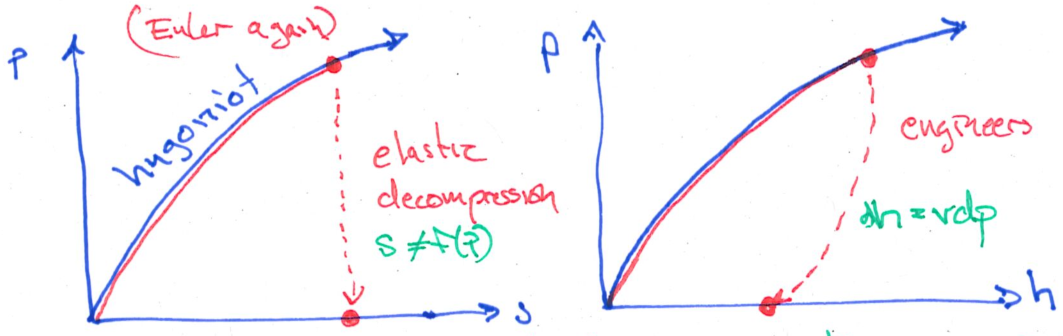
2021 lecture 9.1
(Chapter 5)

A digression: The only open adiabatic system is one that is mechanical eq with its surroundings
eg. mantle upwelling $H(P,S) \rightarrow h = Tds + pdV$



Two basic types of measurement:
Mechanical EoS $V(P,T)$
Caloric EoS $S(P,T)$

Since any phase diagram path depicts a reversible process S is always preferable to h

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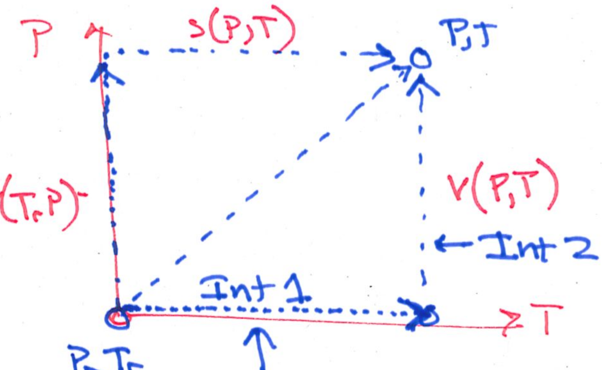
From theory $U(S,V,M)$ to practice (expt) $G(P,T,M) \Rightarrow$
isochemical (pure) homogeneous system $\Rightarrow g(P,T)$

$\cancel{dg = g(P_r,T_r)}$ $\quad g(P,T) = \underline{\underline{g(P_r,T_r)}} + \int_{P_rT_r}^{P,T} dg$

$$\int_{P_rT_r}^{P,T} dg = -\int_{P_rT_r}^{P,T} s(P,T)\,dT + \int_{P_rT_r}^{P,T} V(P,T)\,dP$$

experiment $\Rightarrow$ caloric EoS $\qquad$ mechanical EoS



choose path to use the cheapest/best empirical data

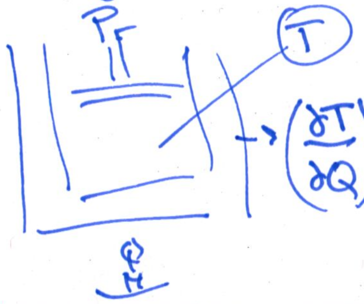
~~Integral 1~~ The beauty is that thermodynamics provides a theoretically exact function for the unmeasured EoS
eg $s(P,T) = -\partial g(P,T)/\partial T$, $c_p(P,T)$ ...

Integral 1 $\quad s(P_r,T) \quad \Rightarrow \quad dU = dQ_p - dW$
$dU = dQ_p - pdV \Rightarrow dQ_p = dU + pdV$

$U - (-P)V$

Legendre Transform

$dH_p = Tds + \cancel{vdp}^{\,0}$



$$\rightarrow \left(\frac{\partial T}{\partial Q}\right)_p = \frac{1}{C_p} = \frac{1}{\left(\frac{\partial h}{\partial T}\right)_p} \Rightarrow s? \Rightarrow \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = C_p$$

$$\Rightarrow dS = \frac{C_p}{T}\,dT$$

Third law entropy :   2021 lecture Q.2

$$S(P_r T) = \int_0^T C_p/T \, dT \quad \leftarrow \text{ fine if no configurational entropy at } 0K$$

$$S(P_r,T) = \underline{\underline{S(P_r T_r)}} + \int_{T_r}^{T} C_p/T \, dT$$

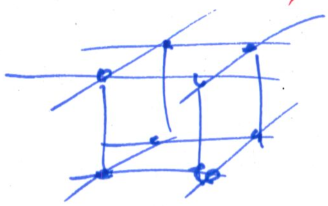
includes S_{conf}

Integral 1 $\Rightarrow$
$$-\int_{T_r}^{T} S(P_r,T)\, dT = -\int_{T_r}^{T}\left(S(P_r,T_r) + \int_{T_r}^{T}\frac{C_p}{T}dT\right) dT$$

$$= -\left(S(P_r,T_r)(T-T_r) + \int_{T_r}^{T}\int_{T_r}^{T}\frac{C_p}{T}\,dT\right)$$

$C_p = f(T) \sim a + bT + cT \ldots$

Integral 2



$V(P,T) \rightarrow$ x-ray diffraction (a little messier for fluids)

The 1st thing we need is $V(P_r T) \leftarrow$ the starting point for integral 2, ie $V(P_r,T)$

$$V(P_r T) = V(P_r T_r) + \int_{P_r T_r}^{P_r T} V dT \Rightarrow \text{what's provided} \Rightarrow$$

$$\alpha_{P_r} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \text{expansivity (isobaric)}$$

$$= \left(\frac{\partial \ln V}{\partial T}\right)_P \Rightarrow \text{simplified notation} \begin{cases} V(P_r T) = V_T \\ V(P_r T_r) = V_0 \end{cases}$$

$$\int_{P_r T_r}^{P_r T} \alpha_{P_r} dT = \int \frac{\partial \ln V}{\cancel{\partial T}} \cancel{dT} = \ln(V(P_r T)) - \ln(V(P_r T_r))$$

$$= \ln(V_T) - \ln(V_0)$$

$$\exp\left(\int \alpha dT\right) = V_T/V_0 \quad \Leftarrow \quad = \ln(V_T/V_0)$$

volumetric strain $\cancel{O(\Delta)}$ $\rightarrow 0$ taylor $\exp(x)$ $f(x) \rightarrow 0$

$$= f_0 + \left.\frac{\partial f}{\partial x}\right|_{x=0} x = 1 + x$$

$$\Rightarrow \left(1 + \int_{T_r}^{T}\alpha\, dT\right) = V_T/V_0 \Rightarrow V_T = V_0\left(1 + \int \alpha dT\right)$$

V_T is the starting point for Int. 2, but the integral itself requires $V(P,T) \Rightarrow V_{PT} \Rightarrow$ The same game

$$\beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \Rightarrow \text{isothermal compressibility}$$
$$= 1/K_T \Rightarrow K_T \text{ isothermal bulk modulus}$$

$$-\int_{P_r}^{P} \beta dP = \ln\left(V_{PT}/V_T\right) \Rightarrow V_{PT}/V_T = \exp\left(-\int \beta dP\right)$$
$$= 1 - \int \beta dP$$

$$V_{PT} = V_T\left(1 - \int_{P_r}^{P} \beta dP\right) = V_0\left(1 + \int_{T_r}^{T} \alpha_{P_r} dT\right)\left(1 - \int_{TP_r}^{TP} \beta\, dP\right)$$

$$= V_0\left(1 + \int_{T_r}^{T} \alpha dT - \int_{TP_r}^{TP} \beta dP - \cancel{\left(\int \alpha dT \int \beta dP\right)}\right)$$

~ 0

$$\text{Int 2} = \int_{P_r T}^{P,T} V dP = \int \left(\quad \right) dP$$

requires $\beta(P,T)$, $\alpha(P_r T)$, $V_0 \Rightarrow$ gives $V(P,T)$, $\underline{\underline{\underline{\alpha(P,T)}}}$!

In petrology β is commonly fit to a 2° polynomial

blows up at $P > \sim 4$ GPa $\Rightarrow$ Mantle pressures require

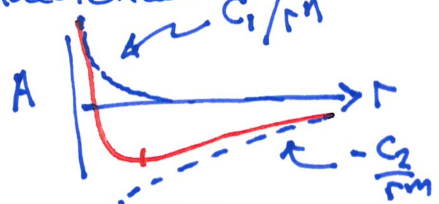
better EoS $\Rightarrow$ Mie - Gruneisen $\Rightarrow$ isothermal EoS

Energy of a crystal lattice at cst T as a function of volume $\Rightarrow \Omega = U - TV = A(V,T) = \Sigma$(repulsive + attractive terms)

$T \to 0 \quad A \to U \to$ "cold" EoS (cold pressure)

$$da = -Pdv - sdT \Rightarrow \left(\frac{\partial A}{\partial V}\right)_T = -p(v) \Rightarrow \text{mechanical EoS}$$

Semi theoretical



isothermal EoS $\rightarrow$ $U - TS = A$

$dA = -pdV + SdT$

$A = C_1/r^n - C_2/r^m$

$A = C_1/V^{n/3} - C_2/V^{m/3}$

$P = -\frac{\partial A}{\partial V} \Rightarrow P = 0,\ V = V_0 \Rightarrow C_2 = C_1 \frac{n}{m} V_0^{(m-n)/3}$

$P = +\frac{C_1 n}{3V}\left(f^{n/3} - f^{m/3}\right) \Rightarrow f = \frac{V_0}{V}$

$K_T = -\frac{\partial P}{\partial V} \cdot V$

$\left.\frac{\partial P}{\partial V}\right|_{P=0} = \frac{C_1(m-n)}{9V_0} \Rightarrow \frac{C_1 n}{3V_0} = -\frac{3K_T(0)}{m-n}\left[\ldots f_0 \ldots\right]$

$P = -\frac{3K_T}{m-n}\left(f^{(m+3)/3} - f^{(m+3)/3}\right)$

$K_T = K_T(0) + K'P + \ldots$

$K' = \frac{\partial K_T(0)}{\partial P} = \frac{m+n+6}{3} = 4 \leftarrow$ experimental

if $n > m$ then

$3 < n < 9$

$V(V_T, K_T, K')$

$V_{T,P_r} = V_{T_r,P_r} \exp\left(\int \alpha dT\right)$

$K_{T,P_r} = f(T)$ at P_r

We need $V(P)$ (VdP) but have 2 powers of V $\Rightarrow$

Birch murnaghan $n = 4$ $m = 2$ $\Rightarrow$ to CMB

Murnaghan $m = -3$ $\Rightarrow$ to ~40 GPa

HP-Murnaghan $n = 9$ $K' = 4$

$$K = K_0 + K'P = -V\frac{\partial P}{\partial V}$$

$$\int_{P_0}^{P}\frac{dP}{K_0+K'P} = \int_{V_0}^{V}\frac{dV}{V}$$

$$\cancel{\ln}\left(\frac{K_0+K'P}{K_0+K'\cancelto{0}{P_0}}\right)^{1/K'} = \frac{V_0}{V}$$

$$K_0+K'P = \left(\frac{V}{V_0}\right)^{-K'}K_0$$

$$K'P = \left(\frac{V}{V_0}\right)^{-K'}K_0 - K_0$$

$$P = \frac{K_0}{K'}\left[\left(\frac{V}{V_0}\right)^{-K}-1\right]$$

$S_0, V_0, G_0 \leftarrow$ integration constants

$G(T), \alpha(T), K_T(T) \leftarrow$ polynomial functions of T

$\downarrow$

$g(P,T)$

$\downarrow$

$$\alpha(P,T) = \frac{1}{V}\frac{\partial V}{\partial T} = \frac{1}{\left(\frac{\partial g}{\partial P}\right)}\left(\frac{\partial\left(\partial g/\partial P\right)}{\partial T}\right)$$

$$G = G_0 - \int_{T_r}^{T}\left(S_0 + \int_{T_r}^{T}\frac{C_p}{T}\,dT\right)dT$$

$$+ \int_{T,P_r}^{T,P}\underbrace{\left[V_0\left(1+\int_{T_r}^{T}\alpha(T)\,dT\right)\right]}_{\neq f(P)}\left(1-\frac{K'P}{\underbrace{K_T}_{\neq f(T)}+K'P}\right)dP$$

UNITS on $\sqrt{\frac{K_{T/S}}{\rho}} \Rightarrow$