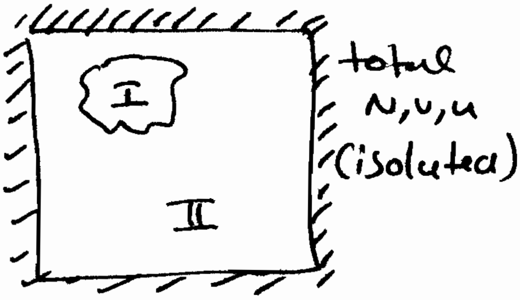
Equilibrium in isolated systems (const. N, V, U)

From 2nd Law $\rightarrow$ Entropy S is max @ equilibrium at const. N, V, U

Internal equilibrium conditions?



$$\delta S = \delta S_I + \delta S_{II}$$

$$\delta S_I = \frac{1}{T_I}\delta U_I + \frac{P_I}{T_I}\delta V_I - \frac{\mu_I}{T_I}\delta N_I$$

$$\delta S_{II} = \frac{1}{T_{II}}\delta U_{II} + \frac{P_{II}}{T_{II}}\delta V_{II} - \frac{\mu_{II}}{T_{II}}\delta N_{II}$$

Constraints $\left\{\begin{array}{l}\delta U_I + \delta U_{II} = 0\\ \delta V_I + \delta V_{II} = 0\\ \delta N_I + \delta N_{II} = 0\end{array}\right)$

$$\therefore \delta S = \left(\frac{1}{T_I} - \frac{1}{T_{II}}\right)\delta U_I + \left(\frac{P_I}{T_I} - \frac{P_{II}}{T_{II}}\right)\delta V_I + \left(\frac{\mu_I}{T_I} - \frac{\mu_{II}}{T_{II}}\right)\delta N_I = 0$$

$\Rightarrow$ all prefactors of independent variations $\delta U_I, \delta V_I, \delta N_I$ must be zero $\Rightarrow$

$$\boxed{\begin{array}{l} T_I = T_{II}\\ P_I = P_{II}\\ \mu_I = \mu_{II}\end{array}}$$

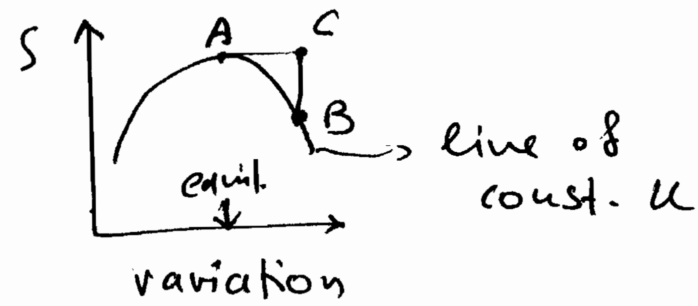
Equilibrium conditions: uniform T, P, μ

(for multicomponent, μ_i's for $i = 1, \dots n$ uniform)

How about U?

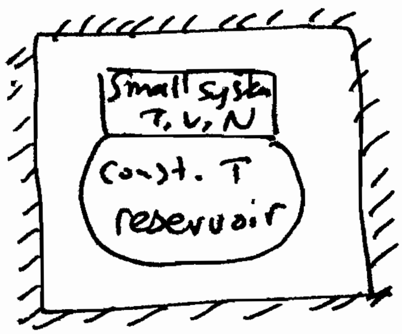
Natural variables $U(S, V, N)$

Can show that S max @ N, V, U $\Rightarrow$ $\boxed{U \text{ min } @ S, V, N}$



Moving off-equilibrium @ const U results in $S \downarrow$
To keep S const for point C must add Q (in reversible process). $U_C > U_A \Rightarrow U$ is min at A

Systems at Const. T, V, N



total system isolated, const N, V, U

$\delta S_{total} = \delta S + \delta S_R$

for any spontaneous process,

$\delta S_{total} > 0$ $\left\{ \begin{array}{c} S_{total} \\ \text{is max} \end{array} \right\}$

$$\left.\delta U_{total} = 0 = \delta U + \delta U_R = \delta U + T\delta S_R \right\} \Rightarrow$$

$$\delta S_R = \delta S_{total} - \delta S$$

$$\delta U + T(\delta S_{total} - \delta S) = 0 \Rightarrow \delta U - T\delta S = \underbrace{-T\delta S_{total}}_{<0}$$

$\Rightarrow$ $\delta A < 0$ { Helmholtz free energy of system is min!

A is minimized at const. T, V, N
U is not minimized at const. T, V, N

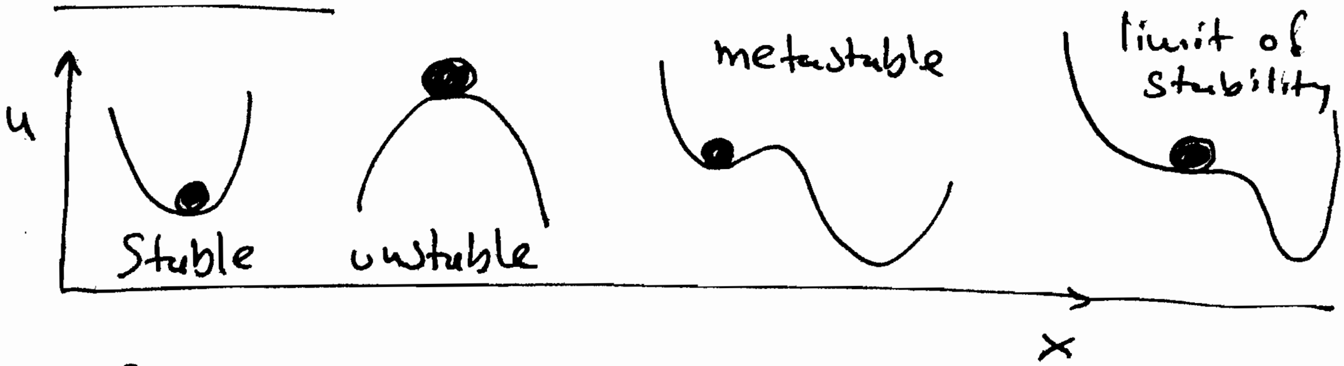
$$\left.\begin{array}{l}(S,V,N) \longrightarrow U \text{ is min} \\ (T,V,N) \longrightarrow A \text{ is min}\end{array}\right\} \text{pattern!}$$

Generalization: For <u>any</u> set of independent variables being held constant, the corresponding Legendre transform is min (starting from U) [or max, starting from S].

E.g. for const. $(T,P,N) \longrightarrow G$ is min
(see proof in book)

$$\left.\begin{array}{ll}\text{for const. } (S,P,N) \longrightarrow ? \\ \qquad (T,V,\mu) \longrightarrow ? \\ \qquad (1/T, P/T, N) \longrightarrow ?\end{array}\right\} \text{Pop quiz, soln. see Example 6.1}$$

Stability



Condition of extremum: $\dfrac{du}{dx} = 0$

For stability (minimum) $\dfrac{d^2u}{dx^2} > 0$ second derivative

Limit of Stability: $\dfrac{d^2u}{dx^2} = 0$

There is no local test for metastability – most thermodynamic systems are metastable with respect to some transformations over long enough time scales.

<u>Always</u> associated with hystereosis/metastability:

→ Phase transitions ←

E.g. $\left\{\begin{array}{l}\text{crystallization}\\ \text{vaporization}\\ \text{condensation}\end{array}\right\}$ can proceed past equilibrium point in the absence of <u>nuclei</u> of the other phase

Examples of superheated/supercooled liquids from YouTube linked from course web site.

Other example: contrails in upper atmosphere (supersaturated water vapor)

<u>Mathematical conditions for stability</u>

$$\delta^2 u > 0 \Rightarrow \frac{\partial^2 u}{\partial s^2}(\delta s)^2 + \frac{\partial^2 u}{\partial v^2}(\delta v)^2 + \frac{\partial^2 u}{\partial N^2}(\delta N)^2$$
$$+ 2\left(\frac{\partial^2 u}{\partial s \partial v}\delta s\,\delta v + \frac{\partial^2 u}{\partial s \partial N}\delta s\,\delta N + \frac{\partial^2 u}{\partial v \partial N}\delta v\,\delta N\right) > 0$$

Since δs, δv, δN are independent variations, <u>all</u> the "unmixed" derivatives must be positive

$$\left.\frac{\partial^2 u}{\partial S^2}\right)_{V,N} > 0 \Rightarrow \left.\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{N C_V} > 0 \Rightarrow \frac{T}{C_V} > 0$$

$$\left.\frac{\partial^2 u}{\partial V^2}\right)_{S,N} > 0 \Rightarrow -\left.\frac{\partial P}{\partial V}\right)_{S,N} > 0 \Rightarrow -\left(\frac{\partial P}{\partial \underline{V}}\right)_{\underline{S}} > 0$$

Similarly, from A min $\Rightarrow \delta^2 A > 0 \Rightarrow$

$$\left.\frac{\partial^2 A}{\partial V^2}\right)_{T,N} > 0 \Rightarrow -\left(\frac{\partial P}{\partial \underline{V}}\right)_T > 0$$ "mechanical" Stability

$$\left\{\begin{matrix} G \text{ min} \Rightarrow \delta^2 G > 0 \\ \text{for binary system} \end{matrix}\right\} \Rightarrow \left.\frac{\partial^2 G}{\partial N_1^2}\right)_{T,P,N_2} > 0 \Rightarrow \left.\frac{\partial \mu_1}{\partial N_1}\right)_{T,P,N_2} > 0$$

"Chemical" stability

__Example 6.2__ Show that $\underbrace{\left.\frac{\partial P}{\partial \underline{V}}\right)_T = 0 \Rightarrow \left.\frac{\partial T}{\partial \underline{S}}\right)_P = 0}_{\text{equivalent stability criteria}}$

$$\left.\frac{\partial P}{\partial \underline{V}}\right)_T = \left.\frac{\partial P}{\partial \underline{S}}\right)_T \left.\frac{\partial \underline{S}}{\partial \underline{V}}\right)_T$$ chain rule

$$\left.\frac{\partial P}{\partial \underline{S}}\right)_T \left.\frac{\partial \underline{S}}{\partial T}\right)_P \left.\frac{\partial T}{\partial P}\right)_{\underline{S}} = -1 \Rightarrow$$ (xyz-1 rule)

$$\Rightarrow \left.\frac{\partial P}{\partial \underline{S}}\right)_T = -\left.\frac{\partial T}{\partial \underline{S}}\right)_P \left.\frac{\partial P}{\partial T}\right)_S$$

$$\therefore \underbrace{\left.\frac{\partial P}{\partial \underline{V}}\right)_T}_{\text{If } \phi} = -\underbrace{\left.\frac{\partial T}{\partial \underline{S}}\right)_P}_{\text{then } \phi} \underbrace{\left.\frac{\partial P}{\partial T}\right)_{\underline{S}} \left.\frac{\partial \underline{S}}{\partial \underline{V}}\right)_T}_{\text{"irrelevant"}}$$

"irrelevant" derivatives – not zero at stability limits