Mineral Physics I
Chapter 4. Equation of State
Section 5. Examination of Birch-Murnaghan equations of state

Significance of Birch-Murnaghan EOS?

- Birch-Murnaghan EOS: the most frequently used
  - Why?
  - Is it more physically meaningful than other EOS's?

- Two assumptions to build BM-EOS's

1. Compression is expressed by a state NOT before BUT after compression as a reference.
2. Discussion starts from change in squared length by compression.

- Examining whether the EOS's built based on these assumptions have a special meaning or not.

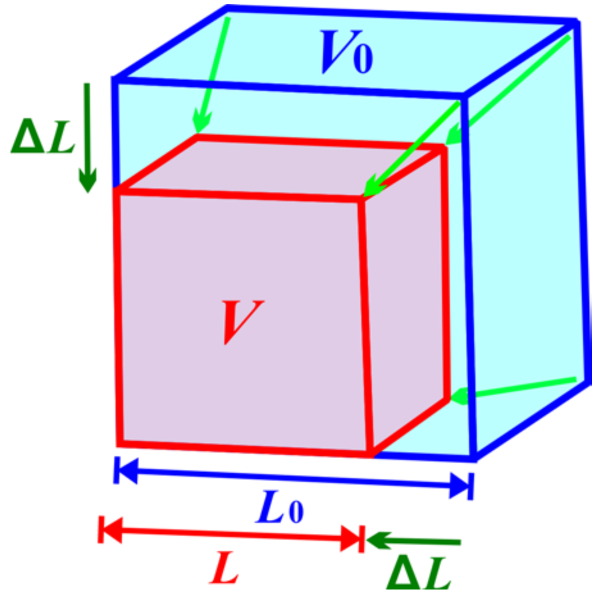
4.5.1 Significance of the Eulerian scheme

Eulerian and Lagrangian schemes

- **Eulerian scheme**:
  - Volume before compression V_0 is described by volume after compression V
    - ✓ Thermodynamic parameters under compression is expressed by V_0/V
    - ✓ $P \rightarrow \infty$ when $V \rightarrow 0$: easy to describe because of $V_0/V \rightarrow \infty$
- **Lagrangian scheme**
  - Volume after compression V is described by volume before compression V_0
    - ✓ Thermodynamic parameters under compression is expressed by V/V_0
- What EOS is obtained under the Lagrange scheme?

Lagrangian finite strain -1

- A cube with edge lengths of L_0 in an unstrained state
  - Volume: $V_0 = L_0^3$ (4.5.1)
- Uniformly compressed to edge lengths of L
  - Volume; $V = L^3$ (4.5.2)
- Displacement ΔL
  - $L = L_0 + \Delta L$ (4.5.3)
- Change in squared edge length
  - $L^2 - {L_0}^2 = (L_0 + \Delta L)^2 - {L_0}^2 = 2L_0\Delta L + \Delta L^2$ (4.5.4)
- The strain should be proportional to the edge length before compression
  - $\Delta L = c_L L_0$ (4.5.5)



Lagrangian finite strain -2

- Eq. (4.5.5) $\Delta L = c_L L_0$ is substituted to Eq. (4.5.4) $L^2 - {L_0}^2 = 2L_0\Delta L + \Delta L^2$
  - $L^2 - {L_0}^2 = 2L_0 c_L L_0 + (c_L L_0)^2 = (2c_L + {c_L}^2)\, {L_0}^2$ (4.5.6)
- Define the Lagrangian finite strain as:
  - $f_L \equiv -\frac{1}{2}c_L^2 - c_L$ (4.5.7)
- Using this definition, Eq. (4.5.6) becomes
  - $L^2 - {L_0}^2 = -2f_L {L_0}^2;\ {L_0}^2 = (1-2f_L){L_0}^2;\ \frac{L^2}{{L_0}^2} = (1-2f_L);\ \frac{L}{L_0} = (1-2f_L)^{\frac{1}{2}}$
  - $\frac{V}{V_0} = \frac{L^3}{L_0^3} = (1-2f_L)^{\frac{3}{2}};\ \left(\frac{V}{V_0}\right)^{\frac{2}{3}} = 1 - 2f_L$
  - $f_L = \frac{1}{2}\left[1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right]$ (4.5.8)
- Lagrangian finite strain expressed by volume compression

2nd-order Lagrangian EOS -1

- P is V derivative of F at constant P
  - $P = -\left(\frac{\partial F}{\partial V}\right)_T$ (4.1.1)
- F is assumed to increase proportionally to the squared f_L with V decrease
  - $\Delta F \cong a{f_L}^2$ (4.5.9)
    - ✓ a: constant
- V derivative of F is expressed by
  - $\left(\frac{\partial F}{\partial V}\right)_T = \left\{\frac{\partial(a{f_L}^2)}{\partial V}\right\}_T = 2af_L\left(\frac{\partial f_L}{\partial V}\right)_T$
  - $P = -2af_L\left(\frac{\partial f_L}{\partial V}\right)_T$ (4.5.10)

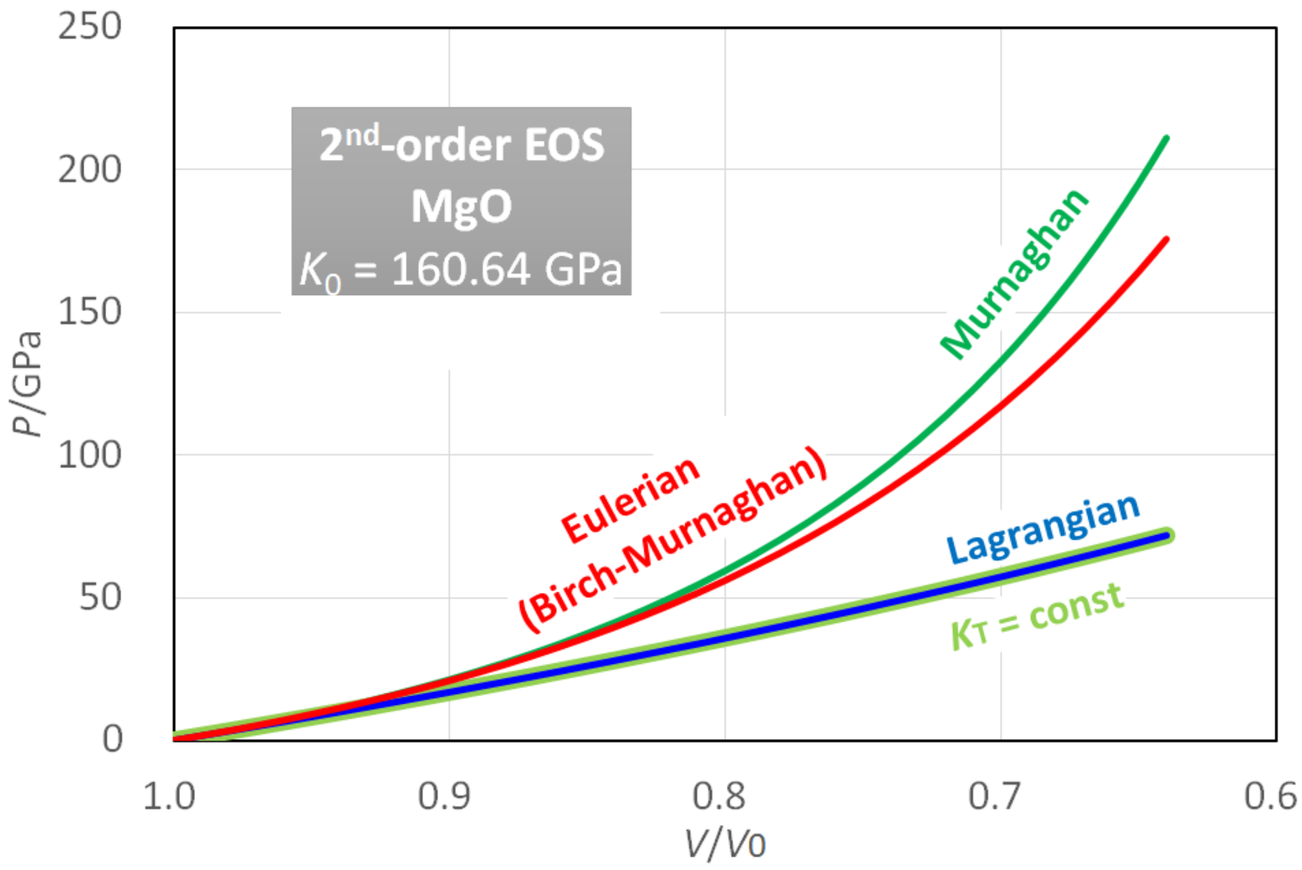
2^{nd}-order Lagrangian EOS -2

- The V derivative of f is:
  - $f_L = \frac{1}{2}\left[1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right] \rightarrow \left(\frac{\partial f_L}{\partial V}\right)_T = \left(-\frac{1}{3V_0}\right)\left(\frac{V}{V_0}\right)^{-1/3}$ (4.5.13)
- The 2^{nd}-order Lagrangian EOS is:
  - $P = -2af_L\left(\frac{\partial f_L}{\partial V}\right)_T$ (4.5.10)

    $P = -2\frac{9}{2}K_{T0}V_0 \times \left\{\frac{1}{2}\left[1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right]\right\}\left\{\left(-\frac{1}{3V_0}\right)\left(\frac{V}{V_0}\right)^{-\frac{1}{3}}\right\} \leftarrow a = \frac{9}{2}K_{T0}V_0$
  - $P = \frac{3}{2}K_{T0}\left[\left(\frac{V}{V_0}\right)^{-\frac{1}{3}} - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right] = \frac{3}{2}K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{1}{3}} - \left(\frac{V_0}{V}\right)^{-\frac{1}{3}}\right]$ (4.5.14)

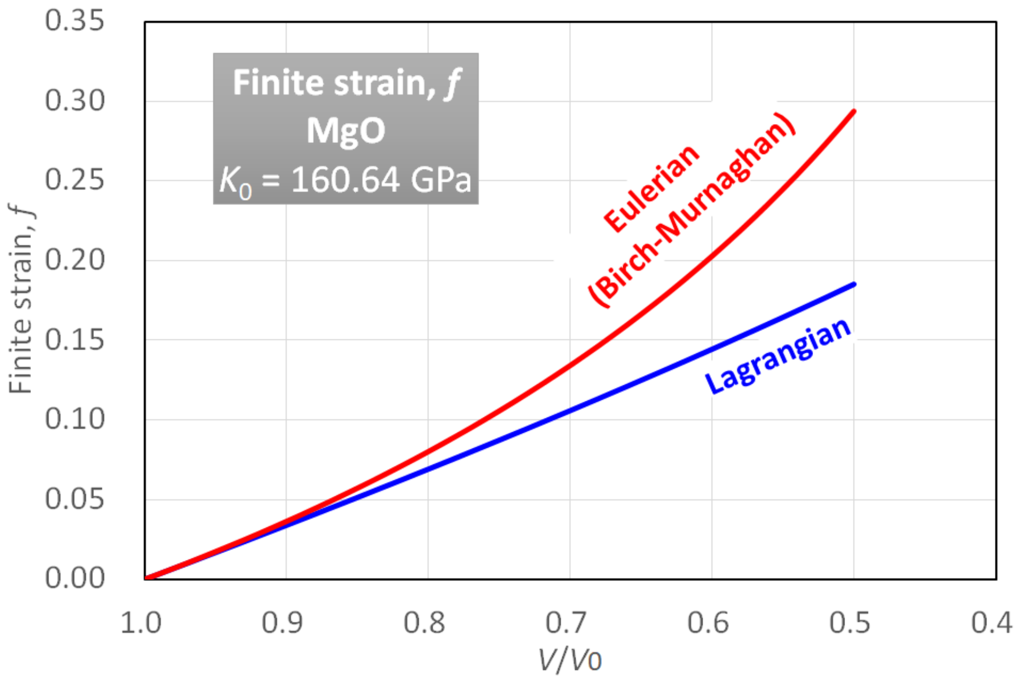
    ✓ 2^{nd}-order BM EOS: $P = \frac{3}{2}K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right] = \frac{3}{2}K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{1}{3}+2} - \left(\frac{V_0}{V}\right)^{-\frac{1}{3}+2}\right]$ (4.2.13)

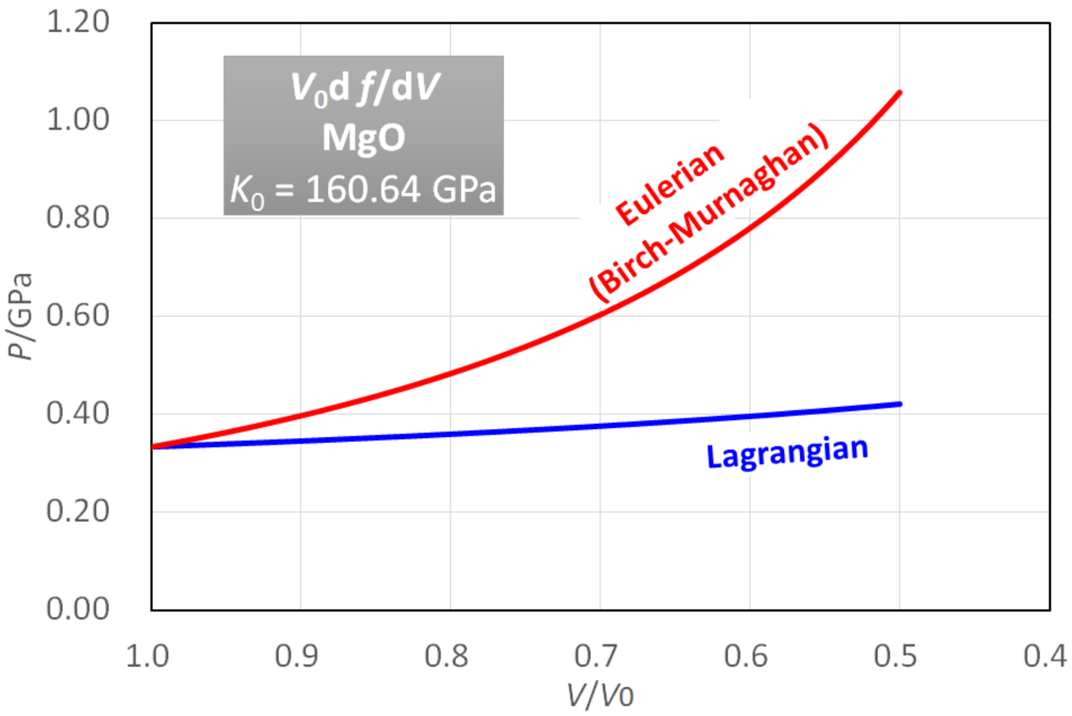
Comparison of 2nd-order EOS's



- ❑ Much less pressure increases in the Lagrangian scheme than the Eulerian scheme
  - ➢ Almost the same as the $K_T = \mathrm{const}$. integration

Comparison of finite strains and its volume derivatives between two schemes



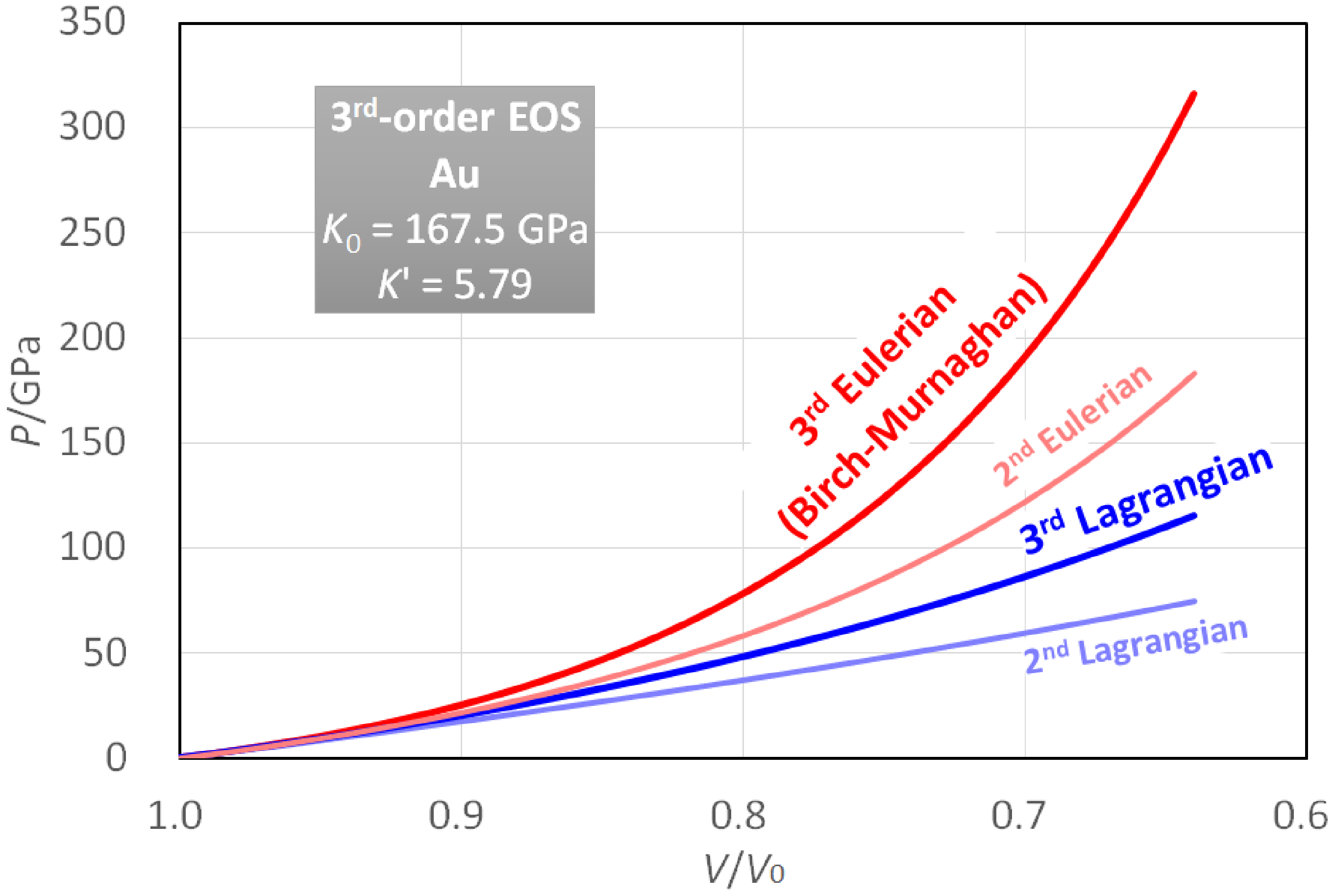


- Both f and $V_0(\mathrm{d}f/\mathrm{d}V)$ much less increase with compression in the Lagrangian scheme than the Eulerian scheme
  - Eulerian: $f_{\mathrm{E}} = \frac{1}{2}\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]$, Lagrangian: $f_L = \frac{1}{2}\left[1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right]$

3rd-order Lagrangian EOS

- 3rd-order Lagrangian EOS
  - $P = \frac{3}{2}K_{T_0}\left[\left(\frac{V}{V_0}\right)^{-\frac{1}{3}} - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\left[1 + \frac{3}{4}K'_{T_0}\left\{1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right\}\right]$ (4.5.15)
  - The 3rd-order Lagrangian EOS becomes identical to the 2nd-order EOS when $K'_{T_0} = 0$
    - ✓ Matters do not become incompressive with compression if the 2nd-order is adopted → identical to (4.1.8) $P = K_{T0}\ln\left(\frac{V_0}{V}\right)$ from $\mathrm{d}P = -K_T\frac{\mathrm{d}V}{V}$
    - ✓ 3rd-order Eulerian (Birch-Marnaghan) EOS
      - $P = \frac{3}{2}K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left[1 + \frac{3}{4}\left(K'_{T_0} - 4\right)\left\{\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right\}\right]$

Comparison of 3rd-order EOS's

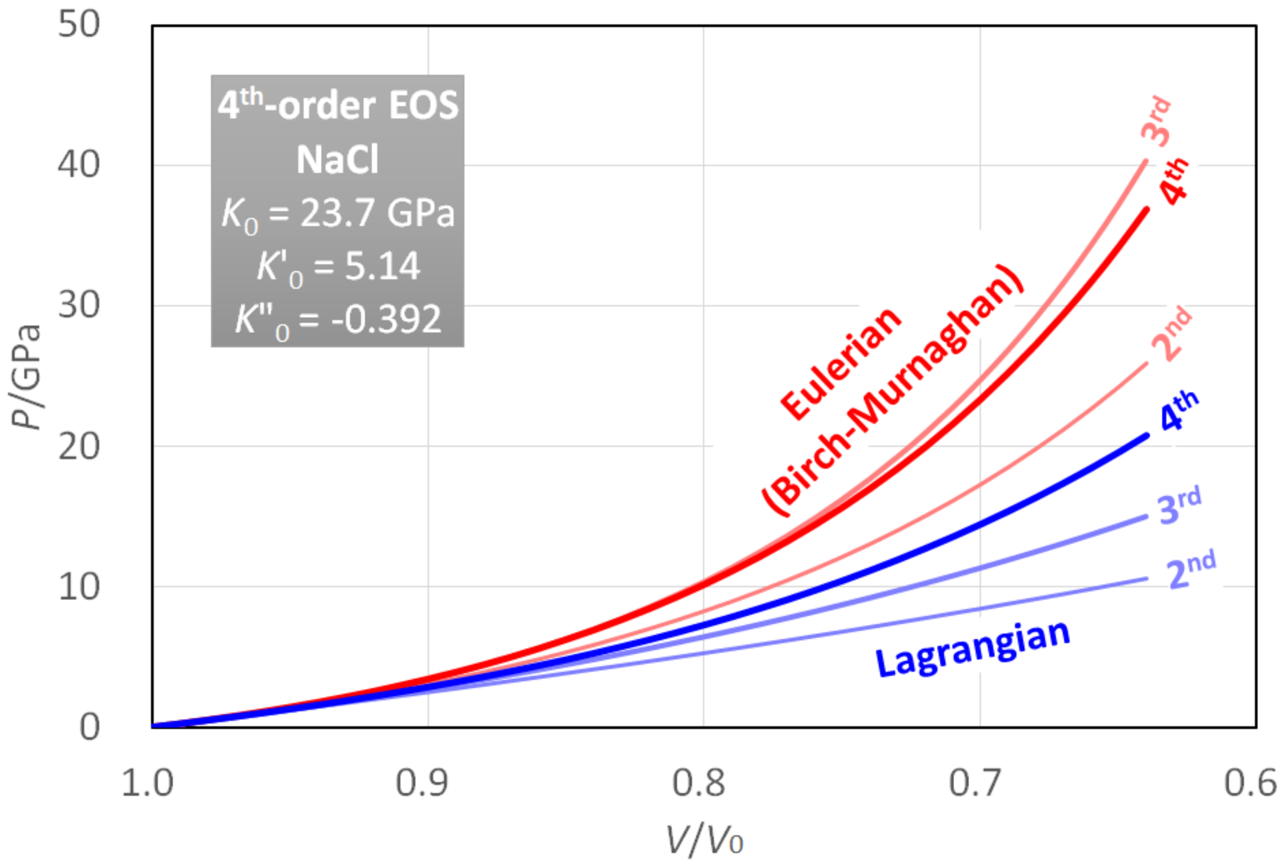


- ❑ Increase of order does not make the difference between the Eulerian and Lagrangian EOS's smaller.
- ❑ The Eulerian and Lagrangian schemes give similar pressures at low compression
  - ➢ $V/V_0 > 0.9$

Higher orders Lagrangian EOS

- 4rd-order Lagrangian EOS
  - $P = \frac{3}{2}K_{T_0}\left[\left(\frac{V}{V_0}\right)^{-\frac{1}{3}} - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]$
  - $\times\left[1 + \frac{3}{4}K'_{T_0}\left\{1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right\} + \frac{9{K'_{T_0}}^2 + 9K'_{T_0} + 9K_{T_0}K''_{T_0} - 1}{24}\left\{1 - \left(\frac{V}{V_0}\right)^{\frac{2}{3}}\right\}^2\right]$ (4.5.16)
    - ✓ 4rd-order Eulerian (Birch-Murnaghan) EOS
      - $P = \frac{3}{2}K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]$
        $\times\left[1 + \frac{3}{4}\left(K'_{T_0} - 4\right)\left\{\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right\} + \frac{9{K'_{T_0}}^2 - 63K'_{T_0} + 9K_{T_0}K''_{T_0} + 143}{24}\left\{\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right\}^2\right]$

Comparison of 4^{th}-order EOS's



- Slightly more agreement between the Eulerian and Lagrangian schemes
  - These EOS may agree at an extremely high order
  - The convergence rate: very slow
    - ✓ Obtaining high order V derivative of K_T is impractical
  - Difference between 3^{rd} and 4^{th} order: larger in Lagrangian than Eulerian
    - ✓ The Eulerian may be a practically better scheme

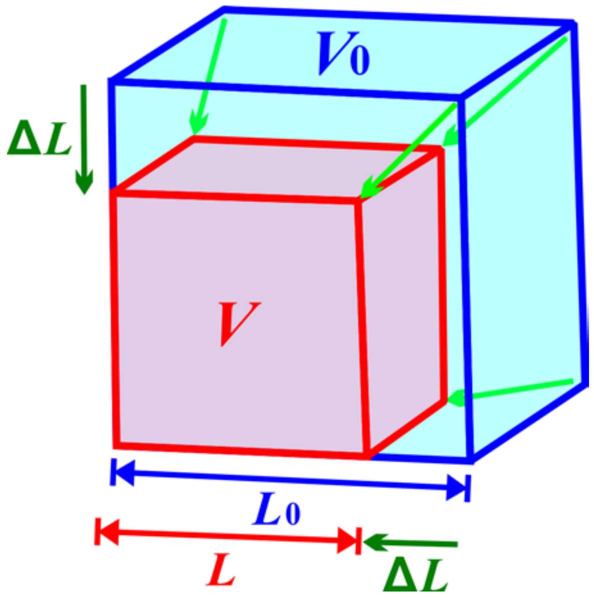
4.5.2 Why expansion of squared length?

Expansion of squared length?

- ❑ Eulerian finite strain: argument starts from change in squared length of the body.
  - ➢ I have no idea why expansion of squared length is essential.
- ❑ Let us see what EOS is obtained if we start from change in
  - ✓ Volume
    - Cubed length
    - This would be a more natural scheme?
  - ✓ Length
    - Linear
    - This would be a more simple scheme?

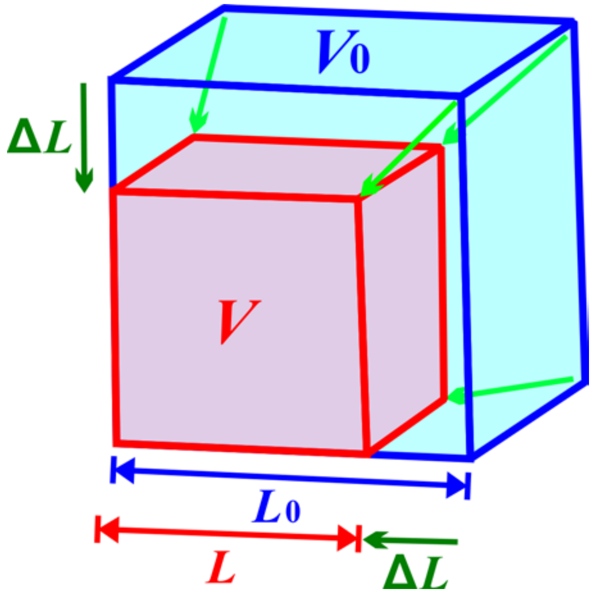
Eulerian EOS from cubed length -1

- The difference in cubed length is:
  - $L_0^3 - L^3 = (L - \Delta L)^3 - L^3 = -3L^2\Delta L + 3L\Delta L^2 - \Delta L^3$ (4.4.17)
- As is in the usual Eulerian finite strain,
  - $\Delta L = c_{\mathrm{E}} L$ (4.2.5)
- By substituting (4.2-5) into (4-12)
  - $L_0^3 - L^3 = (-3c_{\mathrm{E}} + 3{c_{\mathrm{E}}}^2 - {c_{\mathrm{E}}}^3)L^3$ (4.4.18)
- We define a new finite strain
  - $f_{\mathrm{E3}} = -c_{\mathrm{E}} + {c_{\mathrm{E}}}^2 - \frac{1}{3}{c_{\mathrm{E}}}^3$ (4.4.19)



Eulerian EOS from cubed length -2

- According to the Eulerian scheme, we have
  - $L_0^3 - L^3 = 3f_{E3}L^3$ (4.5.20)
  - $\frac{V_0}{V} = \frac{L_0^3}{L^3} = (3f_{E3} - 1)$ (4.5.21)
  - $f_{E3} = \frac{1}{3}\left\{\left(\frac{V_0}{V}\right) - 1\right\}$ (4.5.22)
- The V derivative of f_{E3} is:
  - $\left(\frac{\partial f_{E3}}{\partial V}\right)_T = \frac{\partial}{\partial V}\left[\frac{1}{3}\left\{\left(\frac{V_0}{V}\right) - 1\right\}\right] = -\frac{1}{3V_0}\left(\frac{V_0}{V}\right)^2$ (4.5.23)

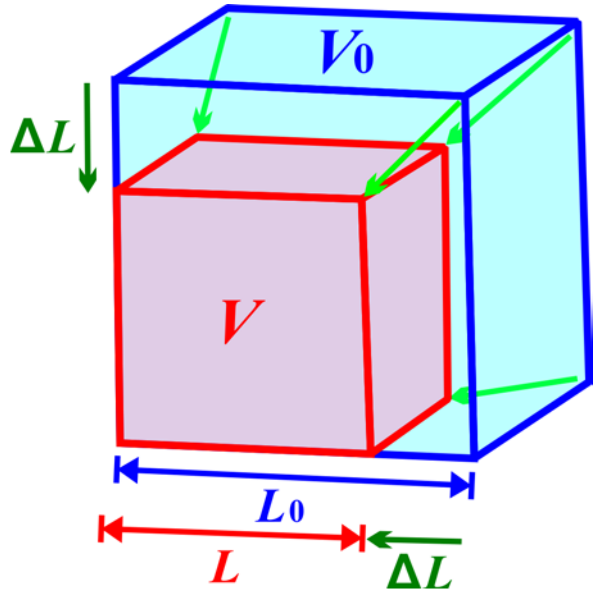


Eulerian EOS from cubed length -3

- As is before, assuming that the increase in F is proportional to f_{E3} squared.
  - $\Delta F \cong a{f_{\mathrm{E3}}}^2$ (4.2.9')
- In this scheme, P is:
  - $P = -\left(\frac{\partial F}{\partial V}\right)_T = -2af_{\mathrm{E3}}\left(\frac{\partial f_{\mathrm{E3}}}{\partial V}\right)_T$ (4.5.10')
- By substituting (4.5.22) and (4.5.23) into (4.5.10'), we have the 2nd-order Eulerian EOS from cubed length.
  - $P = K_{T0}\left[\left(\frac{V_0}{V}\right)^3 - \left(\frac{V_0}{V}\right)^2\right]$ (4.5.24)
- Similarly, the 3rd–order EOS is:
  - $P = K_{T_0}\left[\left(\frac{V_0}{V}\right)^3 - \left(\frac{V_0}{V}\right)^2\right]\left[1 + \frac{1}{2}\left(K'_{T_0} - 5\right)\left\{\frac{V_0}{V} - 1\right\}\right]$ (4.5.25)

Eulerian EOS from (linear) length -1

- The difference in (linear) length is:
  - $L_0 = L - u$ (4.5.26)
- As is in the Eulerian finite strain,
  - $\Delta L = c_{\mathrm{E1}} L$ (4.2.5)
- By substituting (4.2.5) into (4.4.12)
  - $L_0 - L = -c_{\mathrm{E1}} L$ (4.5.27)
- We define a new finite strain
  - $f_{\mathrm{E1}} = -c_{\mathrm{E1}}$ (4.5.28)



Eulerian EOS from (linear) length -2

- According to the Eulerian scheme, we have
  - $L_0 - X = f_{E1}X$ (4.5.29)
  - $\frac{V_0}{V} = \frac{{L_0}^3}{L^3} = (1 + f_{E1})^3$ (4.5.30)
- The new finite strain is therefore:
  - $f_{E1} = \left[\left(\frac{V_0}{V}\right)^{\frac{1}{3}} - 1\right]$ (4.5.31)
- The V derivative of f_{E1} is:
  - $\left(\frac{\partial f_{E1}}{\partial V}\right)_T = \frac{\partial}{\partial V}\left[\left(\frac{V_0}{V}\right)^{\frac{1}{3}} - 1\right] = -\frac{1}{3V_0}\left(\frac{V_0}{V}\right)^{\frac{4}{3}}$ (4.5.32)

Eulerian EOS from (linear) length -3

- As is before, assuming that the increase in F is proportional to f squared.
  - $\Delta F \cong a f_{\mathrm{E1}}{}^{2}$ (4.2.9”)
- In this scheme, P is:
  - $P = -\left(\frac{\partial F}{\partial V}\right)_T = -2a f_{\mathrm{E1}} \left(\frac{\partial f_{\mathrm{E1}}}{\partial V}\right)_T$ (4.2.10”)
- By substituting (4.25) and (4.26) into (2.10), we have the 2nd-order EOS based on the linear length.
  - $P = 3K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{5}{3}} - \left(\frac{V_0}{V}\right)^{\frac{4}{3}}\right]$ (4.5.33)
- Similarly, the 3rd–order EOS is:
  - $P = 3K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{5}{3}} - \left(\frac{V_0}{V}\right)^{\frac{4}{3}}\right]\left[1 + \frac{3}{2}\left(K'_{T_0} - 3\right)\left\{\left(\frac{V_0}{V}\right)^{\frac{1}{3}} - 1\right\}\right]$ (4.5.34)

Comparison of the Eulerian EOS's -1

	Linear	Squared	Cubed
f	$\frac{1}{1}\left[\left(\frac{V_0}{V}\right)^{\frac{1}{3}}-1\right]$	$\frac{1}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]$	$\frac{1}{3}\left[\left(\frac{V_0}{V}\right)^{\frac{3}{3}}-1\right]$
$\left(\frac{\partial f}{\partial V}\right)_T$	$-\frac{1}{3V_0}\left(\frac{V_0}{V}\right)^{\frac{4}{3}}$	$-\frac{1}{3V_0}\left(\frac{V_0}{V}\right)^{\frac{5}{3}}$	$-\frac{1}{3V_0}\left(\frac{V_0}{V}\right)^{\frac{6}{3}}$
2nd-order EOS	$3K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{5}{3}}-\left(\frac{V_0}{V}\right)^{\frac{4}{3}}\right]$	$3K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}}-\left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]$	$3K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{9}{3}}-\left(\frac{V_0}{V}\right)^{\frac{6}{3}}\right]$
3rd-order EOS	$\frac{3}{1}K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{5}{3}}-\left(\frac{V_0}{V}\right)^{\frac{4}{3}}\right]\times\left[1+\frac{3}{2\cdot 1}(K'_{T_0}-3)\left\{\left(\frac{V_0}{V}\right)^{\frac{1}{3}}-1\right\}\right]$	$\frac{3}{2}K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}}-\left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\times\left[1+\frac{3}{2\cdot 2}(K'_{T_0}-4)\left\{\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right\}\right]$	$\frac{3}{3}K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{9}{3}}-\left(\frac{V_0}{V}\right)^{\frac{6}{3}}\right]\times\left[1+\frac{3}{2\cdot 3}(K'_{T_0}-5)\left\{\left(\frac{V_0}{V}\right)^{\frac{6}{3}}-1\right\}\right]$

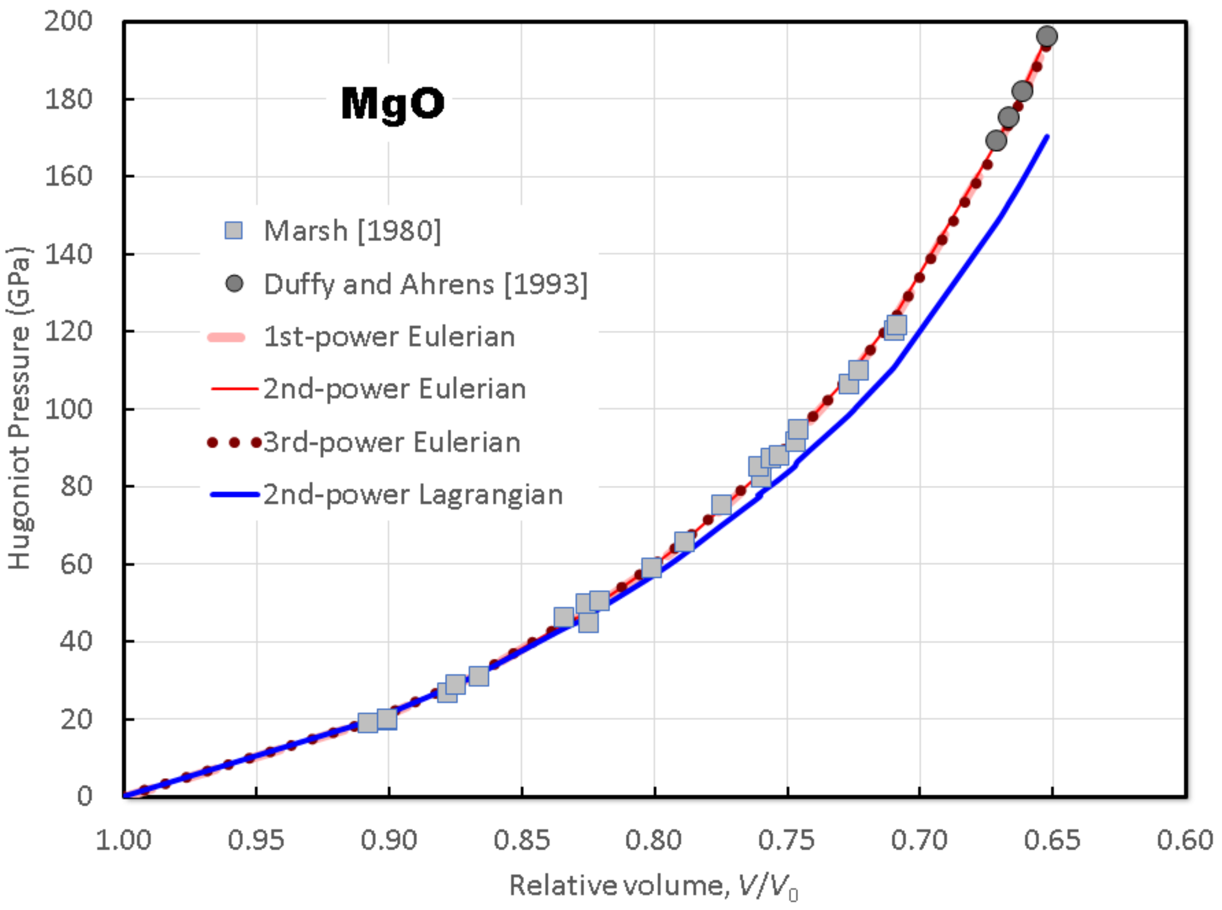
1. The finite strains are proportional to the $n/3$ power of the V ratio.
2. The coefficients to the finite strains are $1/n$.

Comparison of the Eulerian EOS's -2

	Linear	Squared	Cubed
2nd-order EOS	$3K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{5}{3}} - \left(\frac{V_0}{V}\right)^{\frac{4}{3}}\right]$	$3K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]$	$3K_{T0}\left[\left(\frac{V_0}{V}\right)^{\frac{9}{3}} - \left(\frac{V_0}{V}\right)^{\frac{6}{3}}\right]$
3rd-order EOS	$\frac{3}{1}K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{5}{3}} - \left(\frac{V_0}{V}\right)^{\frac{4}{3}}\right]\times \left[1+\frac{3}{2\cdot 1}(K'_{T_0}-3)\left\{\left(\frac{V_0}{V}\right)^{\frac{1}{3}}-1\right\}\right]$	$\frac{3}{2}K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\times \left[1+\frac{3}{2\cdot 2}(K'_{T_0}-4)\left\{\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right\}\right]$	$\frac{3}{3}K_{T_0}\left[\left(\frac{V_0}{V}\right)^{\frac{9}{3}} - \left(\frac{V_0}{V}\right)^{\frac{6}{3}}\right]\times \left[1+\frac{3}{2\cdot 3}(K'_{T_0}-5)\left\{\left(\frac{V_0}{V}\right)^{\frac{6}{3}}-1\right\}\right]$

- The 3rd-order EOS's become identical to the 2nd order EOS's when $K'_{T_0} = 3, 4, \text{and } 5$, respectively, for the linear, squared and cubed cases.
  - Birch-Murnaghan EOS was justified because many materials were considered to have $K'_{T_0} = 4$
  - The cubed case is more appropriate for materials with $K'_{T_0} \approx 5$ like Au?

Comparison among EOSs from different powers

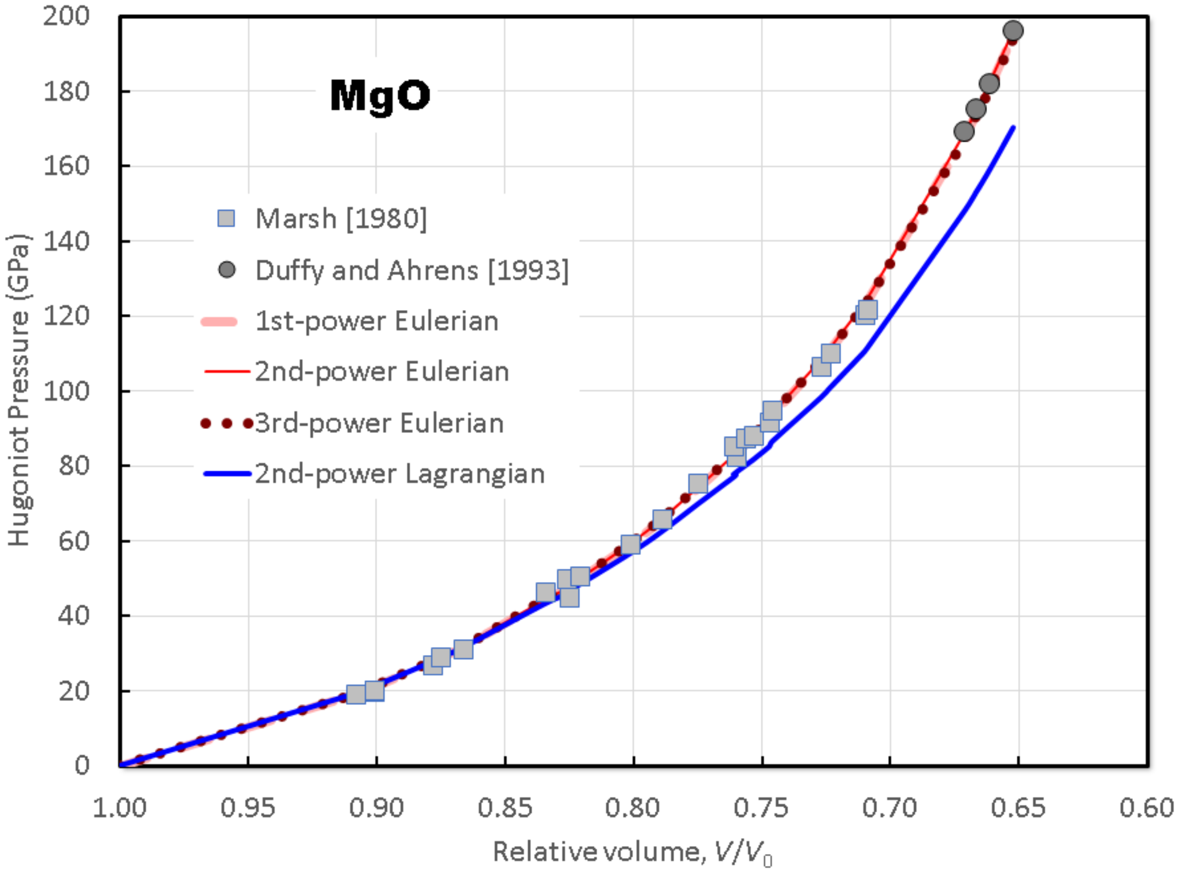


Parameter	2nd-Power (BM)	1st-Power	3rd-Power
V_0 (Å³)	74.698*	74.698*	74.698*
K_{T0} (GPa)	160.64	160.64	160.63
K_{T0}'	4.221	4.293	4.347
θ_0 (K)	761*	761*	761*
γ_0	1.431	1.436	1.440
a	0.29	0.20	0.14
b	3.5	4.4	5.5

* Fixed

- No difference among different powers of Eulerian EOS
- Expansion of squared length to obtain BM EOS has no physical meaning

Comparison among EOSs from different powers



Parameter	2nd-Power Eulerian (BM)	2nd-Power Lagrangian	1st-Power Eulerian	3rd-Power Eulerian
V_0 (Å³)	74.698*	74.698*	74.698*	74.698*
K_{T0} (GPa)	160.64	160.55	160.64	160.63
K_{T0}'	4.221	4.909	4.293	4.347
θ_0 (K)	761*	761*	761*	761*
γ_0	1.431	1.496	1.436	1.440
a	0.29	0 (fixed)	0.20	0.14
b	3.5		4.4	5.5

* Fixed

- The Lagrangian scheme cannot reproduce shock compression data

Conclusion

- ❑ The Eulerian scheme is better than the Larangian scheme to build equations of state to reproduce experimental data with fewer and lower-orders of bulk moduli.
- ❑ The expansion of squared length to define the Eulerian finite strain does not have special physical meaning.

Mineral Physics I

Chapter 4. Equation of state

Section 4. Examination of Birch-Murnaghan equations of state

End