Equation of state and electrical conductivity of expanded Al

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Abstract. Ab-initio molecular dynamics (AIMD) simulations have been performed for generating equation of state (EOS) data as well as atomic configurations of expanded states of Al. The generated atomic configurations have been used for the calculation of electrical conductivity. AIMD simulations have been performed using the ABINIT code and electrical conductivity has been calculated using the Kubo-Greenwood formula as implemented in ABINIT. The generated equation of state data have been fitted to a three-term EOS model using adjustable parameters of ionic and electronic Gruneisen parameters. This three-term EOS model has been used to estimate critical density, temperature and pressure in the liquid-vapour region. The calculated values of critical density, temperature and pressure show good agreement with results available in the literature.

1. Introduction
Experiments and simulations of electrically exploded conductors are of great current interest because of their applications [1]. In such experiments, a large current is passed through a thin foil/wire of some conductor, such as aluminum or copper. This causes intense Joule heating of the conductor on a time-scale that is short in comparison with sound transit time through the conductor. The conductor material thus passes rapidly through the solid, liquid and vapour phases and may even enter the plasma phase. Hydrodynamic simulations of such systems require, as input, electrical conductivity and equation of state (EOS) data of the conductor material for densities ranging from normal density to a fraction of the normal density and temperatures ranging from room temperature to a few thousand Kelvin.

Ab-initio molecular dynamics (AIMD) is a powerful simulation technique for calculating properties of matter such as EOS and electrical conductivity in the density-temperature regime of exploding conductor experiments [2, 3].

In the present work, we have used the AIMD method to generate EOS and electrical conductivity data for expanded states of Al. Using the generated EOS data, we have estimated the critical temperature, density and pressure of Al in the liquid-vapour region.

This paper is organized as follows. In section 2 we have described computational details of generating EOS data and atomic configuration data using AIMD simulations. We also describe the method of computing DC electrical conductivity using the atomic configurations generated by AIMD simulations. In section 3.1 we have compared calculated electrical conductivity results with the reported results for the validation of AIMD simulations. In Section 3.2 we have presented EOS results of AIMD simulations and their fitting to a three-term EOS model. In

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Section 3.3, we describe the procedure for estimating critical density, temperature and pressure and compare these results with those available in the literature. Concluding remarks are presented in Section 4.

2. Computational Details

We used the ABINIT code [4, 5] 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 Perdew-Burke-Ernzerhof (PBE) parametrization [6]. Ion-electron interactions are described by the pseudo-potential generated by Troullier and Martins method [7].

All calculations have been done at the Γ point, i.e., with number of k-points taken as one. A few runs were also done with a higher number of k-points but with no significant effect on the output pressure. In ABINIT, the energy cut off \( e_{cut} \) is an important parameter which controls the number of plane waves and can have an enormous effect on the quality of a calculation. We performed several calculations at various values of \( e_{cut} \) to investigate the convergence needed for reliable results and found that 300 eV is a good value for Al. Runs were done with 108 atoms in an appropriate cubic box to set the required density.

For lower densities (< 1.0 g/cc) runs were done with 32 atoms, as large volume slows down the speed of calculations. For checking the accuracy with only 32 atoms, a few runs were done with 108 atoms. The results were not found to change significantly. We ensured that there were always some unoccupied levels for better convergence of all runs. The convergence criterion for energy was taken as \( 10^{-4} \) eV. The pressure contribution of ions was calculated by using the ideal gas equation.

Out of the atomic configurations generated by AIMD after stabilization of pressure oscillations, 10-15 statistically-independent configurations are used for the calculation of electrical conductivity. Frequency-dependent electrical conductivity of Al is calculated using the Kubo-Greenwood formula as implemented in ABINIT code. Quantities like Fermi-Dirac occupation for each band and each k point, weight of each k point, electronic eigenstate and eigenvalues for each electronic state, and the derivative of the Hamiltonian with respect to the wave vector of the three directions, are required as input for Kubo-Greenwood formula. These quantities are calculated by using ABINIT code. For selected statistically independent atomic configurations of 108 (or 32) atoms, a self-consistent ground state calculation is performed with the ABINIT code to get all these quantities. For conductivity calculations, we found that four k points are necessary for better convergence. We ensured that there were always some unoccupied levels for better convergence of all runs. For calculating the DC electrical conductivity, we extrapolated Kubo-Greenwood results using the Drude formula.

3. Results and discussion

3.1. Validation of AIMD simulations

The electrical conductivity as a function of temperature is plotted in Figure 1. These results are the average of 10-15 calculations, one for each statistically-independent configuration. We can notice that the electrical conductivity as a function of temperature shows a break (change of slope) near 6000 K. The cause for this can be explained using Drude theory. Following the Drude theory, the electrical conductivity can be expressed as

\[
\sigma = \frac{ne^2\tau}{m}
\]  (1)
Here, $n$ is the number density of electrons near Fermi surface, $e$ is the electronic charge, $\tau$ is the relaxation time and $m$ is the mass of electron. Initially conductivity decreases very fast with temperature (up to 6000 K) as shown in Figure 1. This can be understood in a simple manner. The ions vibrate about their equilibrium positions which leads to the thermal vibration of the crystal lattice. The amplitude of the vibration increases with the temperature. The electrons are scattered by collisions with the lattice ions. Consequently with the increase in the amplitude of vibration, the collision frequency increases. This leads to a decrease in the relaxation time $\tau$ and hence to a decrease in the conductivity. At very high temperature (above 6000 K), though the relaxation time $\tau$ is still decreasing with the temperature leading to decrease in the conductivity, but at the same time the number density of electrons near Fermi surface also starts increasing causing increase in the conductivity. These both phenomenas viz. the decrease in the relaxation time $\tau$ and the increase in the number density of electrons near Fermi surface jointly lead to less decrease in the electrical conductivity above the temperature 6000 K as compared to below this temperature. Hence, we see a break in the slope near 6000 K.

For comparison we have also given electrical conductivity data from [3] in Figure 1. Our results show good agreement with the reported results. This confirms the validity of our AIMD simulations.

3.2. EOS results of AIMD simulations and their fitting to three-term EOS model using adjustable parameters

After confirming the validity of our AIMD simulations, we calculated EOS by averaging energy and pressure outputs over 500-1000 steps after equilibration. The calculated pressure as a function of density for temperatures 10,000 K and 15,000 K are shown in Figure 2 with symbols. A three-term EOS model, that was fitted to these AMID data, is given by:

$$P_{TOT}(\rho, T) = \rho \left( f_1 f_2 \rho f_2 - f_3 \rho f_4 \right) + \frac{\rho k T}{AM_P} \left( 1 + \left[ 3 \left( b_1 + b_2 \rho / \rho_0 \right) - 1 \right] w \right) + \frac{1}{2} \gamma_E \beta T^2 \rho \quad (2)$$

Here the first term is cold term $P_C$ which have been represented by a soft sphere function in this model [9], second term is ion-thermal term $P_{IT}$ [8, 9] and third term is electron thermal term $P_{ET}$ [10, 11]. $w = T_m (\rho) / T$, $T_m$ is melting temperature, $3 \left[ b_1 + b_2 \rho / \rho_0 \right] - 1 = \gamma_F$ is lattice Gruneisen parameter and $\gamma_E$ is electronic Gruneisen parameter. The function $P_{TOT}(\rho, T)$ is fitted to AIMD results using adjustable parameters $b_1$, $b_2$ and $\gamma_E$. 
3.3. Estimation of critical point

We used the fitted three-term EOS model to estimate density temperature and pressure at critical point. In Figure 3 we have shown isotherms for temperatures 7458 K, 7923 K, 8387 K and 8851 K for expanded states of Al. We can see that isotherms of temperatures below 8387 K show an oscillatory behaviour (wavelike structure). For example, the 7458 K isotherm shows oscillatory behaviour from point b to point f. In this range of the 7458 K isotherm, the oscillating part can be divided in four parts $b-c$, $c-d$, $d-e$ and $e-f$. In the first part $b-c$ of the oscillating isotherm, the pressure first starts increasing from a value of 2.24 bar at b and reaches a maximum value of 2.89 bar at c. In the second part $c-d$, pressure decreases from this maximum value to 2.24 bar at point d. In the third part $d-e$ of the oscillating isotherm, pressure starts decreasing below 2.24 bar and reaches a minimum value 1.7 bar at e, and in the fourth part $e-f$, pressure starts increasing from the minimum value of third part to the minimum value of the first part i.e. 2.24 bar. Thus it can be readily seen that, for a certain pressure 2.24 bar, there are three values of density marked as $b$, $d$ and $f$. In the density range below starting point of the first part (from point a to b) and in the density range above the maximum density of the fourth part (from point f to g) the expanded state of Al is stable because in these density ranges $\partial P/\partial \rho > 0$. The state in the second and third parts of the oscillating isotherm is unstable because in these states $\partial P/\partial \rho < 0$. First and fourth part of the oscillatory isotherm are metastable states [12]. These represent super-saturated vapour and super heated liquid respectively.

We notice that on 7458 K isotherm, for a pressure 2.24 bar, there are three values of density marked as $b$, $d$ and $f$. If the temperature is decreased the isotherms would move down, loops of the wavelike structure of the isotherms would become larger and larger and the points corresponding to $b$, $d$ and $f$ move farther from one another. As the temperature is raised, the isotherms move up, the loops become smaller and the points corresponding to $b$, $d$ and $f$ get closer to one another. At a certain temperature, the wave-like structure disappears and these three points become identical. The point where these three points merge is shown by the point $x$.

The temperature of this particular isotherm at which critical point lies is the critical
temperature, and the density and pressure corresponding to this point, are the critical density and critical pressure. $\partial P / \partial \rho$ and $\partial^2 P / \partial \rho^2$ are equal to zero at this point. In Table 1, we have given results of estimated critical density, temperature and pressure. For comparison, we have also given results reported in the literature. We can see that our results agree reasonably well with these results.

| Reference | $\rho_c (g/cc)$ | $T_c (K)$ | $P_c (bar)$ |
|-----------|-----------------|----------|------------|
| This work | 0.385           | 8387     | 4.45       |
| Ref [13]  | 0.28            | 8860     | 4.68       |
| Ref [14]  | 0.43            | 8944     | 4.726      |
| Ref [15]  | 0.785           | 8472     | 5.094      |
| Ref [16]  | 0.66            | 7917     | 4.67       |

4. Conclusion
AIMD simulations have been performed for generating EOS and atomic configuration data. Generated atomic configurations have been used for calculating electrical conductivity. Generated EOS data have been used to estimate critical temperature, density and pressure of Al in liquid-vapour region. The electrical conductivity, critical density, critical temperature and critical pressure results show good agreement with the reported results.

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