Grüneisen EOS can work for slightly distended tantalum, however this EOS, as a stand alone model, is inadequate for more porous material. The Rice-Walsh EOS combined with a crush model has very good agreement with experimental data.

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