2020 6.1

sst S?

Stability (Chapter 3)

why wasn't stability an issue in the Al_2SiO_5 phase diagram?

Reversible processes ⇒ $dU = \ldots$ ⇒ external influence required!!

Spontaneous process ⇒ $dS^{universe} > 0$ ⇒ possible w/no external influence.

Isolated system ⇒ no external influence possible, $dQ = dW = 0$, $dS > 0$

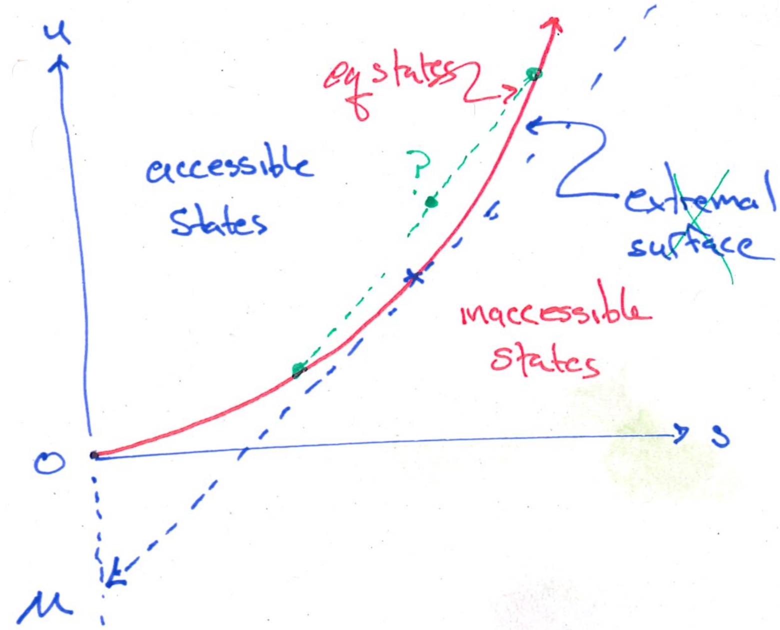
a simplified universe with no mechanics:

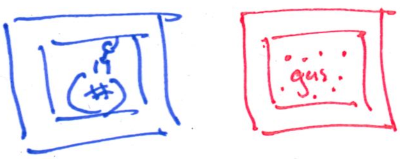
$$U = TS + \mu N \Rightarrow a = N$$

$$u = Ts + \mu \rightarrow k = 1$$

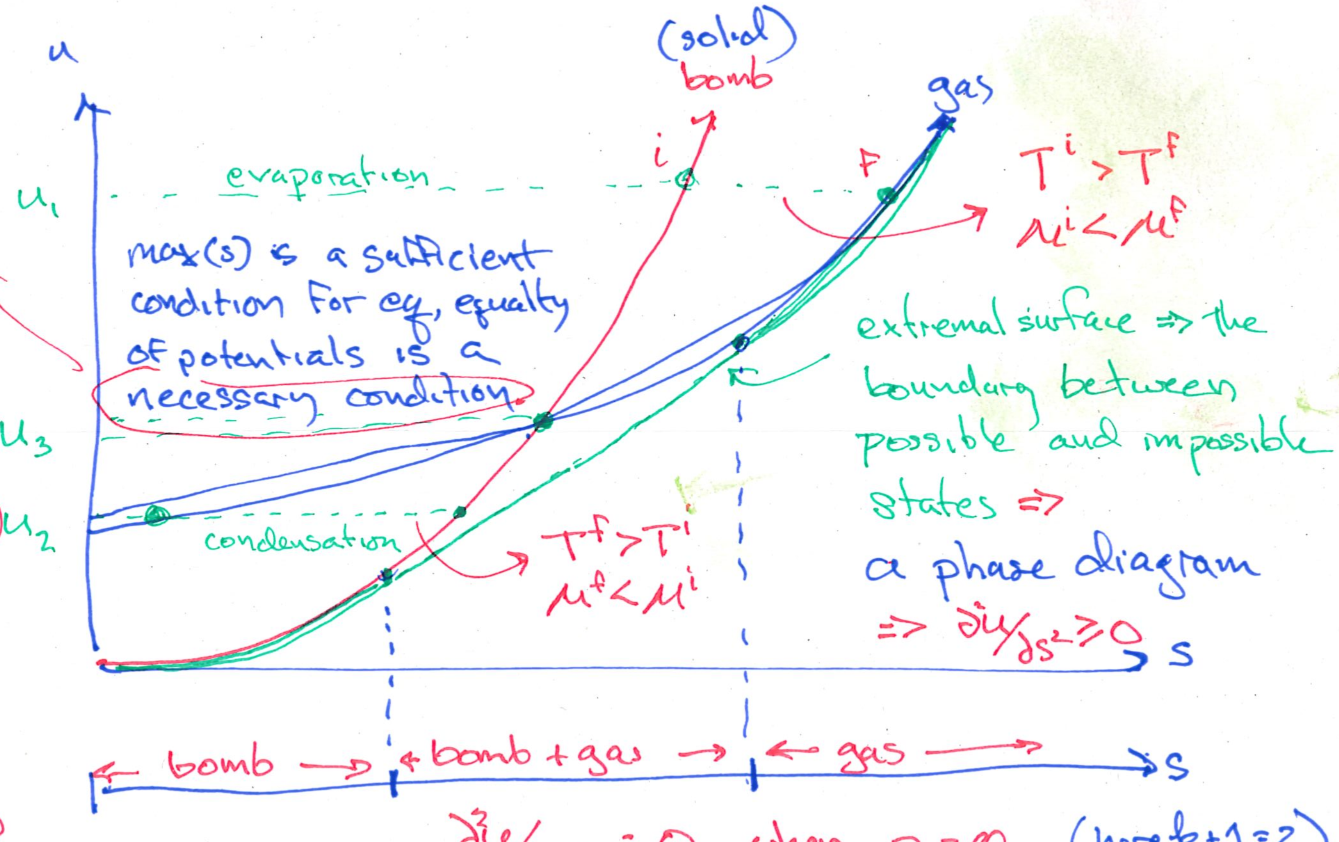
$$p = ?$$

$$du = T ds$$





aka "Kuhn-Tucker" conditions + now + someone else. (Karush!)



$$\partial^2 u/\partial s^2 = \frac{\partial}{\partial s}\left(\frac{\partial u}{\partial s}\right) = \frac{\partial T}{\partial s} \geq 0$$

$\partial^2 u/\partial s^2 = 0$ when $p = \varphi_{max}$ (here $k+1 = 2$)

A family of irrational stability criteria

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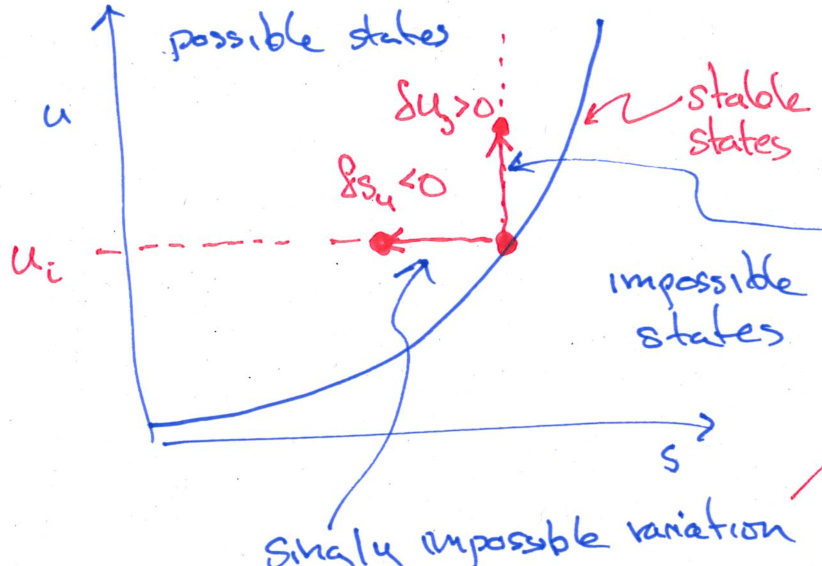
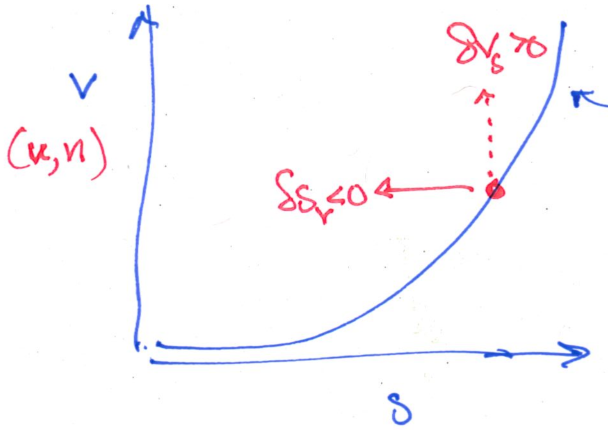


doubly impossible variation the seed of energy min.

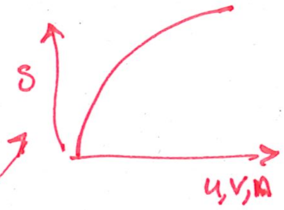
virtual differentials, Tunnell

A system is stable when it has the largest possible entropy consistent with its energy, mass, and volume.



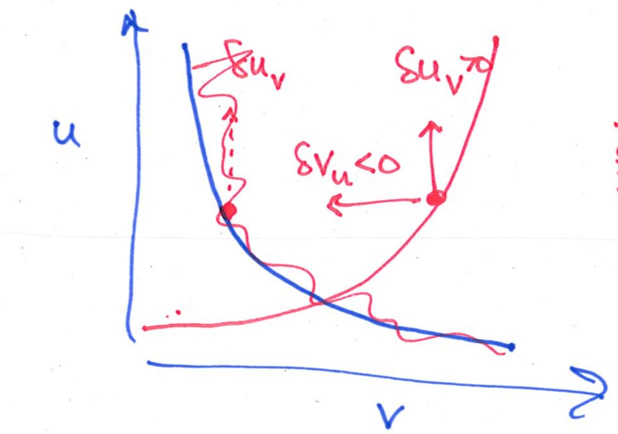
$Tds - pdv = 0$

$ds = \left(\frac{-p}{T}\right) dv$



Tisza: $dS = \underline{\frac{1}{T}} dU + \underline{\underline{\frac{P}{T}}} dV - \underline{\underline{\frac{\mu}{T}}} dM$

potentials for entropy all positive



$du = -pdv \Rightarrow$ if u is a minimum

$\cancel{\frac{\partial u}{\partial v} < 0} \Rightarrow \frac{\partial^2 u}{\partial v^2} = \frac{\partial}{\partial v}\frac{\partial u}{\partial v} = \frac{\partial(-P)}{\partial V} > 0$

$\frac{\partial u}{\partial v} > 0$ $\quad \frac{\partial^2 u}{\partial n^2} = \frac{\partial}{\partial n}\left(\frac{\partial u}{\partial n}\right) = \frac{\partial \mu}{\partial n} > 0$

if $s(v,u,n)$ is convex

$\partial^2 s / \partial \psi^2 < 0$

then $\quad \partial^2 u / \partial \psi^2 > 0$

$u(s,v,n)$

$v(s,u,n)$

$n(s,u,v)$ must be concave

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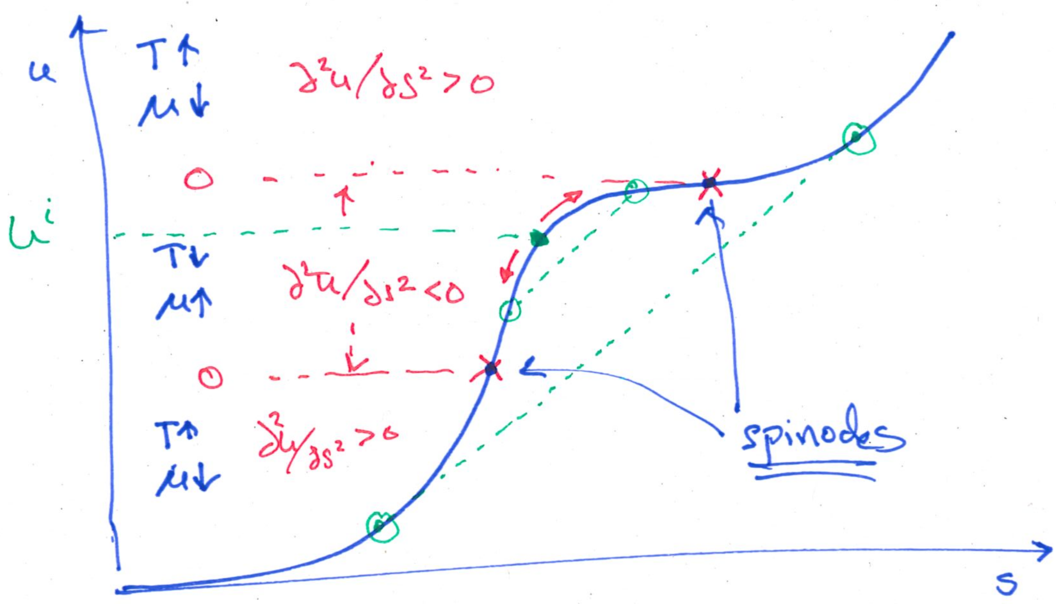
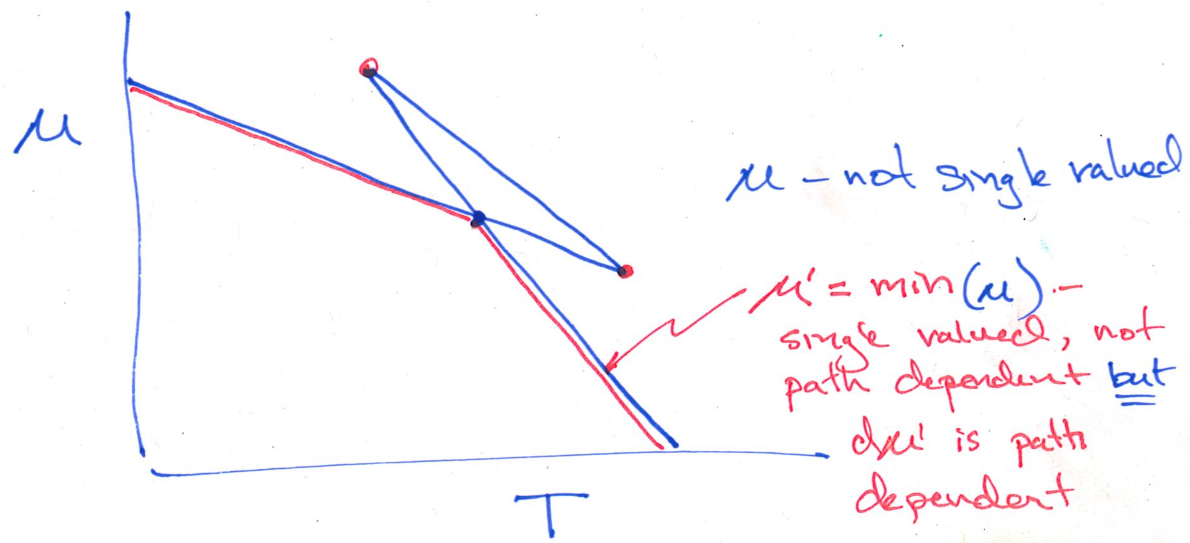
why can't $\partial^2 u/\partial s^2$ be < 0 ?





Stability criterion: a system is stable when **NO** processes are possible

(good) logic

(evil) thermodynamics

if there is a state such that $\delta S_{u,v,M} > 0$ then a process is possible.

$\delta S_{u,v,M} > 0$ is a criterion for possible processes [Clausius]

A system is stable when any variation [by definition an impossible variation] to a possible state at cst U,V,M decreases entropy, ie $\delta S_{u,v,M} < 0$