

## Finite strain High Pressure Equation of State's for Bulk Metallic Glasses

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**Abstract:** The equation of state (EOS) is fundamentally important in studying the high pressure properties of solids, which causes structural transition. The equation of state (EOS) of a solid (pressure–volume relation) plays an important role in condensed matter physics, because the knowledge of the EOS is of central importance for the general understanding of the behaviour and the application of condensed matters and has been a long-standing topic and extensively investigated. Metallic amorphous alloys (i.e. metallic glasses) are comparatively newcomers to the amorphous materials group. Finite-strain theory has been applied extensively to problems in mineral physics. In the present work, pressure of two different bulk metallic glasses viz. Window glass and Water-white glass, has been computed at different compression ranges using three different EOS based on finite strain theory viz. Third order Eulerian EOS, Third order Lagrangian EOS and Third order Birch-Murnaghan EOS. The obtained results are compared with available experimental data to test the validity and success of these equation of states. The obtained result shows that Third order Lagrangian EOS gives better agreement with available experimental data both at high as well as low compressions.

**Key word:** Finite strain theory, Lagrangian Strain, Eulerian Strain, Bulk metallic glass

**Introduction:** The equation of state of compressed solids is fundamentally important in studying the high pressure properties in many fields, such as condensed matter physics and geophysics including applied sciences. A relation between pressure and volume which is capable of predicting P-V behaviour of a substance at constant temperature is known as an isothermal equation of state. Up to now a number of workers have endeavoured to search for a simple form of the equation of state (EOS) of solids which has a small number of parameters and predicts correct high pressure behaviours irrespective of the material. The parameters are determined by using available low pressure data such as the volume  $V_0$ , isothermal bulk modulus  $K_0$  and its pressure derivative  $K_0'$  at zero pressure.

With the development of high pressure techniques, pressure is becoming an important processing variable just like that of temperature or chemical composition for condensed phases. High pressure, which can cause a larger change of atom spacing, chemical bonding and Gibbs free energy, has been found to be a powerful tool for affecting and controlling the nucleation and growth of the metallic glasses [1, 2]. For example, since high pressure can promote local atomic

rearrangement and suppress the long-range atomic diffusion in super cooled liquid state, BMGs can be crystallized under high pressure to very fine-grained nanostructured materials. Contamination and grain growth that often occur during consolidation of nanoparticles could be avoided in the nanostructured material derived from BMG [3].

In the present work, pressure of two different bulk metallic glasses viz. Window glass and Water-white glass, has been computed at different compression ranges using three different EOS based on finite strain theory viz. Third order Eulerian EOS, Third order Lagrangian EOS and Third order Born-Mie EOS. The obtained results are compared with available experimental data to test the validity and success of these equations of states.

**Theory:** The practical expression for Finite strain were developed by Birch [20,21]. The classical theory of infinitesimal elasticity is based on two assumptions:

- (1). The strains are uniquely determined by stresses and are reversible.
- (2). The strains are limited to linear elasticity.

Birch used Murnaghan's basic theory, but restricted it to the case where the initial stress is a large hydrostatic pressure. The crucial assumption in finite strain theory is in the formal

Relationship between compressions and co-ordinate displacement [22], one form is

$$\frac{V}{V_0} = \eta = (1 + 2\varepsilon)^{3/2} \quad (1)$$

where  $\varepsilon$  is strain. The relationship between  $\eta$  and  $\varepsilon$  is not unique. Another alternative is [23]

$$\eta = (1 - 2\varepsilon)^{-3/2} \quad (2)$$

Equation (1) is Lagrangian formulations where as (2) is Eulerian formulation.

### A series in strain ( $\varepsilon$ ) for the energy function

A simple relationship between the compression  $\eta$  and strain variable [23] is given by

$$\varepsilon = f(\eta)$$

Let the symbol  $\varepsilon'$  denote  $d\varepsilon/dv$ ,  $\varepsilon''=d^2\varepsilon/dv^2$  etc. Take the expansion in the potential as a Taylor's series in the equation

$$E(\varepsilon) = K_{T0} V_0 \sum_{P=2}^{\infty} \left( \frac{C_P}{P!} \right) \varepsilon^P \quad (3)$$

where P denotes a power. The condition  $P(1)=P_0=0$  is satisfied by ignoring the term  $P=1$  the factor  $K_{T0}V_0$  has the dimensions of energy so that all coefficients  $C_P$  and  $\epsilon$  are dimensionless.

Further  $E'=P$  where

$$E' = (\partial E/\partial V)_T, \quad E'' = -(K/V) \quad (4)$$

$$E''' = \frac{K}{V^2} \left( \frac{VK'}{K} + 1 \right) \quad (5)$$

The derivatives of equation (3) is

$$E' = K_{T0} V_0 \epsilon \epsilon' C_2 \left\{ 1 + \sum_{P=3} \frac{C_P}{C_2} \left[ \frac{\epsilon^{P-2}}{(P-1)!} \right] \right\} \quad (6)$$

$$E'' = K_{T0} V_0 C_2 \left[ (\epsilon' \epsilon' + \epsilon \epsilon'') + \sum_{P=3} \frac{C_P}{C_2} \left\{ \left[ \frac{\epsilon' \epsilon'}{(P-2)!} + \frac{\epsilon \epsilon''}{(P-1)!} \right] \right\} \epsilon^{(P-2)} \right] \quad (7)$$

$$E''' = K_{T0} V_0 C_2 \left[ 3\epsilon' \epsilon'' + \sum_{P=3} \frac{C_P}{C_2} \left\{ \left[ \frac{\epsilon' \epsilon' \epsilon'}{(P-3)!} + \frac{3\epsilon \epsilon' \epsilon''}{(P-2)!} + \frac{\epsilon''' \epsilon^2}{(P-1)!} \right] \right\} \epsilon^{(P-3)} \right] \quad (8)$$

For  $P=0$ ,  $\epsilon=\epsilon_0=0$

since  $E'' = K_T/V$

Then  $E_0'' = (K_{T0}/V_0) \quad (9)$

Another expression for  $E_0''$  is found from equation (7) for  $n=2$  and  $\epsilon_0=0$  the terms behind the summation sign in equation (7) vanishes &  $E_0''$  becomes

$$E_0'' = K_{T0} C_2 V_0 (\epsilon_0')^2 \quad (10)$$

From equation (9) and equation (10)

$$C_2 = \frac{1}{(V_0 \epsilon_0')^2} \quad (11)$$

Similarly  $E_0''' = -\frac{K_T}{V^2} (1 - K_0')$

where 
$$\mathbf{K}'_0 = \left( \frac{\partial \mathbf{K}_T}{\partial \mathbf{P}} \right)_T \text{ at } \mathbf{P} = 0$$

For  $n=3$  &  $\epsilon_0=0$ , the  $\epsilon\epsilon''\epsilon^2$  term in equation (8) vanishes and all but the  $(\epsilon')^3$  term behind the summation sign in equation (8) vanish leaving

$$E''' = K_{T0} V_0 C_2 \left[ 3\epsilon_0' \epsilon_0'' + \frac{1}{2} C_3 (\epsilon_0')^3 \right] \quad (12)$$

Equating equation (25) and equation (26),  $C_3$  becomes

$$C_3 = - \left[ \left\{ \frac{(1 - K'_0)}{(\epsilon' V_0)^3} \right\} + \frac{3C_2 \epsilon_0'''}{(\epsilon_0')^2} \right] \quad (13)$$

The pressure equation to third order is

$$\begin{aligned} P = E' &= K_{T0} V_0 \epsilon \epsilon' \left( C_2 + \frac{1}{2} C_3 \epsilon \right) \\ &= \frac{K_{T0} V_0 \epsilon \epsilon'}{(\epsilon_0' V_0)^2} \left\{ 1 - \frac{\epsilon}{2} \left( \frac{1 + K'_0}{\epsilon_0' V_0} + \frac{3\epsilon_0''}{(\epsilon_0')^2} \right) \right\} \end{aligned} \quad (14)$$

The energy equation for third order is

$$\begin{aligned} E(\epsilon) &= \frac{1}{2} K_{T0} V_0 E^2 \left( C_2 + \frac{1}{3} C_3 \epsilon \right) \\ &= \frac{1}{2} K_{T0} V_0 \epsilon^2 \left\{ \frac{1}{(\epsilon_0' V_0)^2} - \frac{\epsilon}{3} \left[ \frac{1 - K'_0}{\epsilon_0' V_0^3} + \frac{3}{(\epsilon_0' V_0)^3} \frac{\epsilon_0'''}{(\epsilon_0')^2} \right] \right\} \\ &= \frac{1}{2} \frac{K_{T0} V_0 \epsilon^2}{(\epsilon' V_0)^2} \left\{ 1 - \frac{\epsilon}{3} \left[ \frac{1 + K'_0}{\epsilon_0' V_0} + \frac{3\epsilon_0''}{(\epsilon_0')^2} \right] \right\} \end{aligned} \quad (15)$$

***Equation of state based on Eulerian Strain***

The Eulerian strain for  $\epsilon(\eta)$

$$\epsilon(\eta) = \frac{1}{2}(1 - \eta^{-2/3}) = \left(\frac{1}{2}\right) \left[ 1 - \left(\frac{V_0}{V}\right)^{2/3} \right] \quad (16)$$

we have

$$\epsilon' = \frac{1}{3V_0} \eta^{-5/3} \quad \epsilon'_0 = \frac{1}{3V_0} \quad (17a)$$

$$\epsilon'' = -\frac{5}{9V_0^2} \eta^{-8/3} \quad \epsilon''_0 = -\frac{5}{9V_0^2} \quad (17b)$$

$$\frac{\epsilon'}{\epsilon'_0} = \eta^{-5/3} \quad \frac{\epsilon''_0}{(\epsilon'_0)^2} = -5 \quad (17c)$$

where  $\epsilon' = (\partial\epsilon/\partial V)$  and  $\epsilon'' = (\partial\epsilon'/\partial V)$

Now from equations (13), (17a), (17b) and (17c) the third order coefficient can be written as

$$C_3 = -27(K'_0 - 4)$$

Thus, from equation (15) the third order in Eulerian strain Energy (at T=0)

$$E(\epsilon) = U - E_{ST} = \frac{9}{2} K_{T0} V_0 \epsilon^2 \left[ 1 - \frac{3}{2} (K'_0 - 4) \epsilon \right] \quad (18)$$

and the EOS is

$$P(\varepsilon,0) = -3K_{T0}(1-2\varepsilon)^{-5/2} \varepsilon \left[ 1 - \frac{3}{2}(K'_0 - 4)\varepsilon \right] \quad (19)$$

### *Equation of state based on Lagrangian Strain*

The Lagrangian strain is given by

$$\varepsilon = \frac{1}{2}(\eta^{2/3} - 1) = \frac{1}{2} \left[ \left( \frac{V}{V_0} \right)^{2/3} - 1 \right]$$

$$\varepsilon' = \frac{1}{3V_0} \eta^{-1/3}$$

$$\varepsilon'_0 = \frac{1}{3V_0}$$

$$\varepsilon'' = -\frac{1}{9V_0^2} \eta^{-4/3}$$

$$\varepsilon''_0 = -\frac{1}{9V_0^2}$$

$$\frac{\varepsilon'}{\varepsilon'_0} = \eta^{-1/3}$$

$$\frac{\varepsilon''}{(\varepsilon'_0)^2} = -1$$

Now from equation (28) the pressure equation for third order is

$$P = K_{T0} V_0 \varepsilon \varepsilon' \left( C_2 + \frac{1}{2} C_3 \varepsilon \right)$$

where

$$C_2 = \frac{1}{(V_0 \varepsilon_0)^2} = 9$$

and

$$C_3 = - \left[ \frac{1}{(V_0 \varepsilon_0')^3} (1 - K_0') + \frac{\varepsilon_0'' 3C_2}{(\varepsilon_0')^2} \right] = -27K_0'$$

using above, the EOS in third order

$$P(\varepsilon, 0) = -9K_{T0} V_0 \varepsilon \varepsilon' (1 - 3K_0' \varepsilon) \quad (20)$$

In terms of compression  $\eta$  it is [24]

$$P(\eta, 0) = -\frac{3}{2} K_{T0} \left( \eta^{1/3} - \eta^{-1/3} \right) \left[ 1 - \frac{3}{4} K_0' \left( \eta^{2/3} - 1 \right) \right] \quad (21)$$

### ***Birch - Murnaghan Isothermal Equation of state***

Birch original derivations were based on Murnaghan's theory of finite elasticity. The EOS presented by Birch in terms of parameter  $\varepsilon$  is

$$\varepsilon = \frac{3}{4} (4 - K_0')$$

In terms of the compression  $\eta$  and the experimentally determined  $K_{T0}$  and  $K_0'$  the isothermal B-M EOS to second order is

$$P(\eta, 0) = \frac{3}{2} K_{T0} \left( \eta^{-7/3} - \eta^{-5/3} \right) \quad (22)$$

Isothermal B-M equation of state to the third order is

$$P(\eta, 0) = (-3/2) K_{T0} (\eta^{-5/3} - \eta^{-7/3}) [1 - (3/4)(K_0' - 4)(1 - \eta^{-2/3})] \quad (23)$$

### **Results and Discussion**

The variation of pressure with unit cell volume of two different BMG's viz Window glass and Water-white have been computed by using third order Eulerian EOS, third order Lagrangian EOS and third order B-M EOS and compared with their experimental values [13]. The values of

isothermal bulk modulus ( $K_0$ ) and its first pressure derivative ( $K_0'$ ) at zero pressure are used as input parameter for these BMG's , displayed in table (1) obtained from literature [14]. The values of pressure computed by using equations (19), (21) and (23) at different compressions with their experimental values are listed in tables (2-3). It is evident from the table (2-3) that the third order Lagrangian and third order Birch-Murnaghan EOS give the best agreement with experimental values for window glass where only Third order Lagrangian EOS gives better agreement with experimental values. The Eulerian EOS fails hopelessly in the case for calculating pressure at extreme compressions. The order of superiority can be arranged as follows on the basis of EOS used in present study for the calculation of pressure at different compressions for Bulk metallic glasses.

Third order Lagrangian EOS > Third order Birch-Murnaghan EOS > Third order Eulerian EOS



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**Table-1**

**The input values of isothermal bulk modulus ( $K_0$ ) & its first pressure derivative ( $K'_0$ ) at zero pressure**

S.No.	Sample	$K_0$ (GPa)	$K'_0$ (GPa)
7.	Window glass	38.70	2.88
8.	Water-white glass	45.70	1.78

**Table- 2**

**Calculated values of pressure (P) in GPa as a function of  $V/V_0$  at different compressions using different equation of state from equations (19, 21, 23) for bulk metallic glass "Window glass"**

$V/V_0$	P (Gpa) Third order Eulerian EOS (19)	P (GPa) Third order Lagrangian EOS (21)	P (GPa) Third order Birch- Murnaghan EOS (23)	Experimental [3]
1.00	0.00	0.00	0.00	0.00
0.90	3.33	4.68	4.73	4.74
0.80	5.55	11.22	11.69	11.86
0.70	6.66	20.16	21.87	22.80
0.60	6.63	32.25	36.37	40.15
0.50	5.44	48.70	54.84	68.95
0.40	3.11	71.57	65.89	120.21

**Table – 3**

**Calculated values of pressure (P) in GPa as a function of  $V/V_0$  at different compressions using different equation of state from equations (19, 21, 23) for bulk metallic glass "Water-white glass"**

<b><math>V/V_0</math></b>	<b>P (Gpa) Third order Eulerian EOS (19)</b>	<b>P (GPa) Third order Lagrangian EOS (21)</b>	<b>P (GPa) Third order Birch- Murnaghan EOS (23)</b>	<b>Experimental</b>
1.00	0.00	0.00	0.00	0.00
0.90	3.68	5.25	5.23	5.30
0.80	5.56	12.09	11.69	12.51
0.70	5.62	20.95	18.44	22.68
0.60	3.85	32.50	21.14	37.60
0.50	0.28	47.75	2.81	60.70
0.40	-5.04	68.48	-106.84	99.34