2021 8.1

isolated system $U(S, \Psi_2, \dots, \Psi_{k+2})$

$c = k+2$ = # of conservative properties, ie $U, \Psi_2 \dots \Psi_{k+2}$

real processes : $\delta S_{U\dots} > 0$ stable system: $\delta S_U < 0$

system open with respect to $\Psi_{c+1} \dots \Psi_{k+2}$ $\Rightarrow$

$\Omega(\Psi_1, \dots \Psi_c, \Theta_{c+1} \dots \Theta_{k+2})$ = Legendre Transform $\Omega \equiv \underbrace{U - \sum_{i=c+1}^{k+2} \Theta_i \Psi_i}_{U + \sum W_{rev} = 0}$

Can only be used to predict stability at constant $\Theta_{c+1} \dots \Theta_{k+2}$

Two cases :

only case of interest is $H(S, M_1, \dots M_k, -P)$

Adiabatic $\Omega(S, \Psi_2 \dots \Psi_c, \Theta_{c+1}, \dots \Theta_{k+2})$ ($S \to \Psi_1$)

$c = \cancel{k+1}$ $(\Omega, \Psi_2, \dots, \Psi_c)$

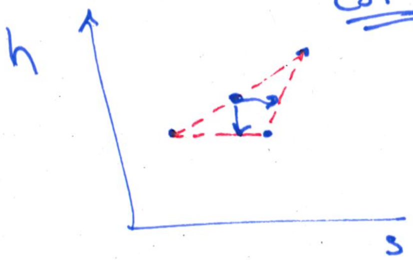
real processes $dS > 0$, $d\Omega = 0$, stability ...

Diathermal $\Omega(\Psi_1, \dots \Psi_c, \cancel{T}, \Theta_{c+2}, \dots, \Theta_{k+2})$ ($T \to \Theta_{c+1}$)

conservative properties $\Psi_1 \dots \Psi_c$

real processes $d\Omega = -T dS^{int} < 0$

stability $d\Omega_{\cancel{\Theta_{c+1}} \dots \Theta_{k+2}} > 0$ ($\Theta_{c+1} \to T$)



cst P!

$c = \{H, N\}$

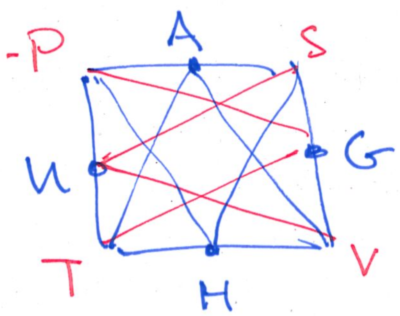
$\Theta_{c+1} = -P$

$u = Ts + Pv + \mu n$

$h = Ts + \mu n$ $\{= u - (-P) v\}$

$$\begin{bmatrix} s & n \\ \vdots & \vdots \end{bmatrix} \begin{bmatrix} T \\ \mu \end{bmatrix} = \begin{bmatrix} h \\ \vdots \end{bmatrix} = \begin{bmatrix} u + Pv \\ \vdots \end{bmatrix}$$

Born Square ?



2021 8.2

Legendre Transform defines the natural variables of the new function $\Omega(\psi_1 \ldots \psi_c, \Theta_{c+1} \ldots \Theta_{k+2})$

$\rightarrow$ normal math one never differentiates a function with respect to anything other than a natural variable, eg $\partial U / \partial T = ?$

$\rightarrow$ Thermodynamics all the time

$\frac{\partial U}{\partial S}$ unadorned means differentiating w/ ~~resp~~ natural variables held constant, ie $= \left(\frac{\partial U}{\partial S}\right)_{V,N}$

$\neq \left(\frac{\partial U}{\partial S}\right)_{P,N}$ if variables that are held cst are not natural variables then they must be indicated.

$\rightarrow$ Theory $U(S,V)$ $dU = TdS + (-P)dV$

$\Rightarrow T(S,V), -P(S,V)$

$\rightarrow$ Practice $G(P,T)$ $dG = VdP - SdT$

$\Rightarrow V(P,T), S(P,T)$

$\downarrow$

$g = g_0 + c_0 T + c_1 P + c_2 P,T$

$S(P,T) = ?$

$V(P,T) = ?$

Why bother with P.D. transformations? Knowledge of one function gives all functions.

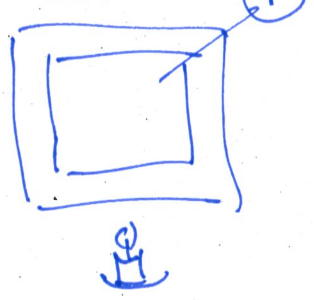
Some examples:

= Problems 4.5 – 4.8 $\rightarrow$ to be assigned

2021 8.3

Calorimetry – Problem 4.6

cst V



$$\left(\frac{\partial T}{\partial q}\right)_V = \frac{1}{\left(\frac{\partial q}{\partial T}\right)_V} = \frac{1}{C_V}$$

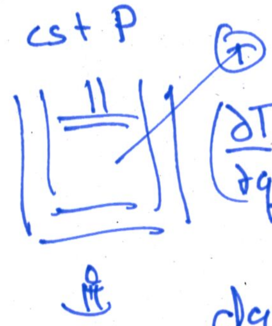
$$du = dq - dw$$

$$du_V = dq_V$$

$$C_V = \left(\frac{\partial u}{\partial T}\right)_V = \left(\frac{TdS - \cancel{PdV}}{\partial T}\right)_V$$

$$= T\left(\frac{\partial S}{\partial T}\right)_V \Rightarrow S(T,V)$$

cst P



$$\left(\frac{\partial T}{\partial q}\right)_P = \frac{1}{\left(\frac{\partial q}{\partial T}\right)_P} = \frac{1}{C_P}$$

$$dq = du + dw$$

$$= du + pdV = dh$$

$$dh = Tds + Vdp$$

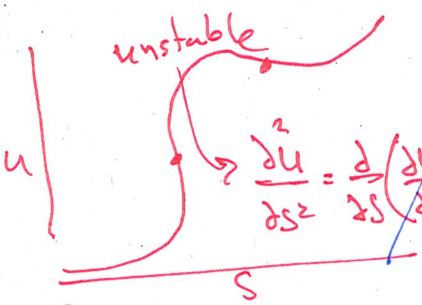
$$C_P = \left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{Tds + \cancel{Vdp}}{\partial T}\right)_P$$

$$= T\left(\frac{\partial S}{\partial T}\right)_P \Rightarrow S(P,T)$$

$$C_P - C_V = T\left(\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V\right)$$

Stability of a state of matter

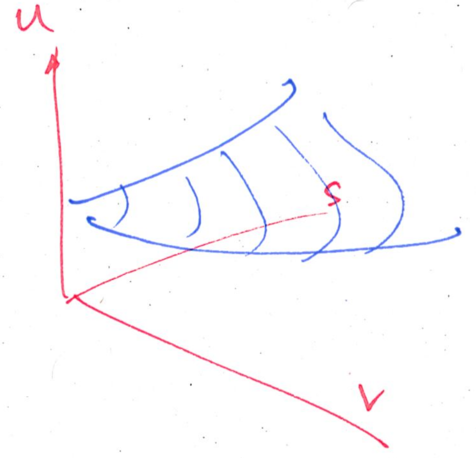
Problem 4.8



$$\frac{\partial^2 U}{\partial S^2} = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial S}\right) \quad T$$

$$\Downarrow$$

$$= \left(\frac{\partial T}{\partial S}\right)_V = T/C_V > 0$$



$$C = \begin{bmatrix} \partial^2 U/\partial S^2 & \partial^2 U/\partial S \partial V \\ \partial^2 U/\partial V \partial S & \partial^2 U/\partial V^2 \end{bmatrix} = \mathrm{Det}\ C \geq 0$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial V}\right) = \left(\frac{-\partial P}{\partial V}\right)_S$$

$$= \frac{1}{\left(\frac{\partial V}{\partial P}\right)_S} \Rightarrow V(P,S)$$

$$|C| = 1\Big/\left(V\frac{C_P}{K_T T} - V\alpha_P^2\right)$$

→ a state of matter is only stable if

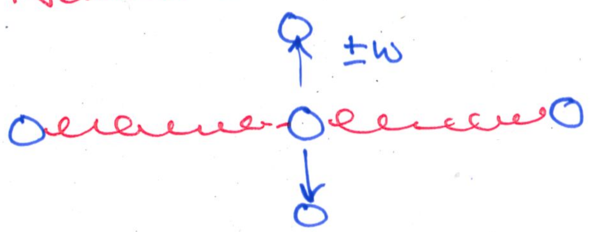
$$C_P\Big/K_T T > \alpha_P^2$$

2021 8.4

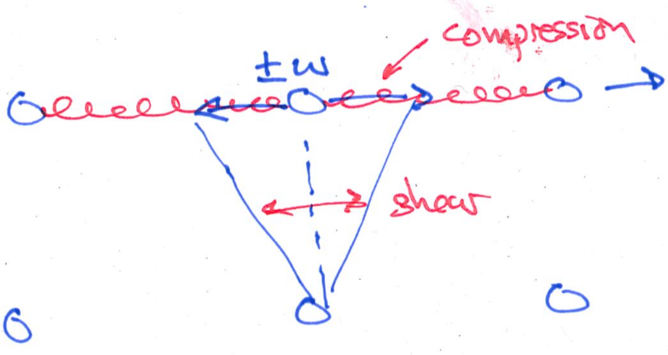
Problem 4.5 Seismic waves $\cong$ Elastic waves = Thermodynamic waves

Hookes law $\Rightarrow F = k\,\delta x$

Newtons law $\Rightarrow F = ma$



$\rightarrow C_s \Rightarrow$ shear wave



$\rightarrow C_p \Rightarrow$ compressional wave

if no shear strength $C_p = C_\varphi$ sound

$$C_{1D}^2 = \frac{\partial F}{\partial x} x \Big/ \rho_{1D} \qquad \rho_{1D} = M/x$$

$\frac{\delta x}{x}$: strain

(−F)

$$\text{(Euler 1756)} \rightarrow C_{3D}^2 = -\frac{\partial P}{\partial V} V \Big/ \rho_{3D} \qquad \rho_{3D} = M/V$$

$\frac{\delta V}{V}$ - bulk strain

$$-\frac{\partial P}{\partial V} V = K$$

↳ bulk modulus

$$C_\varphi = \sqrt{K/\rho} = \sqrt{\Phi_s}$$

$$\Phi_s = V_p^2 - \frac{4}{3} V_s^2$$

$$K_T = -\left(\frac{\partial P}{\partial V}\right)_T V$$

$1\Big/\left(\frac{\partial V}{\partial P}\right)_T \Rightarrow V(P,T)$

$$K_S = -\left(\frac{\partial P}{\partial V}\right)_S V$$

$1\Big/\left(\frac{\partial V}{\partial P}\right)_S \Rightarrow V(P,S)$

which is a better spring?

would you expect Quality to be frequency dependent?

2021 8.5

differentiation rules in chapter 4:

x, y, z variables that can be used for differentiation (P, T)

F, g, z all the others (S, V)

Rule 0 (4.39) $1/\partial x/\partial y = \partial y/\partial x \Rightarrow \left(\frac{\partial T}{\partial V}\right)_P = 1 \Big/ \left(\frac{\partial V}{\partial T}\right)_P = 1 \Big/ \partial^2 g/\partial P^2$

Rule 1 (4.43) $\frac{\partial F/\partial x}{\partial g/\partial x} = \partial F/\partial g \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \frac{(\partial S/\partial P)_T}{(\partial V/\partial P)_T}$

Rule 3 Euler's criterion

Rule 4 Euler's chain rule (4.40) $\left(\partial y/\partial x\right)_z = -\left(\frac{\partial z}{\partial x}\right)_y \Big/ \left(\frac{\partial z}{\partial y}\right)_x$

1 variable you can't handle

Problem 4.7 $\rightarrow \left(\frac{\partial P}{\partial T}\right)_S \rightarrow \left(\frac{\partial P}{\partial T}\right)_V$. $\Rightarrow V(P,T) \Rightarrow$

$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$

at cst V $= 0$

$\left(\frac{\partial V}{\partial P}\right)_T dP_V = -\left(\frac{\partial V}{\partial T}\right)_P dT_V$

$\left(\frac{\partial P}{\partial T}\right)_V = -(\partial V/\partial T)_P \Big/ (\partial V/\partial P)_T$

Rule 5 (4.42) – two variables you can't handle $\left(\frac{\partial S}{\partial T}\right)_V$

$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$

$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial S}{\partial T}\right)_P \cancel{\left(\frac{\partial T}{\partial T}\right)_V}$ 1

Not Problem 4.4

$\rho = N/V$ ← molar mass a cst; V ← specific volume

→ 4.5, 4.7

problem 4.7 g – gravitational acceleration a cst.

Make script g(P,T)

2021 8.6

Maple script

```
g:= G(P,T);        <= makes g a symbolic f(P,T)
S:=-diff(g,T);     <= makes S, V functions of PT
V = diff(g,P);     <=

dsdpt := diff(S,P);    ....
dpdst := 1/dsdpt;      ....
```

Useful to have the solutions in Maple for chapter 5.