Ion Equation of State using scaled binding energy model

Chandrani Bhattacharya and M. K. Srivastava

Theoretical Physics Division, Bhabha Atomic Research Centre, Mumbai-400085
E-mail: bchandra@barc.gov.in

Abstract. Global Equation of State models are used to carry out hydrodynamic calculations of inertial confinement fusion systems. There are some such models like QEOS which are used quite routinely in ICF simulations. The empirical content of QEOS, which otherwise does have a strong theoretical basis, provides scope for further research aiming at making the EOS theoretically more sound by reducing the empirical nature of the EOS. To this end, we have made some progress by developing an equation of state which uses a more accurate form for the zero temperature isotherm and a method to calculate the Grüneisen parameter so as to yield an ion equation of state which is better than the Cowan’s model used in QEOS. The parameters of the model are taken from experiments or electronic structure calculations. The EOS is verified against the shock Hugoniot data and the melting data of Pb and U, and the phase diagram and Hugoniot of Hf. The stability analysis of some metals like Cu and Mo had also been carried out. The agreement of the calculated results with available experimental data is reasonably good.

1. Introduction
Development of advanced theoretical as well as experimental techniques in the field of high energy density physics which deals with matter under application of very high pressures and temperatures has gained tremendous importance in various disciplines such as astrophysical phenomena, inertial confinement fusion (ICF), nuclear explosions etc. In all these cases, a large amount of energy is concentrated in a very small region at a very fast rate leading to generation of very high pressures and temperatures and subsequent hydrodynamic motion. The Equation of State of materials is an important ingredient for the hydrodynamic simulation of these systems. A proper understanding of extreme states of matter requires development of Equation of state models valid over wide ranges of thermodynamic conditions. Materials also undergo structural phase transitions when subjected to these conditions. It is obvious that due to these complications, a single generalized formula cannot be used to describe the EOS of materials. Hence there is always a need for global EOS models which can explain the physical processes in the various thermodynamic regimes appropriately. For more details, one can refer [1].

The quotidian equation of state (QEOS) is one of such models. In spite of a strong theoretical basis, QEOS [2] uses some empirical corrections for obtaining agreement with measured shock wave data. One of these corrections is used for all materials while the other is used to account for structural phase transitions. Evaluation of these corrections requires a priori knowledge of experimental data. We have developed a method wherein we can avoid the usage of these empirical corrections.

In our model we express the total free energy of a system as a sum of the zero temperature isotherm and thermal contributions from ions and electrons. Though the zero temperature isotherms can be determined accurately from electronic structure theory, it is customary to parameterize it with semi-
analytical models. Several such semi analytical formulae which use data from experiments or theory are available to describe the zero temperature isotherm. A universal scaled binding energy model applicable to various classes of materials in the absence of phase transitions was proposed by Rose et al. [3]. This model uses three parameters of solid at ambient conditions, namely, the equilibrium density, cohesive energy and bulk modulus. We present an improvement in the ‘universal’ EOS by incorporating the strong compression limit wherein the solid behaves like a free electron gas and using the pressure derivative of bulk modulus to improve the predictive power of the EOS [1].

Apart from the zero temperature isotherm, a proper account of nuclear motions and thermal excitations of electrons is required to study the temperature dependence of materials. Systematic calculations of these properties using statistical mechanics and computer simulations are difficult because this needs proper incorporation of the complicated inter-particle interactions. A well known approach to solve this problem is to use the Debye Grüneisen theory. We have used this approach wherein the Grüneisen parameter \( \gamma \) is expressed in terms of the 0-K pressure and bulk modulus and a free parameter, \( \tau \). This parameter is chosen to be 0, 1 or 2 corresponding to the lattice vibration theories of Slater [4], Dugdale and McDonald [5], and Vashchenko and Zubarev [6]. However, it is observed from various theoretical and experimental analyses that a constant value for \( \tau \) is inadequate and that it should increase with density. We have derived an expression for \( \tau \) vs density in such a way that the limiting values of \( \gamma \) at ambient conditions (known experimentally) and very high density were included. This model, together with the electronic part obtained from the low temperature specific heat constant was verified against the Hugoniot and melting curves of many materials and the agreement was found to be quite good [1].

2. The Equation of State model

2.1. Energy \( E_c \) and Pressure \( P_c \)

Though the energy and pressure in a solid at zero temperature can be accurately determined from electronic structure calculations, it is common practice to use analytical expressions, which contain the relevant parameters at ambient conditions. One of such expressions, called the universal scaled binding energy [3], has been found to agree quite well with the results of electronic structure calculations, and is expressed as

\[
E_c = E_{coh}[1 + \varepsilon(a)]; \quad a = \frac{r - r_0}{l},
\]

where, \( E_{coh} \) is the cohesive energy per unit mass, which is the energy required to vaporize the material completely. The Wigner Seitz cell radius \( r_0 \) corresponds to the normal density \( \rho_0 \). The scale length \( l \) is expressed as

\[
l = \left[ \frac{E_{coh}Am_p}{12\pi B_0r_0} \right]^{1/2}
\]

where, \( A \) is the atomic weight, \( m_p \) is the mass of proton, and \( B_0 \) is the bulk modulus at normal density. The equilibrium conditions expressed in terms of the function \( \varepsilon(a) \) yield the relations

\[
\varepsilon(0) = -1, \quad \varepsilon'(0) = 0, \quad \varepsilon''(0) = 1.
\]

Then, the pressure and the bulk modulus are given by

\[
P_c = -Am_p\left[ \frac{dE_c}{dV} \right]; \quad B = -V\left[ \frac{dP_c}{dV} \right].
\]

2.1.1. Expression for \( \varepsilon(a) \). The functional form of \( \varepsilon(a) \) used in the subsequent analysis is of the form
where, \( R = 1 + ka \) and \( k = l / r_0 \). The equilibrium conditions mentioned earlier show that the parameters \( \alpha, \beta \) and \( \lambda \) are given by

\[
\alpha = -1; \quad \beta = -(1 + 2k); \quad \lambda = -k^2 - 2k.
\]

The fourth parameter \( \mu \) is obtained using the experimentally/ theoretically known value of \( B_0' \) which is related to \( e^m(0) \) as

\[
e^m(0) = -3k(B_0' - 1).
\]

In earlier applications of the binding energy formula, the value of the parameter \( \mu \) is taken as -0.05 [3] for all metals. This choice is quite arbitrary and it yields the universal binding energy formula. The use of the pressure derivative of bulk modulus to obtain the parameter \( \mu \) destroys the universal nature of the scaled binding energy formula. This is found from detailed calculations that universality is true only approximately. Finally, inclusion of the \( R^2 \) term in the denominator ensures that pressure varies as \( \sim V^{-5/3} \) as \( V \) approaches zero which is the required limiting behaviour for the free electron gas.

### 2.2. Ionic free energy

The total free energy consists of ionic contributions from lattice vibrations and electronic thermal excitations. The ionic part obtained within the Debye model [8] is

\[
F_i(V, T) = \frac{k_B T}{A m_p} f(u), \quad u = \vartheta(V) / T,
\]

\[
f(u) = \frac{9u}{8} + 3 \ln(1 - e^{-u}) - D(u),
\]

\[
D(u) = \frac{3}{u^3} \int_0^u dx \frac{x^3}{e^x - 1}.
\]

The ionic contribution to the internal energy \( E_i \) and pressure \( P_i \) can now be obtained as

\[
E_i(V, T) = -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{F_i}{T} \right) \right]_V = \frac{k_B T}{A m_p} u f'(u),
\]

\[
P_i(V, T) = -\left( \frac{\partial F_i}{\partial V} \right)_T = \gamma \rho E_i(V, T).
\]

Here, \( \gamma \) is called the Grüneisen parameter which is related to the Debye temperature as

\[
\gamma = \frac{d \ln \vartheta_D}{d \ln V}. \tag{8}
\]

#### 2.2.1. Grüneisen parameter.

Several models for \( \gamma(\rho) \) are available in literature. The most commonly used formulas for \( \gamma \) are expressions given by Slater [4], Dugdale and McDonald [5], and Vashchenko and Zubarev [6]. The expressions can be written in a single generalized form as

\[
\gamma(V) = -\frac{1}{6} - \frac{1}{2} \frac{d \ln(B - 2l / 3 P_i)}{d \ln V}.
\]
Here, the parameter ‘$t$’ takes the values 0, 1 and 2 corresponding to the formulas given by Slater, Dugdale and McDonald, and Vashchenko and Zubarev respectively. However, the constant value for ‘$t$’ is not found to agree well with the analyses of many of the Hugoniot and melting curves. In fact, it is found that an increasing variation of ‘$t$’ with density yields better results.

2.2.2. Expression for $t(a)$. The functional form for $t(a)$ has to be chosen such that $\gamma \to \infty$ as $\rho \to \infty$ or $R \to 0$. Employing the limiting condition on $\gamma(\rho)$ we find that ‘$t$’ should vary as a power law

$$t(a) = \frac{5}{2} - \eta R^\delta.$$  

A similar expression for $t(a)$ has been found by some other authors also. The limiting value of $\gamma(\rho) \to \infty$ is 0.5. This gives a value of 1 for $\delta$. The value of $\eta$ can be obtained from the value of $\gamma(\rho_0)$ i.e. its value at normal density which is an experimentally known quantity.

2.3. Electronic free energy

The electronic free energy is obtained using the Thomas Fermi model in global theoretical EOS models like the QEOS. However, for moderate pressures, of the order of Mbars, and temperature of the order of few eV, $F_e \ll F_i$. So, it is adequate to use an approximate expression for $F_e$ given by

$$F_e(V, T) = -\frac{1}{2} N \Gamma T^2.$$  

(9)

Here, $\Gamma$ is the Sommerfield’s coefficient for specific heat and $N$ is the Avogadro number. $\Gamma$ is proportional to the electronic density of states at Fermi energy. The dependence of $\Gamma$ on $V$ is given by

$$\Gamma = \Gamma(V_0)(V/V_0)^\kappa,$$

where, $\Gamma(V_0)$ and $\kappa$ are determined from electronic structure calculations.

3. Results and Discussion

Before application to hydrodynamic simulations, extensive verification of the EOS using available experimental / theoretical data is mandatory. Seven independent parameters, viz., density, cohesive energy, bulk modulus, pressure derivative of bulk modulus, Grüneisen parameter, and Debye temperature and Sommerfield coefficient are needed for using the EOS model discussed above. Their values for lead and uranium are given in Table I and for hafnium in Table II.

3.1. Melting curve

Lindemann’s criterion can be used to determine the melting curve of solids. This is expressed in the form of Gilvarry law which relates melting temperature $T_m$ and $\gamma$ as

$$\frac{d \ln T_m}{d \ln V} = 2 \left[ \gamma - \frac{1}{3} \right].$$  

(10)

Knowing the volume dependence of $\gamma$, the expression for the melting temperature can be derived by performing one integration. The knowledge of the melting temperature at some reference density can be used to obtain the entire melting curve of the material. The melting curves for Pb and U are calculated and compared with available experimental / theoretical data. The theoretical curve is well within the experimental error bars. (see figure-(1-2))
3.2. **Hugoniot curve**

Another test for the EOS model is to reproduce the experimental Hugoniot data. The Hugoniot relations are based on the conservation laws of mass, momentum and energy [8] given by

\[
\begin{align*}
U_p & = U_s \left(1 - V / V_0 \right), \\
P_H & = U_p U_s / V_0, \\
E_H & = \frac{1}{2} \left( P_H + P_0 \right) \left( V_0 - V \right).
\end{align*}
\]

where, \( U_p \) and \( U_s \) are, respectively, the particle and shock velocities. \( P_H \) and \( E_H \) denote the pressure and specific internal energy behind the shock wave. In addition to this, the knowledge of the EOS can be used to determine all the variables. The Hugoniot curve calculated by this method was verified against available experimental data for Pb and U and good agreement was noted. (see figure-(3-4))
3.3. Phase transition
The EOS model can be used to characterize materials undergoing structural phase transitions, if the parameters of both the phases are known. In addition, an additive constant, \( \phi_0 \) needs to be added to the zero temperature energy of the high-pressure phase.

\[
E_{\text{cold}} = \phi_0 + E_{\text{coh}} \left[ 1 + \varepsilon(a) \right].
\]

\( \phi_0 \) is to account for the difference in the ground state energies of the two phases, and needs to be adjusted in order to get the correct transition pressure. The curve in the P-T plane separating the two phases is determined by the condition, \( G_\alpha(P,T) = G_\beta(P,T) \), where \( G \) is the Gibbs free energy. Hafnium undergoes two transformations when subjected to high pressures. The first transition is from \( \alpha \) to \( \omega \) phase occurring at 35 GPa and the next transition is from the \( \omega \) to \( \beta \) phase occurring at 70 GPa. The appearance of kink in the Hugoniot indicates the occurrence of structural phase transition in the solid. The figure 5 shows the 300K isotherm of Hf. The experimental points (open circles) are from Reference [11].
Figure 5. 300 K isotherm for Hf. Open circles are data from Reference [11] and solid line is the result of present calculations.

Table 2. Input parameters for various phases of Hf used in the model

| Phase | $\rho_0$ (g/cc) | $E_{\text{coh}}$ (Terg/g) | $\beta_0$ (erg/K$^2$) | $\gamma_0$ | $B_0$ (Mbar) | $B_{\beta_0}$ | $\theta_0$ (K) | $\phi_0$ (Terg/g) |
|-------|----------------|--------------------------|----------------------|-----------|--------------|--------------|-------------|-----------------|
| $\alpha$ | 13.08 | 0.03468 | 121.02 | 1.3 | 1.125 | 4.8 | 207 | 0 |
| $\omega$ | 13.27 | 0.07 | 84.714 | 1.42 | 1.188 | 4.5 | 211.3 | 0.0004 |
| $\beta$ | 13.20 | 0.09 | 67.771 | 1.49 | 81.5 | 5 | 175 | 0.0011 |

The input data for the various phases were from reference [12].

3.4. Stability of shock waves

The conditions for the occurrence of the corrugation instability and spontaneous emission of sound waves from intense shock waves were formulated by Dyakov and Kontorovich. However, the precise determination of the unstable regions needs an accurate EOS model. The EOS model described was used to obtain the variation of Mach number, entropy and the sound velocity behind the shock front. With these results, it became possible to apply the ‘Kontorovich criterion’ for the spontaneous emission of sound from the shock front. This phenomenon can also be interpreted as a resonant reflection of the acoustic wave from the shock since for some angle of incidence the reflection coefficient becomes infinite. The criterion for SE obtained by Kontorovich is

$$h_c(\rho_2, M_2) < h < 1 + 2M_2, \quad h = -V_2^2 \left( \frac{d\rho_2}{d\rho_2} \right)_h.$$  \hspace{1cm} (11)

Here, $\rho_2 / \rho_1 > 1$ is the ratio of the densities on both sides of the shock, $V_2 = U_S - U_p$, and $M_2 = V_2/c_2 < 1$, are the flow velocity behind the shock in the frame of reference which is stationary with respect to the shock wave and the Mach number for this flow, $c_2$ is the sound velocity in the shock compressed medium, $h$ is the Dyakov parameter defined along the Hugoniot adiabat. The critical value $h_c$ of parameter $h$ determining the threshold of SE is given by

$$h_c = \frac{1 - M_2^2(\rho_2 + 1)}{1 + M_2^2(\rho_2^2 - 1)}.$$  \hspace{1cm} (12)
Contrary to the results published by Rutkevich et al. [13], we have not found any instabilities for Mo in the range of pressures investigated by these authors. This maybe attributed to the inaccuracies in the EOS model used by them. In figures (6-7), we show the stability curves of Cu and Mo calculated using our EOS model.

However, we expect that these metals will exhibit such instabilities if the shock wave pressures are much higher so as to cause ionization or dissociation in the medium. These ranges of shock pressures can be investigated with the new model if a more accurate model for the electronic contribution to the EOS, than what we use at present, is made use of. This is because at very high temperatures and pressures, the electronic part dominates the behaviour of materials. Work along this direction is in progress.

**Figure 6.** Stability curve of Cu.  
**Figure 7.** Stability curve of Mo.

### 4. Conclusion

The EOS model formulated in this article has excellent predictive capabilities. This has been achieved partly due to the inclusion of pressure derivative of bulk modulus and the limiting form of free electron pressure in the universal scaled binding energy. Next, the constraints imposed in developing the Grüneisen coefficient, through the non-central force parameter $t$, make it accurate right from ambient conditions to high compression states. The set of seven parameters needed in the model can be obtained either from experimental databases or electronic structure calculations. Experimental / theoretical results on melting curves of several materials, over a wide range of volumes, are also accurately predicted by the model. The model is validated using data for normal solids such as Pb and U as well as Hf which undergoes structural phase transitions. The stability of shock waves at high pressures and temperatures for some metals are also studied.

### References

[1] Bhattacharya C and Srivastava M K 2007 *J. Appl. Phys.* 102 064915.  
[2] More R M, Warren K H, Young D A, and Zimmerman G B 1988 *Phys. Fluids* 31 3051.  
[3] Rose J H, Smith J R, Guinea F, and Ferrante J 1984 *Phys. Rev. B* 29 2963.  
[4] Slater J C 1939 *Introduction to Chemical Physics* Mc Graw Hill New York Chapter XII.  
[5] Dugdale J S and Mc Donald K C 1953 *Phys. Rev.* 89 832.  
[6] Vashchenko V Ya and Zubarev V N 1963 *Sov. Phys. Solid State* 5 653.  
[7] Burakovsky L and Preston D L 2004 *J. Phys. Chem. Solids* 65 1581.
[8] Zeldovich Ya B and Raiser Yu P 1996 *Physics of Shock waves and High Temperature Hydrodynamic Phenomena* Academic Press New York Vol.-I.

[9] Akella J, Ganguly J, Grover R and Kennedy G 1973 *J. Phys. Chem. Solids* **34** 631.
Millet L E 1968 unpublished dissertation Brigham Young University Provo Utah.

[10] Ganguly J and Kennedy G C 1973 *J. Phy. Chem. Solid (Technical notes)* 2272-2274.

[11] Hui X, Parthasarthy G, Luo H, Vohra Y K, and Ruoff A 1990 *Phys. Rev. B* **42** 6736.
Hui X, Parthasarthy G, Luo H, Vohra Y K, and Ruoff A 1996 *Phys. Rev. Lett.* **77** 3865.
Vohra Y K and Spencer P T 2001 *Phys. Rev. Lett.* **86** 3068.

[12] Joshi K D, Jyoti G, Gupta S C, and Sikka S K 2002 *J. Phys.: Condens. Matter* **14** 10921
The parameters in the Table II were communicated to us by Dr. K. D. Joshi.

[13] Rutkevich I, Zaretsky E, and Mond M 1997 *J. Appl. Phys.* **81** 11.