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Thermodynamics Starting Point

1st Law: $dU = \delta q - \delta w$

Combined Statement of 1st + 2nd Laws:

$$dU = T\,dS - \sum_{j=1}^{J} Y_j\, dX_j$$

Work terms

$$\sum_{j=1}^{J} Y_j\, dX_j$$

X_j, Y_j conjugate variables (energy)

Doing Thermo = integrating $dU = T\,dS - Y_j\, dX_j$

Need:

$T(S, X_1, X_2 \ldots X_j)$

$Y_1(S, X_1, X_2 \ldots X_j)$

$Y_2(S, X_1, X_2 \ldots X_j)$

$\vdots$

$Y_j(S, X_1, X_2 \ldots X_j)$

Practical Approach : Taylor's expansion.

$$Y_j = Y_{j0} + \sum_{k=1}^{n} \frac{1}{k!}\left(\sum_{i=0}^{I} \delta X_i \frac{\partial Y_j}{\partial X_i}\right)^k$$

$\uparrow$ reference state

$\uparrow$
$n = 1$ linear
$n = 2$ harmonic approx
$n = 3$ "anharmonic terms"

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Mechanical Equations of State

$$dU = \bar{\bar{\sigma}}_{ij}\, d\bar{\bar{\varepsilon}}_{kl}$$

$$\bar{\bar{\sigma}}_{ij} = \bar{\bar{\sigma}}^{\circ}_{ij} + \delta\bar{\bar{\varepsilon}}_{kl}\frac{\partial\bar{\bar{\sigma}}_{ij}}{\partial\bar{\bar{\varepsilon}}_{kl}} + \frac{1}{2}\delta\bar{\bar{\varepsilon}}_{kl}^{2}\frac{\partial^2\bar{\bar{\sigma}}_{ij}}{\partial\bar{\bar{\varepsilon}}_{kl}^{2}}$$

Linear approximation: Hooke's law

$$\underbrace{\sigma_{ij}}_{\text{6 component stress tensor}} = \underbrace{C_{ijkl}}_{\text{36 component constitutive tensor}}\ \underbrace{\varepsilon_{kl}}_{\text{6 component strain tensor}}$$

For a material in equilibrium: C_{ijkl} symmetric : 21 components

	SYMMETRY	# Independent C_{ijkl}'s	
crust rocks (	triclinic	21	
	monoclinic	13	
Mantle Pv.	orthorhombic	9	
	tetragonal	7	
	hexagonal	5	"A, C, F, L, N"
Transition Zone Materials	* cubic	3	C_{11}, C_{12}, C_{44}
	isotropic	2	$C_{11} - C_{12} = 2C_{44}$

* cubic does not necessarily mean elastically isotropic * (e.g. Pt ~ 15-20% A_U)

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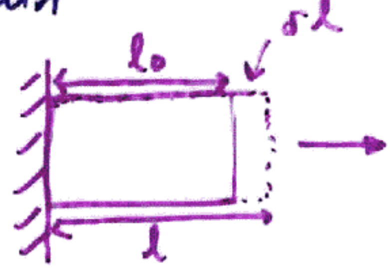
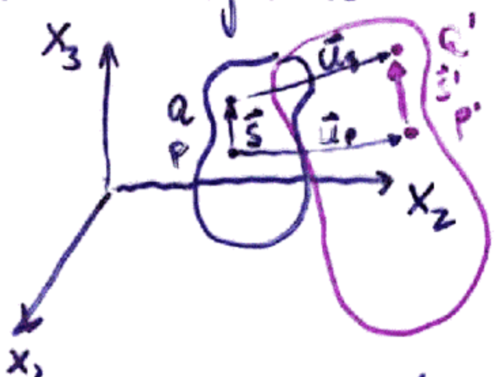
Definition of Strain

1. Linear (infinitesimal)

$$\varepsilon = \frac{l - l_0}{l_0} = \frac{\delta l}{l_0}$$



2. More general (Finite)



Object: find $\delta \bar{s} = \bar{s}' - \bar{s}$

<u>Undeformed</u>

$P(x_i)$

$Q(x_i + d\vec{s}_i)$

<u>Deformed</u>

$P'(x_i + d\vec{u}_P)$

$Q'(x_i + d\vec{s} + d\vec{u}_P + d\vec{s}')$

Need to choose a coordinate System for Bookkeeping.

Lagrangian: unstrained reference frame

$$x_i' = x_i + \vec{u}_i$$

Eulerian: strained reference frame

$$x_i = x_i' - \vec{u}_i$$

ICBS:

Total displacement $= \varepsilon_{ij} + \omega_{ij}$

ε_{ij}: strain – hydro, deviatoric

ω_{ij}: rigid body – trans, rot

ICBS:

Eulerian Finite Strain $= \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) - \frac{1}{2}\sum_k \frac{\partial u_k}{\partial x_i} \cdot \frac{\partial u_k}{\partial x_j}$

cross terms.

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Birch's Equation of State

Strain Energy: $E(\varepsilon) = \sum_{m=1}^{\infty} c_m \frac{\varepsilon^m}{m!}$

$\uparrow$ strain energy either Helmholtz (S const) or Internal (T const)

Strain defn: Eulerian finite strain:

$$\varepsilon_{hydro} = \frac{1}{2}\left(1 - \left(\frac{V}{V_0}\right)^{-2/3}\right) = -f$$

as $P\uparrow$, $\varepsilon\downarrow$ as $P\uparrow$, $f\uparrow$

$$E(\varepsilon) = C^0 + C_1\varepsilon + \frac{C_2\varepsilon^2}{2} + \frac{C_3}{6}\varepsilon^3 + \frac{C_4\varepsilon^4}{24} + \dots$$

$$E(f) = C^0 - C_1 f + \frac{C_2}{2}f^2 - \frac{C_3 f^3}{6} + \frac{C_4 f^4}{24} - \dots$$

$$P = \left.\frac{-\partial E}{\partial V}\right)_{T \text{ or } S,\, N \text{ or } \mu} = \frac{\partial E}{\partial f}\cdot\frac{\partial f}{\partial V} = \frac{\partial E}{\partial f}\left(\frac{(1+2f)^{5/2}}{3V_0}\right)$$

$\uparrow$ from Thermo $\uparrow$ chain rule $\uparrow$ differentiate strain defn. wrt V

$$\frac{\partial E}{\partial f} = -C_1 + C_2 f - \frac{1}{2}C_3 f^2 + \frac{1}{6}C_4 f^3$$

$\uparrow$ choose $\emptyset$

3rd-order Birch finite strain Eulerian E.O.S.

$$\boxed{P = \frac{(1+2f)^{5/2}}{3V_0}\left(C_2 f - \frac{1}{2}C_3 f^2 + \dots\right) \quad C_2 = 9K_0 \quad C_3 = 3(4-K_0')\cdot C_2}$$

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High Pressure, High Temperature Equations of state.

$$E = ST + \sum_i X_i Y_i$$

1. Pick Conjugate Variables
2. Do a series expansion around a convenient reference state
3. Solve!

Ideal Properties for a thermal Eqn. of state.

Reference

- Surface of the Earth, adiabat / P=0, T=300
- mantle adiabat
- experiments
- hugoniot

Constitutive properties

- non-dimensional
- orthogonal
- converge
- V_s, V_p