A comparison of quotidian equation of state of aluminium with ab-initio calculations

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Abstract. We present results of theoretical calculation of the equation of state of Al covering several orders of magnitude of density and temperature. The data is generated using a QEOS model. The QEOS data have been used to calculate $U_s - U_p$ and $P - V$ hugoniots. The calculated hugoniots show good agreement with the experimental hugoniots. The cold curve generated by QEOS model has been compared with FP-LAPW results for compressed states and good agreement has been found. The QEOS data has also been compared with AIMD simulation results for expanded states – agreement is not good. These comparisons confirm that QEOS results are accurate for compressed states and less accurate for low temperature expanded states of Al.

1. Introduction
The equation-of-state (EOS) which defines the pressure and energy as functions of density and temperature is important in high pressure studies. It depends on the nature of the inter-atomic interactions and thus provides a test of fundamental condensed matter theories. At the same time, it can be used to determine thermodynamic properties. The metal EOS is an essential input to the hydrodynamic simulations of pulse power experiments such as metallic liner acceleration [1] and exploding wires/foils [2].

The EOS of metals have three contributions [3, 4]:

$$E_{TOT}(\eta,T) = E_C(\eta,T) + E_{IT}(\eta,T) + E_{ET}(\eta,T)$$

$$P_{TOT}(\eta,T) = P_C(\eta,T) + P_{IT}(\eta,T) + P_{ET}(\eta,T) \quad \eta = \rho/\rho_0$$

Here the first term (T = 0 or cold term) $P_C$ and $E_C$ are the electronic pressure and specific internal energy at zero Kelvin (cold-curve). Second term $P_{IT}$ and $E_{IT}$ are the contribution of ionic vibrations to the pressure and energy at finite temperatures, and third term $P_{ET}$ and $E_{ET}$ are the electron thermal contributions. This representation of EOS is known as three-term EOS model. In QEOS, Thomas - Fermi (TF) model is used for both contributions of electrons viz cold as well as thermal [5]. Cowan model is used for ion thermal contribution [5, 6]. TF model does not consider quantum mechanical structure of atom therefore it does not give correct results near cold solid. TF theory predicts a few megabar pressure for the cold solid where the actual pressure should be zero due to attractive forces. In order to obtain an approximately correct equation of state in this region, an empirical bonding correction is applied to remove
this inaccuracy. This correction is applied in such a way that pressure and bulk modulus are made to match the experimental value under normal conditions and the correction term has little effect away from the region near the cold solid. Hence the total energy and pressure are given by the following equations in QEOS [5, 6]

\[ E_{TOT}(\eta, T) = E_B(\eta, T) + E_{IT}(\eta, T) + E_E(\eta, T) \]  

(3)

\[ P_{TOT}(\eta, T) = P_B(\eta, T) + P_{IT}(\eta, T) + P_E(\eta, T) \]  

(4)

\( E_B \) is the binding correction term and \( E_E \) is the electron contribution to EOS which is calculated by using Thomas - Fermi model.

2. Computational Details

We have used More’s methodology for performing QEOS calculations to generate EOS data of Al. For comparing QEOS data for T=0, we have performed first principles calculations using Full Potential Linearized augmented plane wave (FP-LAPW) method [7]. For comparing QEOS data in expanded states we have performed Ab-Initio Molecular Dynamics (AIMD) simulations. The details of QEOS, FP-LAPW and AIMD calculations are described in this section.

2.1. QEOS code using More’s methodology

We have developed a quotidian equation of state (QEOS) code, based on the methodology of More, for generating EOS tables, specific heat and sound speed over a wide range of temperatures and densities, including compressed as well as expanded states. This yields the pressure, energy, entropy and free energy, taking into account density-dependent melting temperature, Debye temperature and Gruneisen parameter for any material. Cold and electron thermal terms are given by the TF model itself, a binding correction is applied to correct the cold - curve. Ion-thermal term is calculated separately using Cowan model as described in [5]. In this model energy and pressure are calculated by using following expressions:

\[ E_{IT}(\eta, T) = \frac{3kT}{2AM_P} \left(1 + \frac{w}{3}\right), \quad w = \frac{T_m(\rho)}{T} \]  

(5)

\[ P_{IT}(\eta, T) = \frac{\rho kT}{AM_P} \left(1 + \gamma_F w^{1/3}\right) \]  

(6)

Here \( T_m \) is melting temperature, \( \gamma_F \) is Gruneisen parameter.

Using More’s technique, we have incorporated a thermodynamically consistent interpolation scheme for calculating EOS, and density and temperature derivatives of pressure and energy.

2.2. Full Potential Linearized Plane Wave (FPLAPW) Calculations

For validation of the QEOS results, we have performed first principles calculations to generate cold-curve for Al. For this purpose we used WIEN-2k [7] code which is based on full potential linear augmented plane wave (FP-LAPW) method within the framework of density functional theory. The exchange correlation potential within GGA is calculated using the scheme of Perdew - Burke- Ernzerhof [8]. These calculations have been done using a constant muffin-tin radius \( R_{mt} \) of 1.7 a.u. In the WIEN2k code, it is very important to select a good basis set and k mesh size for getting accurate results. We start by taking a low value \( R_{ml}K_{max} = 7.0 \). For purposes of determining a suitable k -mesh size, we then calculate the total energy as a function of the size of the k -mesh increasing the size by 1000 at each step. We find that 10,000 k-points are sufficient. Having determined a good k-mesh, we now vary \( R_{ml}K_{max} \) from 7 to 12, and find that 9.5 is a good choice. Selected k-mesh size and \( R_{ml}K_{max} \) correspond to an energy accuracy
of $10^{-4}$ Ry. We have selected an energy cut-off of 6.0 Rydberg to separate the core from the valence states.

2.3. Ab-Initio Molecular Dynamics (AIMD) Simulations
We used the ABINIT code [9] for performing AIMD simulations, in isokinetic ensemble. The simulations are first run until equilibration is achieved, i.e., until the variations in pressure stabilize to an oscillatory pattern, without any long-term trend. Following equilibration, the pressure and energy are calculated by averaging over the next 500-1000 time steps of 1 femtosecond (fs) each. The exchange correlation interactions of electrons are treated in generalized gradient approximation (GGA), using PBE parametrization [8]. Ion-electron interactions are described by the pseudo-potential generated by Troullier and Martins method [10]. All calculations have been done at the $\Gamma$ point, i.e., with number of k-points taken as one.

3. Results and Discussion
3.1. QEOS-Results
In figure 1 we have shown the TF as well as QEOS pressures as functions of density at $T=200$ K. The TF pressure is approximately 1 megabar at normal density. The binding correction term makes pressure zero at normal density. Binding correction has little effect at higher densities. Hence QEOS and TF models give similar representation of electron contribution at very high density. TF model is accurate in high density limit. In order to get zero pressure at standard conditions, the cold energy should have a minimum at normal density. However, as shown in figure 2, the TF cold energy does not exhibit a minimum at normal conditions. The binding correction removes this discrepancy.

The EOS generated using QEOS model is combined with the three hugoniot equations viz.,
$\rho_0U_s = \rho_1 (U_s - U_p)$,
$P_1 - P_0 = \rho_0U_sU_p$
and
$E_1 - E_0 = \frac{1}{2} (P_1 + P_0) (V_0 - V_1)$
to get the $P - V$ and $U_s - U_p$ hugoniots [4]. In these equations, $\rho$, $E$, $P$ and $V$ have same meaning as in equations 1, $U_s$ and $U_p$ are shock and particle velocities respectively. The suffixes 1 and 0 represent the quantities in the shocked and the un-shocked regions. The calculated $U_s - U_p$ and $P - V$ hugoniots are plotted in figure 3 and figure 4 respectively. For comparison experimental shock compression data [11, 12, 13] are also shown. Good agreement with the experimental hugoniot can be seen.
3.2. Comparison of QEOS results with ab-initio calculations

We next compare the cold curve generated by QEOS by first-principles calculations using the FP-LAPW method within the framework of density functional theory. For generating cold curve using FP-LAPW method we have assumed Al to exist in FCC structure at all pressures. Although pressure-induced FCC-HCP and HCP-BCC structural transformations occur at high pressures, the differences in the energies of FCC and HCP structures and HCP and BCC structures are so small near the transition pressure that these structures coexist over a wide range of pressures [14, 15, 16]. This has been confirmed experimentally using X-ray powder diffraction experiments performed by Akahama [14]. In our calculations, we observed that differences in the energies of three structures were very small, and density of states curves of FCC and HCP structures at Fermi level were similar near the transition pressure [15, 16]. Therefore for the calculation of cold contribution we ignored structural transformation and assumed Al to exist in the FCC structure. In figure 5 we can see that there is a very good agreement between first principles results and QEOS results. These results match well with reported experimental data obtained by powder x-ray diffraction experiments [14]. The QEOS cold curve also agrees well with the cold-curve deduced from shock wave experiments [17, 18].

In figure 6 we have shown a comparison of QEOS results with AIMD simulation results for temperature 10000 K and expanded states. AIMD simulations are known to yield an accurate EOS in this regime, especially for \( T < 5 \text{eV} \) [19, 20]. It can be seen from figure 6 that QEOS results do not show good agreement with the results of AIMD simulations. Hence, QEOS results are less accurate for expanded metals at low temperatures.

4. Conclusion

We presented equation of state results of Al using quotidian equation of state model and from first principles calculations. QEOS calculations have been performed using More’s methodology. Full potential linearized augmented plane wave (FPLAPW) calculations have been performed within the framework of density functional theory for accurate calculations of cold curve. Ab-initio molecular dynamics simulations have been performed for calculating EOS for expanded metals. FPLAPW and AIMD simulation results have been compared with the QEOS results. The cold curves generated by using QEOS and FPLAPW methods for compressed states show good agreement, implying that QEOS results are accurate for compressed Al. QEOS results
Figure 5. Cold curve generated by QEOS and FP-LAPW calculations and their comparison with experimental results [14, 17, 18].

Figure 6. Isotherm (10000 K) generated by QEOS and AIMD simulations do not show good agreement with the AIMD simulations for expanded states, indicating that QEOS method gives less accurate results for the expanded states and low temperatures.

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