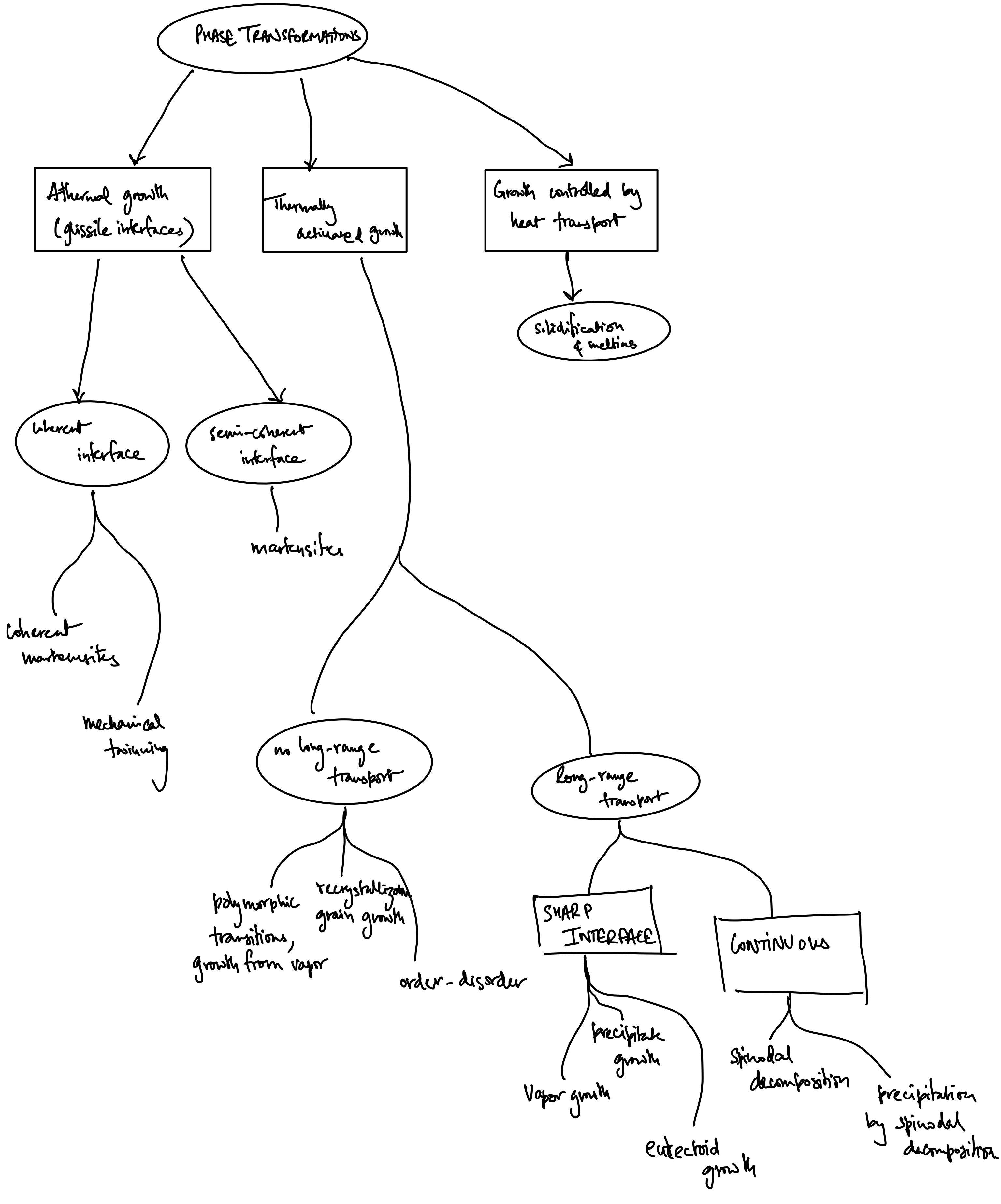
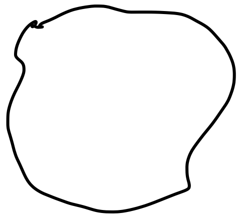
PHASE TRANSFORMATIONS:

- phase transformations in the solid state (involving crystalline solids)
  - * metals (alloys)
  - * ceramics, oxides, battery materials
  - * compound semiconductors, thermoelectrics, memory devices.
- An attempt @ classification



* Consider the following experiments:

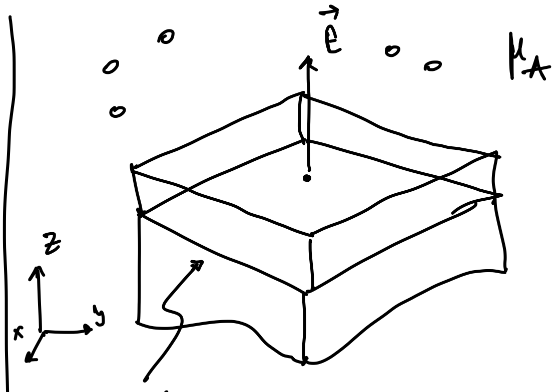


T, p = constant

how do we determine which phase is stable?

→ minimize Gibbs free energy wrt internal degrees of freedom (i.e. various possible crystal structures/phases)

$$G = U - TS + pV$$



epitaxially constrained.

experimentally you are controlling

$$T, \vec{E}, \varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{xy}, \sigma_{zz}, \mu_A$$

→ how do we determine which phase is stable?

→ minimize what?

G? F? ...

→ if the epitaxial film undergoes a phase transformation, how much heat is exchanged with the environment?

* FIRST PART OF THE COURSE:

Develop the thermodynamic tools to analyze arbitrarily complex boundary conditions.

THERMODYNAMICS:

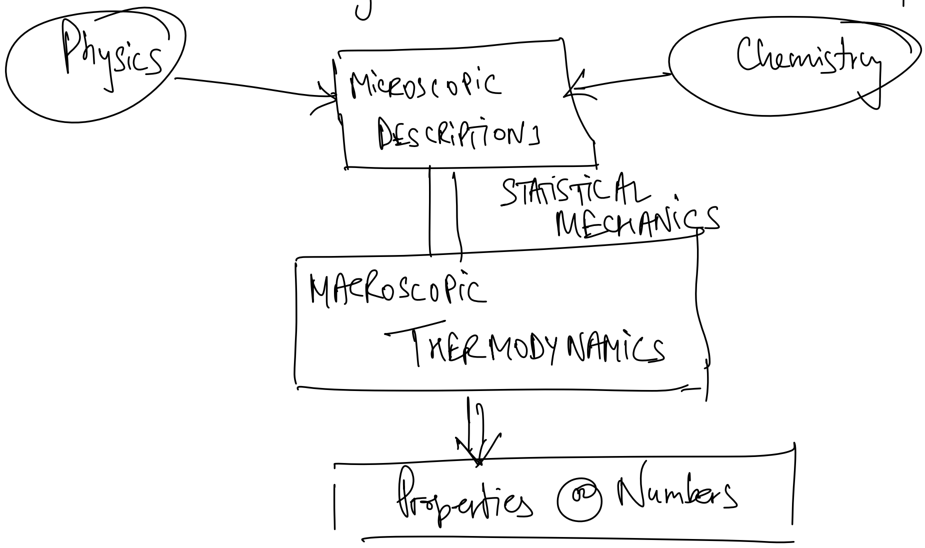
What is thermodynamics?

Macroscopic framework of energy flows, and how they affect the properties of the system

- Macroscopic theory → no atomic scale information
- deals only with macroscopic variables
  (eg) Volume (V)
  pressure (p)
  temperature (T) . . .
- Completely general framework that does not rely on atomic details.
- Thermodynamics is a "processor" or "accountant"
  ⇒ You have to put some information | physics into the framework to get other properties out

RELATION TO OTHER FIELDS:

Can derive thermodynamic relations from atomic | electronic



THERMO: determines the equilibrium states and free energy landscape between phases

KINETICS: determines the mechanisms and rates.

DEFINITIONS:

* **SYSTEM**: Any collection of matter that can be uniquely specified (and over which macroscopic averages can be specified)
* **SURROUNDING / ENVIRONMENT**: Universe − System
* **VARIABLES**:
  - extensive: scale with the size of the system
    $(S, V, \vec{M}, N_i, V_0\varepsilon_{ij})$ $\Longrightarrow$ normalized extensive variables: $\frac{N_i}{V} = x_i$ $\downarrow$ "densities"
  - intensive: do not scale with the size of the system
    $(T, p, \vec{H}, \mu_i, \sigma_{ij})$

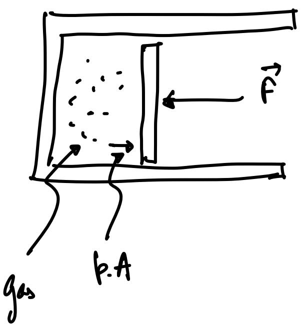
extensive and intensive variables always come in conjugate pairs

$$(\underset{\text{extensive}}{X}, \underset{\text{intensive}}{Y})$$

* **CHANGE OF STATE** → by exchanging heat or work between the system and the environment

* **TYPES OF PATHS**:
  - reversible → mathematical idealisation where the system and the environment are always in eq^n with each other
  - irreversible → all real and spontaneous changes of state

EXAMPLE: piston work (work is $\delta w = \vec{f}\cdot d\vec{l}$)



- real compression $f > p.A$
- real expansion $f < pA$

$\Rightarrow$ real changes of state need an imbalance between the system and the environment

REVERSIBLE WORK

$$f = pA$$

$$\delta w = \vec{f}\cdot d\vec{l} = p\underbrace{A\,dl}_{-dV} = -p\,dV$$

$$\boxed{\begin{array}{c}\text{Reversible } p\text{-}V \text{ work}\\ \delta w = -p\,dV\end{array}}$$

→ Expressed in terms of STATE VARIABLES of the system.

In general: REVERSIBLE work is "force" applied by the environment on the system times "displacement"

$$\delta W_{\text{reversible}} = \underbrace{Y}_{\substack{\text{intensive}\\ \text{(force)}}}\, d\overbrace{X}^{\substack{\text{extensive}\\ \text{(displacement)}}}$$

HEAT: exchange of energy between system and the environment due to a temperature difference

REVERSIBLE: $\Rightarrow \Delta T \to 0$

LAWS OF THERMODYNAMICS:

1st law: $\Delta U = Q + W$ U → internal energy

$$\underbrace{dU}_{\substack{\text{NEW STATE}\\ \text{VARIABLE}}} = \underbrace{\delta q + \delta w}_{\text{path variables.}}$$

2nd law: $\Delta S \geq \frac{Q}{T}$ S = entropy

$>$ for irreversible

$=$ for reversible.

$$dS \geq \frac{\delta Q}{T}$$

$$\frac{\delta Q_{\text{reversible}}}{T} = dS \Rightarrow \boxed{\delta Q_{\text{reversible}} = TdS}$$

COMBINED 1st AND 2ND LAW:

$$\boxed{dU = \underbrace{TdS}_{\delta Q_{\text{rev}}} + \underbrace{\sum_i Y_i\, dX_i}_{\delta W_{\text{reversible}}}}$$

ASIDE:

for macroscopic systems

$$N \to 2N \Rightarrow \left.\begin{array}{l} V \to 2V \\ U \to 2U \\ S \to 2S \end{array}\right\} \text{EXTENSIVITY}$$

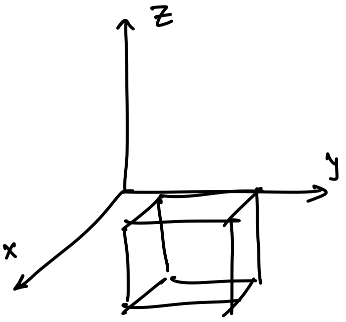
* REVERSIBLE WORK

$$\boxed{\delta W = \underbrace{Y}_{\text{intensive force}} . \underbrace{dX}_{\text{extensive displacement}}}$$

Y & X are state variables of the system.

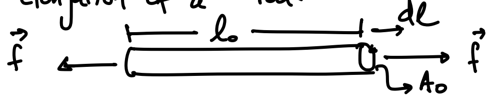
① STRAIN WORK:

$$\boxed{\delta W = V_0 \sum_i \sum_j \sigma_{ij} \, d\varepsilon_{ij}}$$



Special cases

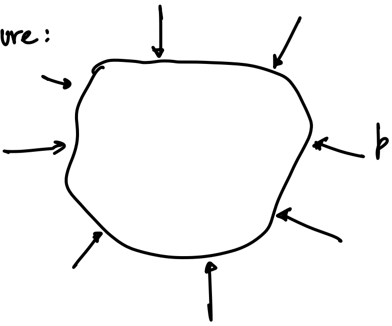
* elongation of a rod:



A_0 ⟶ area of the rod cross-section

$$\delta W = f dl = f . l_0 \frac{\delta l}{l_0} = \underbrace{\left(\frac{f}{A_0}\right)}_{\sigma_{xx}} \underbrace{\left(A_0 l_0\right)}_{V_0} \underbrace{\left(\frac{\delta l}{l_0}\right)}_{d\varepsilon_{xx}} = V_0 \sigma_{xx} \, d\varepsilon_{xx}$$

* hydrostatic pressure:



$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \overset{\text{sign convention}}{-p}$$

$$\sigma_{xy} = \sigma_{xz} = \sigma_{yz} = 0$$

$$V = \overset{\text{reference volume}}{V_0} \underbrace{\left(1 + \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}\right)}_{\text{hydrostatic stress/strain}}$$

$$dV = V_0 d\left(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}\right)$$

$$\delta W = V_0 \sum_i \sum_j \sigma_{ij} \, d\varepsilon_j = V_0 \left(\sigma_{xx} d\varepsilon_{xx} + \sigma_{yy} d\varepsilon_{yy} + \sigma_{zz} d\varepsilon_{zz}\right)$$

$$= V_0 (-p) d\left(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}\right) = -p \, dV$$

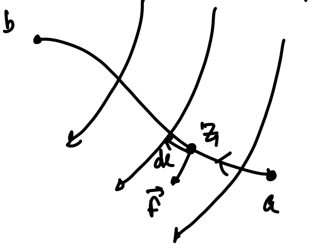
$$\boxed{\delta W = -p \, dV}$$

* Electrical Work :

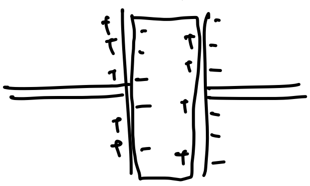
- moving charge from one potential to another

$$\delta W = \Delta\phi \, d Z_1$$

$$\vec{E} = -\nabla \phi$$



- work to polarize a material



$$\boxed{\delta W = \vec{E} . d\vec{P}}$$

$d\vec{P}$ ⟶ total dipole moment of the material

* **Magnetic Work**:

$$\boxed{\delta W = H\, dM}$$

total magnetic moment

applied magnetic field

* **Chemical Work**:

$$\delta W = \mu_i\, dN_i$$

chemical potential of element i

\# of atoms of element i

SUMMARY:

form of work	δW	state variables				
– lengthen rod	$\vec{f}\cdot d\vec{l}$	f	l	or	σ	$V_0\varepsilon$
– hydrostatic pressure	$-p\cdot dV$	p	V			
– general strain work	$V_0\sum_{ij}\sigma_{ij}\,d\varepsilon_{ij}$	σ_{ij}	$V_0\varepsilon_{ij}$			
– moving charge through a potential	$\phi\, dZ_1$	ϕ	Z_1			
– electric polarization	$\vec{E}\cdot d\vec{P}$	$\vec{E}$	$\vec{P}$			
– magnetization	$\vec{H}\cdot d\vec{M}$	$\vec{H}$	$\vec{M}$			
– chemical	$\mu_i\, dN_i$	μ_i	N_i			
		INTENSIVE VARIABLES	EXTENSIVE VARIABLES			

CONJUGATE PAIRS

GENERAL: $\delta W = Y\, dX$ → reversible work expressed in terms of state variables of the system.

Y: intensive

X: extensive.

FUNDAMENTAL RELATION IN THERMO:

$$\boxed{dU = T\underset{\uparrow}{dS} + \sum_i Y_i\, \underset{\uparrow}{dX_i}} \longrightarrow \text{connects all state variables of a system.} \quad ①$$

differentials are all extensive

$$\Rightarrow U(\underbrace{S, X_1, X_2, \dots}_{\text{"natural variables" of internal energy.}})$$

$$\Rightarrow \boxed{dU = \left(\frac{\partial U}{\partial S}\right)_{X_1, X_2, \dots} dS + \sum_i \left(\frac{\partial U}{\partial X_i}\right)_{X_{j\neq i}, S} dX_i} \quad ②$$

Comparing eqns. ① & ②

$\rightsquigarrow$ EQUATIONS OF STATE

$$T = \left(\frac{\partial U}{\partial S}\right)_{X_1, X_2, \dots}$$

$$Y_i = \left(\frac{\partial U}{\partial X_i}\right)_{S, X_{j\neq i}}$$

All intensive variables are partial derivatives w/ respect to the conjugate extensive variable.

- if U is known in terms of S and X_i $\Rightarrow$ all thermodynamic properties can be extracted from U.
- if all EOS are known $\Rightarrow$ U can be determined through integration.

* EULER RELATION: $\boxed{U = TS + \sum_i Y_i X_i}$

extensivity: $U(\lambda S, \lambda X_i) = \lambda U(S, X_i)$

take derivative wrt to λ

$$\left(\frac{\partial U}{\partial(\lambda S)}\right)_{X_i} \left(\frac{d(\lambda S)}{d\lambda}\right) + \sum_i \left(\frac{\partial U}{\partial(\lambda X_i)}\right)_{\lambda S, \lambda X_j} \left(\frac{\partial(\lambda X_i)}{\partial \lambda}\right) = U(S, X_i)$$

evaluate for $\lambda = 1$

$$\underbrace{\left(\frac{\partial U}{\partial S}\right)_{X_i}}_{T} \cdot S + \sum_i \underbrace{\left(\frac{\partial U}{\partial X_i}\right)_{S, X_{j\neq i}}}_{Y_i} X_i = U(S, X_i)$$

* GIBBS-DUHEM :

Start with Euler: $U = TS + \sum_i Y_i X_i$

Take differential: $dU = TdS + SdT + \sum_i \left(Y_i dX_i + X_i dY_i \right)$

fundamental eqⁿ of thermo ⇒ $dU = TdS + \sum_i Y_i dX_i$

$$\Rightarrow \boxed{SdT + \sum X_i dY_i = 0}$$

all intensive

LEGENDRE TRANSFORM:

⟶ gives us the "characteristic potential".

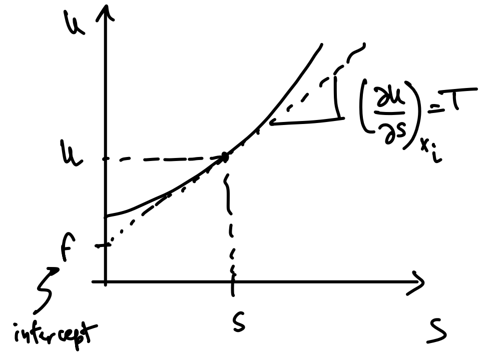
$U(S, X_i)$ ⟶ U is the characteristic potential when we control (S, X_i) ie extensive quantities.

Controlling extensive quantities in experiment may be difficult.

(eg) controlling S is difficult.

Say I want to run an experiment where we control (T, X_i) instead of (S, X_i)

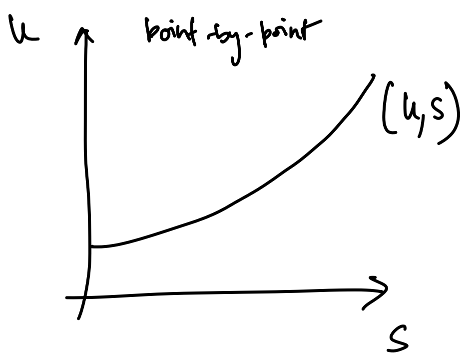
⇒ I would like a state function that has (T, X_i) as natural variables ⟹ How do we obtain this from U?



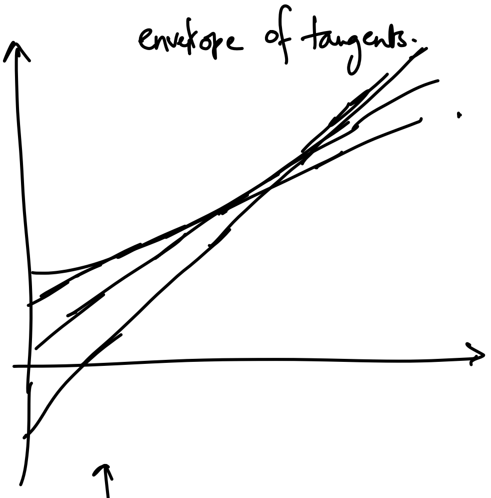
$$\frac{U - F}{S} = \left(\frac{\partial U}{\partial S}\right)_{X_i} = T$$

$$\Rightarrow \boxed{F = U - TS}$$

Two ways to represent a curve



OR



Specify slope (T) and intercept (F)

F = U − TS

The two curves have the same information content.

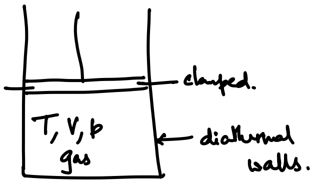
Whenever an INTENSIVE variable is experimentally controlled, we have to perform a LEGENDRE TRANSFORM

In general: $\phi = U - Y_i X_i$ $\left\{ \begin{array}{l} X_i = \text{extensive} \\ Y_i = \text{intensive.} \end{array} \right.$

char. potential under the experimental conditions.

EXAMPLES:

* Constant T, V:



(perfect heat transfer between system and environment)

* start with fundamental equation:

$$dU = TdS - pdV \longrightarrow U(\underset{\text{good}\checkmark}{S}, \overset{\text{need to replace this with conjugate } T}{V})$$

Legendre transform:

$$f = U \underbrace{- TS}_{\text{Legendre transform.}}$$

$$df = dU - TdS - SdT$$

$$= TdS - pdV - TdS - SdT$$

$$\boxed{df = -SdT - pdV} \longrightarrow f(T, V)$$

$$df = \left(\frac{\partial f}{\partial T}\right)_V dT + \left(\frac{\partial f}{\partial V}\right)_T dV \Rightarrow \boxed{\left(\frac{\partial f}{\partial T}\right)_V = -S \qquad \left(\frac{\partial f}{\partial V}\right)_T = -p}$$

EQUATIONS OF STATE

(eg) IDEAL GAS: from statistical mechanics.

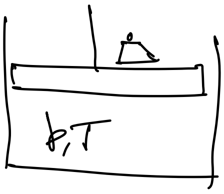
$$F(T, V) = -nRT\left[\log V - \frac{3}{2}\log T + \frac{3}{2}\log\left(\frac{m}{2\pi k_B \hbar^2}\right)\right]$$

$$p = -\left(\frac{\partial f}{\partial V}\right)_T = \frac{nRT}{V}$$

$$S = -\left(\frac{\partial f}{\partial T}\right)_V = nR\left[\log V - \frac{3}{2}\log T + \frac{3}{2}\log\left(\frac{m}{2\pi\hbar^2 k_B}\right)\right] - \frac{3}{2}nR$$

$$U = F + TS = \frac{3}{2}nRT = U(T)$$

2. Constant T, p



fundamental equation: $dU = TdS - pdV$

$U(S, V) \longrightarrow$ replace both variables with their conjugates

$$G = U - TS + pV$$

$\hookrightarrow$ sign because $Y_i = -p$

$$dG = -SdT + Vdp$$

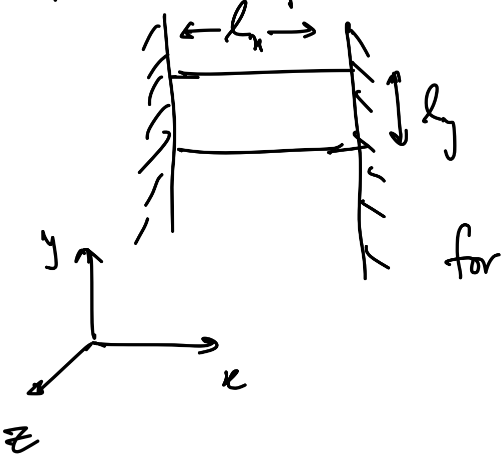
$G(T,p) \longrightarrow$ GIBBS FREE ENERGY

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

EQUATIONS OF STATE:

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \qquad V = \left(\frac{\partial G}{\partial p}\right)_T$$

③ Clamped block of material @ constant T, p



generalized stress/strain work

$$\sum_i \sum_j V_0 \sigma_{ij} d\varepsilon_{ij}$$

for simplicity, assume no shear stress/strain

$$\delta W = V_0\left(\sigma_{xx} d\varepsilon_{xx} + \sigma_{yy} d\varepsilon_{yy} + \sigma_{zz} d\varepsilon_{zz}\right)$$

fundamental equation:

$$dU = TdS + V\sigma_{xx} d\varepsilon_{xx} + V\sigma_{zz} d\varepsilon_{zz} + V\sigma_{yy} d\varepsilon_{yy}$$

$$U(S, V\varepsilon_{xx}, V\varepsilon_{zz}, V\varepsilon_{yy})$$

we control:

$$\left(T, \underset{\text{extensive}}{V\varepsilon_{xx}}, \underbrace{\sigma_{zz}, \sigma_{yy}}_{-p}\right)$$

$$\Lambda = U - TS - V\sigma_{yy}\varepsilon_{yy} - V\sigma_{zz}\varepsilon_{zz} = U - TS + pV(\varepsilon_{yy} + \varepsilon_{zz})$$

$$d\Lambda = -SdT + \sigma_{xx} V d\varepsilon_{xx} - V(\varepsilon_{yy} + \varepsilon_{zz})dp$$

EQUATIONS OF STATE:

$$S = -\left(\frac{\partial \Lambda}{\partial T}\right)_{V\varepsilon_{xx}, p} \qquad \sigma_{xx} = \left(\frac{\partial \Lambda}{\partial \varepsilon_{xx}}\right)_{T,p} \cdot \frac{1}{V}$$

$$V(\varepsilon_{xx} + \varepsilon_{yy}) = -\left(\frac{\partial \Lambda}{\partial p}\right)_{T, V\varepsilon_{xx}}$$