Thermodynamic formulation of enthalpy-based equation of state for condensed substances

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Abstract. Thermodynamic formulation has been made for the enthalpy-pressure-volume equation of state for condensed substances based on the assumptions proposed by Rice and Walsh in 1957. We found a thermodynamic constraint that must be imposed on the specific heat at constant pressure and a material parameter defined by them and later in another form by Wu and Jing. Behavior of this material parameter has been calculated based on the calculation of the Grüneisen parameter. Comparison of this material parameter along shock Hugoniot and an isentrope revealed that this parameter depends on entropy as well as pressure, but entropy dependence is very small. This result strongly suggests that this parameter as a function of only pressure will give sufficient description of high-pressure behavior of solid materials within appropriate range of pressure.

1. Introduction

In 1957, Rice and Walsh have published twin papers, the first one of which is the representation of their shock wave data for liquids including water [1, 2]. Their data have been obtained by the state of the art at that time in experiments through the use of argon flash gap technique analyzed by shock impedance matching method. In the second paper, they have formulated an equation of state based on their measurements of principal and reflected shock wave data for water. Their analysis was based on an equation of state (EOS) in terms of pressure, volume and enthalpy. Specific enthalpy is introduced into the equation of state for solid materials instead of specific internal energy. Their choice of thermodynamic state variables is natural in that flow equations describing shock propagation in terms of internal energy, pressure and volume (or density) can easily be transformed into the form by using enthalpy, pressure and volume.

Wu and Jing have proposed a simple theoretical model to predict shock Hugoniot for porous solids [3]. Their model was based on an EOS in terms of pressure, volume and enthalpy. The EOS itself is basically the same as the Rice-Walsh EOS. In their scheme of EOS discussions, a new non-dimensional material parameter $R$ is defined instead of the Grüneisen parameter in the Grüneisen EOS. Isobaric process instead of isochoric process can naturally be applied to reach the high-temperature states attained by shock compression of porous materials. Use of pressure as an independent variable instead of volume or density is very convenient for the numerical simulation of shock wave propagation, and especially useful to reactive flow problems including detonation wave simulation.
In this paper, Rice-Walsh type EOS and Wu and Jing’s assumptions were examined in detail by thermodynamics and the enthalpy-based EOS is reformulated and it is compared with the corresponding Grüneisen EOS. Calculation of the non-dimensional material parameter for high-pressure states and the results have been discussed to know the feasibility of the Rice-Walsh type EOS for the description of high-pressure states in condensed materials.

2. Definition of non-dimensional material parameter

According to the papers by Rice and Walsh [2], a material parameter $\xi$ is defined as

$$\xi(p,v) \equiv \left( \frac{\partial h}{\partial v} \right)_p = C_p \left( \frac{\partial T}{\partial v} \right)_p.$$  \hspace{1cm} (1)

This definition can be read that the parameter $\xi$ is a function of pressure and volume, having the dimension of pressure. In their formulation of EOS, they assumed that it is a function only of pressure.

Wu and Jing [3] used somewhat different definition of another material parameter $R$ as

$$R(p,h) = p \left( \frac{\partial v}{\partial h} \right)_p.$$  \hspace{1cm} (2)

This definition is physically equivalent to the definition of equation (1) and can be read that the parameter $R$ is a function of pressure and enthalpy. Wu and Jing assumed that it is a function only of pressure.

$$R = R(p).$$  \hspace{1cm} (3)

The definition of equation (2) resembles to the definition of the Grüneisen parameter

$$\gamma(v,\varepsilon) = v \left( \frac{\partial p}{\partial \varepsilon} \right)_v,$$  \hspace{1cm} (4)

where the Grüneisen parameter is a function of volume and internal energy. This definition leads us to the so-called Grüneisen type equation of state, if the Grüneisen parameter defined by equation (4) is a function only of volume. (Grüneisen law)

$$\gamma = \gamma(v).$$  \hspace{1cm} (5)

Wu and Jing claimed that the parameter $R$ is one of material parameters equivalent to the Grüneisen parameter. Important difference between them is the change in the thermodynamic state variables from the specific volume to the pressure.

By combining equations (2) and (3), one has the EOS of the form,

$$v = F(p) + \frac{R(p)}{p} h,$$  \hspace{1cm} (6)

which is reached by the integration of the following equation derived from equation (2) along an isobaric.

$$dv = \frac{R(p)}{p} dh.$$  \hspace{1cm} (7)
A pressure function \( F(p) \) in equation (6) is an integration function. Although Wu and Jing demonstrated that constancy of specific heats leads to equation (6), the present discussion shows that constancy of specific heats is not required to reach the Rice-Walsh type equation of state.

3. Relationship between the Grüneisen EOS and Rice-Walsh type EOS

In this section, Wu-Jing definition, equation (2) is studied thermodynamically in detail. Based on the Debye model for the specific heat at constant volume, \( C_v \), isothermal compression leads to the shrinkage in lattice spacing, thereby making the fundamental frequency to increase. As a result, the Debye temperature increases upon compression. This results makes two specific heats \( C_v, C_p \) decrease.

General relationship between the Grüneisen parameter and the specific heat at constant volume was discussed by the present author through the following equation [4],

\[
\frac{dT}{T} = -\left( \frac{\partial p}{\partial \varepsilon} \right)_v dv + \frac{dS}{C_v} = -\frac{\gamma(v,S)}{v} dv + \frac{dS}{C_v(v,S)}. \tag{8}
\]

This is a thermodynamic identity and contains both \( C_v \), and the Grüneisen parameter. Note that the lhs of equation (8) is a total differential. Then a Maxwell’s relation pertinent to this equation is written by

\[-\left( \frac{\partial}{\partial S} \left( \frac{\gamma(v,S)}{v} \right) \right)_v + \left( \frac{\partial}{\partial v} \left( \frac{1}{C_v(v,S)} \right) \right)_S, \tag{9}\]

which clearly shows the mutual dependence between the Grüneisen parameter and the specific heat, \( C_v \). If one starts with the Grüneisen law, i.e., equation (5), equation (9) gives the following.

\[ C_v = C_v(S). \tag{10}\]

Volume dependent Debye temperature in the Debye model is compatible with this result. Namely, the Grüneisen law, equation (5), and the entropy dependent specific heat, equation (10) are physically equivalent.

Corresponding identity for parameter \( R \) does exist, which is written as

\[
\frac{dT}{T} = \left( \frac{\partial v}{\partial h} \right)_p dp + \frac{dS}{C_p} = -\frac{1}{\xi(p,S)} dp + \frac{dS}{C_p(p,S)} = \frac{R(p,S)}{p} dp + \frac{dS}{C_p(p,S)}. \tag{11}\]

One may note again that this equation is a thermodynamic identity containing the specific heat at constant pressure, \( C_p \), and the parameter, \( R \). Note that the lhs of equation (11) is again the same total differential. Then a Maxwell’s relation pertinent to this equation is written by

\[ +\left( \frac{\partial}{\partial S} \left( \frac{R(p,S)}{p} \right) \right)_v = \left( \frac{\partial}{\partial p} \left( \frac{1}{C_p(p,S)} \right) \right)_S, \tag{12}\]

which clearly shows the mutual dependence between \( R \) and \( C_p \). If one starts with the Wu-Jing assumption, equation (3), equation (12) gives the following.

\[ C_p = C_p(S), \tag{13}\]

which gives the sufficient and necessary condition to reach the Wu-Jing assumption, equation (3).
In order to show whether equation (13) is a physically acceptable assumption, one may discuss the difference between two identities, equations (8) and (11). If one combines these two equations, it is shown that the parameter \( R \) is directly connected to the Grüneisen parameter through the relation
\[
\frac{\partial v}{\partial h}_p = \frac{R}{p} = \frac{\Gamma v}{c_b^2}.
\] (14)

In equation (14), \( c_b \) denotes bulk sound velocity.
\[
c_b^2 = \left( \frac{\partial p}{\partial \rho} \right) = -\nu^2 \left( \frac{\partial p}{\partial v} \right)_S.
\] (15)

From equation (14), parameter \( R \) can be calculated using this equation by the knowledge of the Grüneisen parameter. It should be emphasized that this relationship is a thermodynamic identity and is completely independent of the Wu-Jing assumption, equation (3) or the Grüneisen law, equation (5) and also on the assumption of entropy-dependent specific heats. Furthermore, we can obtain the relation of the difference in two specific heats in terms of Grüneisen or parameter \( R \) as
\[
\frac{1}{C_p} - \frac{1}{C_v} = -\left( \frac{\partial v}{\partial h}_p \right)^2 \frac{2 c_b^2}{v^2} = -\frac{R^2 T c_b^2}{p^2 v^2} = -\frac{\gamma^2 T}{c_b^2}.
\] (16)

Equation (16) shows that \( C_p \) may not be described by one entropy function, since rhs of the equation cannot be written in terms only of entropy even when \( C_v \) is described by the Debye model. This shows that Wu-Jing assumption, equation (3) is not valid in general sense. Discrepancy between the Wu-Jing assumption and the real behaviour of \( C_p \) depends on the range of high-pressure states. The Wu-Jing assumption, however, may be a good approximation for wide high-pressure range, which will be shown in the next section.

4. Behaviour of the parameter \( R \) along Hugoniot and an isentrope

This section is devoted to investigate whether the Wu-Jing assumption can be a good approximation for the description of high-pressure states reached by shock or isentropic compression of solid materials. In order to study the behaviour of the parameter \( R \), we will start the discussion for the EOS based on the Grüneisen law, equation (5). Since the Grüneisen law has some theoretical and experimental basis. Starting from the Grüneisen EOS, we will seek the way to reach the Rice-Walsh type EOS. This is the way Wu and Jing adopted in their paper.

We have estimated the value of the parameter \( R \) by using equation (14) based on the knowledge of the Grüneisen parameter as well as bulk sound velocity at compressed states on shock Hugoniot and on an isentrope. Our strategy to investigate the feasibility of Wu-Jing assumption is the comparison of estimated parameter \( R \) on the Hugoniot and an isentrope. By doing so, one may see how large is the entropy dependence of the parameter. Since the entropy dependence of parameter \( R \) must be small in order for the Wu-Jing assumption to be a good approximation for high pressure EOS of materials. We have performed the calculations of the Grüneisen parameter, two specific heats, \( C_v \) and \( C_p \) along Hugoniot and an isentrope centering an uncompressed state for aluminum. Calculation of the Grüneisen parameter is based on three theoretical models, Slater [5], Dugdale-MacDonald [6], and Vaschenko-Zubarev model [7].

Figure 1 shows the calculated result of the parameters. Parameter \( R \) tends to zero with decreasing pressure, but it is seen from these figures that \( R/p \) may have a finite value from equation (14). One may note from figure 1 that the \( R/p \) is a monotonically decreasing function. By the comparison of the differences in \( R \) along Hugoniot and an isentrope, one may see the entropy dependence of the parameter, since entropy increases along shock Hugoniot. Wu and Jing assumed that the parameter
has no entropy dependence, but this assumption is not correct for Debye solids. Figure 1 shows, however, entropy dependence of $R$ is rather small. It is found from figure 1 that more important parameter $R/p$ exhibits less entropy dependence.

We also have studied the change in two specific heats $C_p$ along shock Hugoniot and an isentrope. They were calculated using Debye model. $C_p$ slightly decreases along an isentrope, and is not a function only of entropy, showing slight dependence on pressure. Along shock Hugoniot, $C_p$ increases with increasing pressure. In this case, entropy along Hugoniot also increases. Behavior of $C_p$ along Hugoniot shows both entropy and pressure dependence.

![Figure 1](image.png)

**Figure 1** Calculated pressure dependence of the parameter, $R(pH)$ and $R(pH)/pH$ along shock Hugoniot and an isentrope for aluminum. Broken and solid lines show values on corresponding isentropes.

5. **Conclusion**

Equation of state in terms of enthalpy introduced by Rice and Walsh has been examined thermodynamically in detail. Comparison of a non-dimensional parameter $R$ along shock Hugoniot and an isentrope revealed that parameter $R$ depends on entropy as well as pressure, but its dependence is very small, which strongly suggests that parameter $R$ as a function of only pressure will give sufficient description of high-pressure behavior of solid materials within appropriate range of pressure.

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