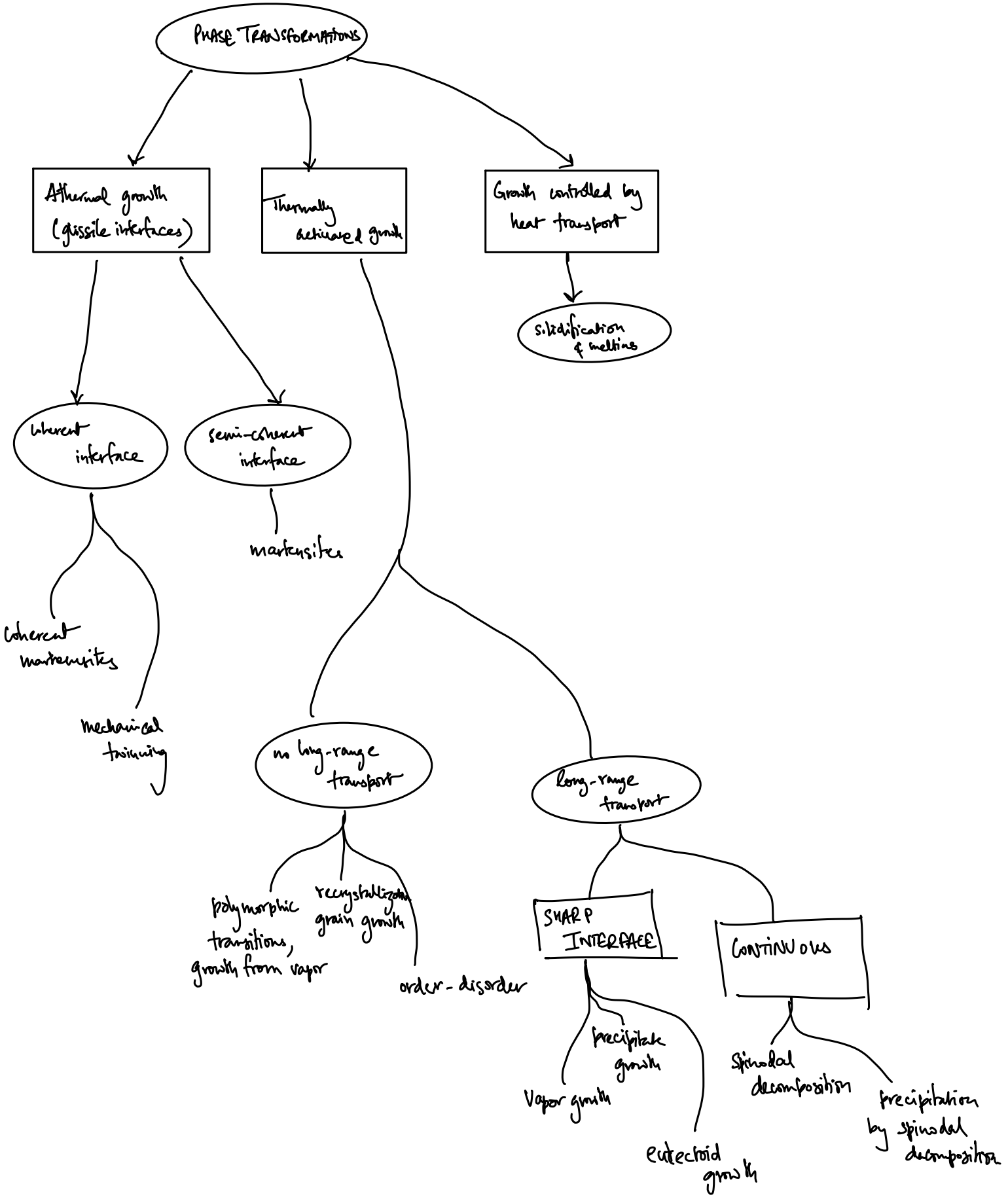
PHASE TRANSFORMATIONS:

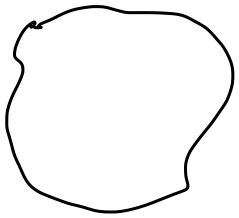
- phase transformations in the solid state (involving crystalline solids)
  - * metals (alloys)
  - * ceramics, oxides, battery materials
  - * compound semiconductors, thermoelectrics, memory devices.

- An attempt @ classification



* Consider the following experiments:

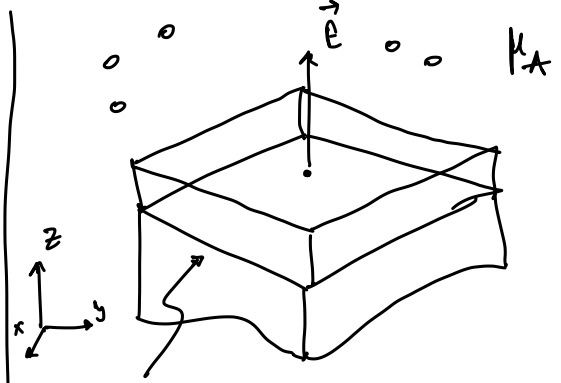
T, p = constant



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:

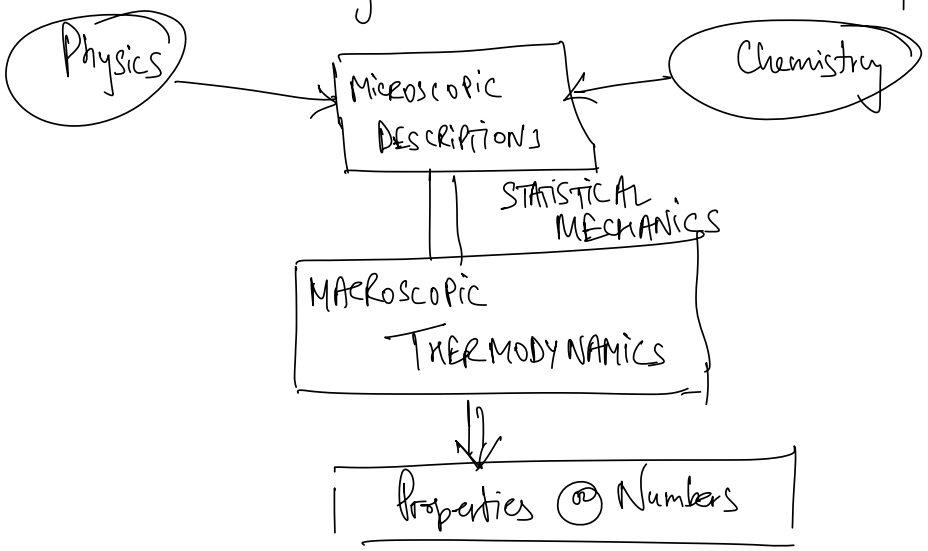
What is thermodynamics?

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" @ "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:

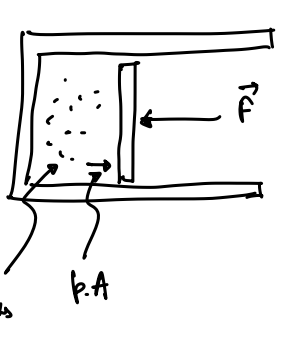
* SYSTEM: Any collection of matter that can be uniquely specified (and over which macroscopic averages can be specified)
* SURROUNDING / ENVIRONMENT: Universe − System
* VARIABLES:
  - extensive: scale with the size of the system
    $(S, V, \vec{M}, N_i, V_0 \varepsilon_{ij})$ $\Longrightarrow$ normalized extensive variables: $\frac{N_i}{V} = x_i$ ↓ "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

(X, Y) — X: extensive, Y: intensive

* 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 eqm with each other
  - irreversible → all real and spontaneous changes of state

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



- 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

$F = pA$

$\delta W = \vec{F} \cdot d\vec{\ell} = p\underbrace{A d\ell}_{-dV} = -p dV$

Reversible p-V work
$\delta W = -p dV$

→ Expressed in terms of STATE VARIABLES of the system.

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

$$\delta W_{\text{reversible}} = Y\,dX$$

Y: intensive (force); dX: extensive (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: $\Delta U = Q + W$ $\quad U \to$ internal energy

$$dU = \delta q + \delta w$$

dU: NEW STATE VARIABLE; $\delta q + \delta w$: both variables.

2nd law: $\Delta S \geq \frac{Q}{T}$ $\quad S =$ entropy $\quad >$ for irreversible, $=$ for reversible.

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

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

COMBINED 1st AND 2ND LAW:

$$\boxed{dU = T\,dS + \sum_i Y_i\,dX_i}$$

$T\,dS \to \delta Q_{rev}$; $\sum_i Y_i\,dX_i \to \delta W_{\text{reversible}}$

ASIDE:

for macroscopic systems

$N \to 2N \Rightarrow$ $V \to 2V$, $U \to 2U$, $S \to 2S$ } EXTENSIVITY

* REVERSIBLE WORK

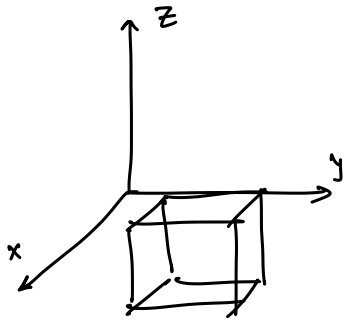
$$\delta W = Y \cdot dX$$

Y & X are state variables of the system.

- Y: intensive force
- X: extensive displacement

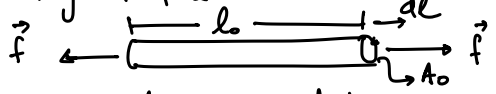
① STRAIN WORK:

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



Special cases

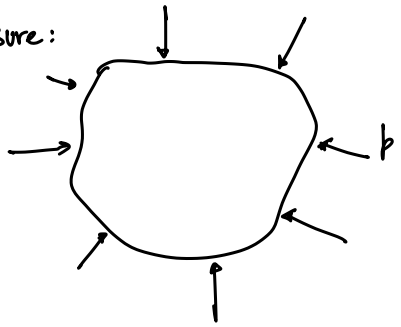
* elongation of a rod:



$A_0 \rightarrow$ area of the rod cross-section

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

* hydrostatic pressure:



$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = -p \quad \text{(sign convention)}$$

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

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

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

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

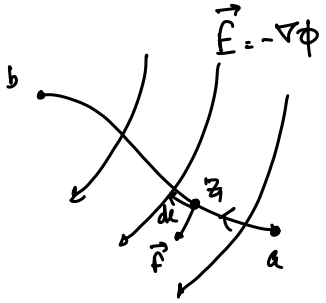
$$= V_0 (-p)\, d\left(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}\right) = -p\, dV$$

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

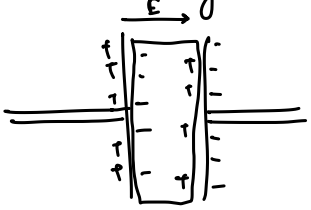
* Electrical Work:

- moving charge from one potential to another

$$\delta W = \Delta\phi \, dZ$$



- work to polarize a material



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

$\rightarrow$ total dipole moment of the material

* **Magnetic Work:**

$$\delta W = H\, d\mathcal{M}$$

$\mathcal{M}$: total magnetic moment

H: applied magnetic field

* **Chemical Work:**

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

μ_i: chemical potential of element i

N_i: # of atoms of element i

SUMMARY:

form of work	δW	state variables				
– lengthen rod	$\vec{f}\cdot d\vec{l}$	f	l	@	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	$\oint d'\mathcal{E}_1$	Φ	$\mathcal{E}_1$			
– electric polarization	$\vec{E}\cdot d\vec{\mathcal{P}}$	$\vec{E}$	$\vec{\mathcal{P}}$			
– magnetization	$\vec{H}\cdot d\vec{\mathcal{M}}$	$\vec{H}$	$\vec{\mathcal{M}}$			
– chemical	$\mu_i\, dN_i$	μ_i	N_i			

CONJUGATE PAIRS

μ_i: INTENSIVE VARIABLES

N_i: EXTENSIVE VARIABLES

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

Y: intensive

X: extensive.

FUNDAMENTAL RELATION IN THERMO:

$$dU = TdS + \sum_i Y_i dX_i \quad \text{(1)}$$

→ connects all state variables of a system.

differentials are all extensive

$$\Rightarrow U(S, X_1, X_2, \cdots)$$

"natural variables" of internal energy.

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

Comparing eqns. (1) & (2)

→ EQUATIONS OF STATE

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

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

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

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

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

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 $\Rightarrow$ $dU = TdS + \sum_i Y_i dX_i$

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

all intensive

LEGENDRE TRANSFORM: ⟶ gives us the "characteristic potential".

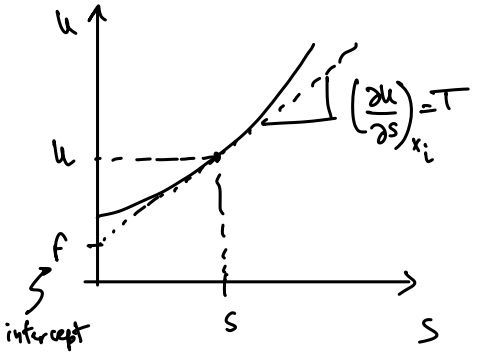
$U(S, X_i)$ ⟶ U is the characteristic potential when we control (S, X_i) ie extensive quantities.

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)

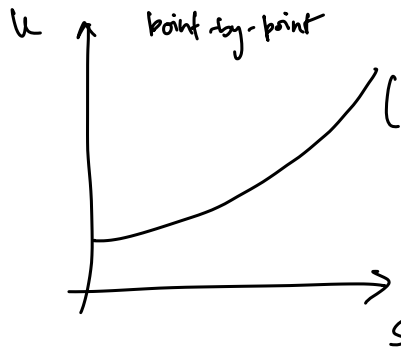
$\Rightarrow$ I would like a state function that has (T, X_i) as natural variables $\Rightarrow$ How do we obtain this from U?



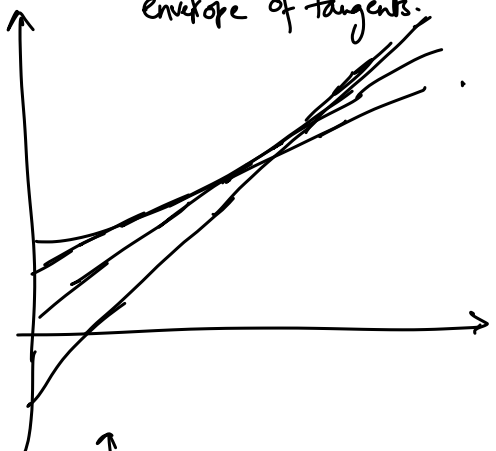
$$\frac{U - f}{S} = \left(\frac{\partial U}{\partial S}\right)_{X_i} = T$$

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

Two ways to represent a curve



OR



The two curves have the same information content.

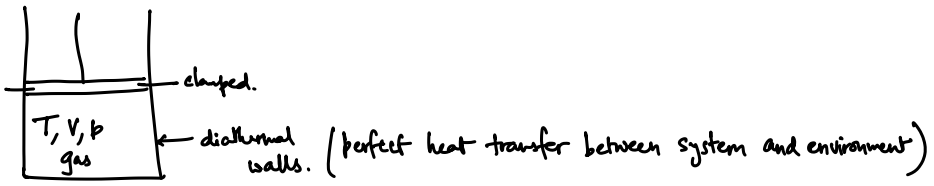
Whenever an INTENSIVE variable is experimentally controlled, we have to perform a LEGENDRE TRANSFORM

In general: $\phi = U - Y_i X_i$ (chor. potential under the experimental conditions.)

$\begin{cases} X_i = \text{extensive} \\ Y_i = \text{intensive.} \end{cases}$

EXAMPLES:

* Constant T, V:



* start with fundamental equation:

$dU = TdS - pdV \longrightarrow U(S,V)$ (need to replace this with conjugate T; good ✓)

Legendre transform:

$F = U - TS$ → 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