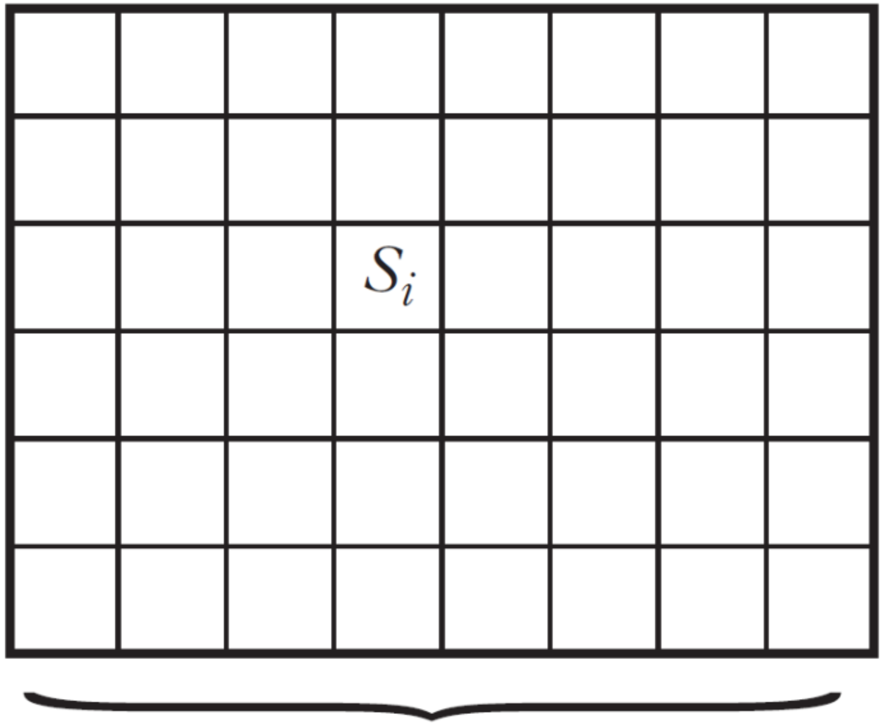
Thermodynamics lecture 11. Stability and free energy

1. Treating a system out-of-equilibrium; equilibrium conditions for isolated system
2. Minimum energy principle
3. Stability conditions; le Chatalier’s principle
4. Consequences of an entropy wiggle
5. Availability and minimum free energy

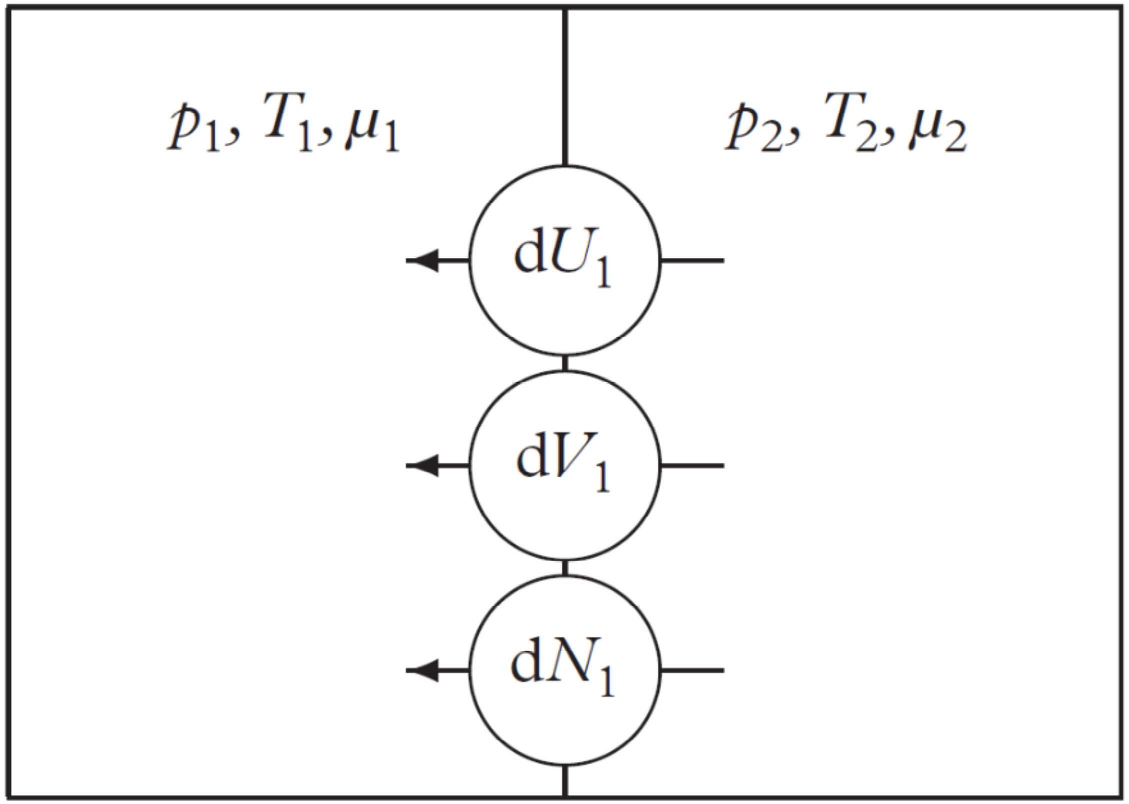
Subjects for next week: mainly Phase change; a little on radiative heat transfer and greenhouse effect; some general insights into the structure of scientific reasoning.

Applying thermodynamic reasoning to a system out of equilibrium

- System is NOT in equilibrium overall!
- Divide it into parts
- Each part is large enough to be treated using thermodynamics, and is in internal equilibrium with itself (e.g. has well-defined T, p) but is not necessarily in equilibrium with its neighbours
- We can treat many (but not all) out-of-equilibrium situations this way



Total entropy $\tilde{S} \equiv \sum_i S_i.$



An example involving just two parts

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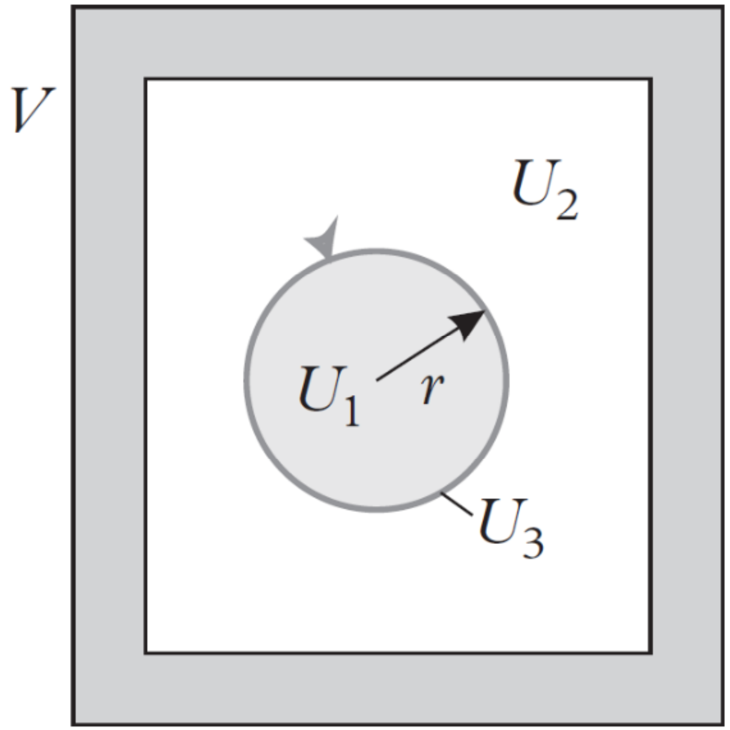
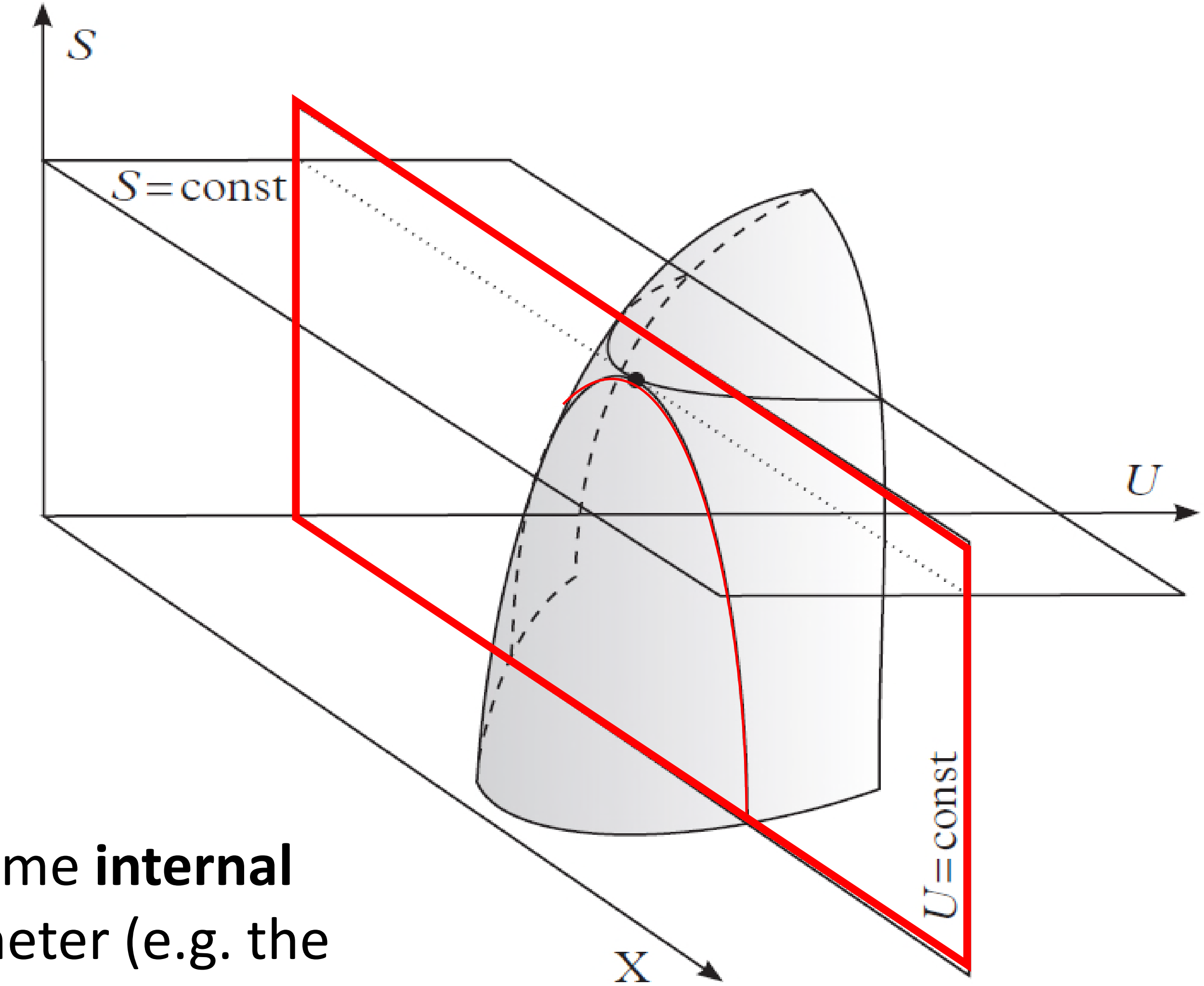


An example system with internal parts:
a rubber balloon floating in a fluid, with some other fluid inside it.

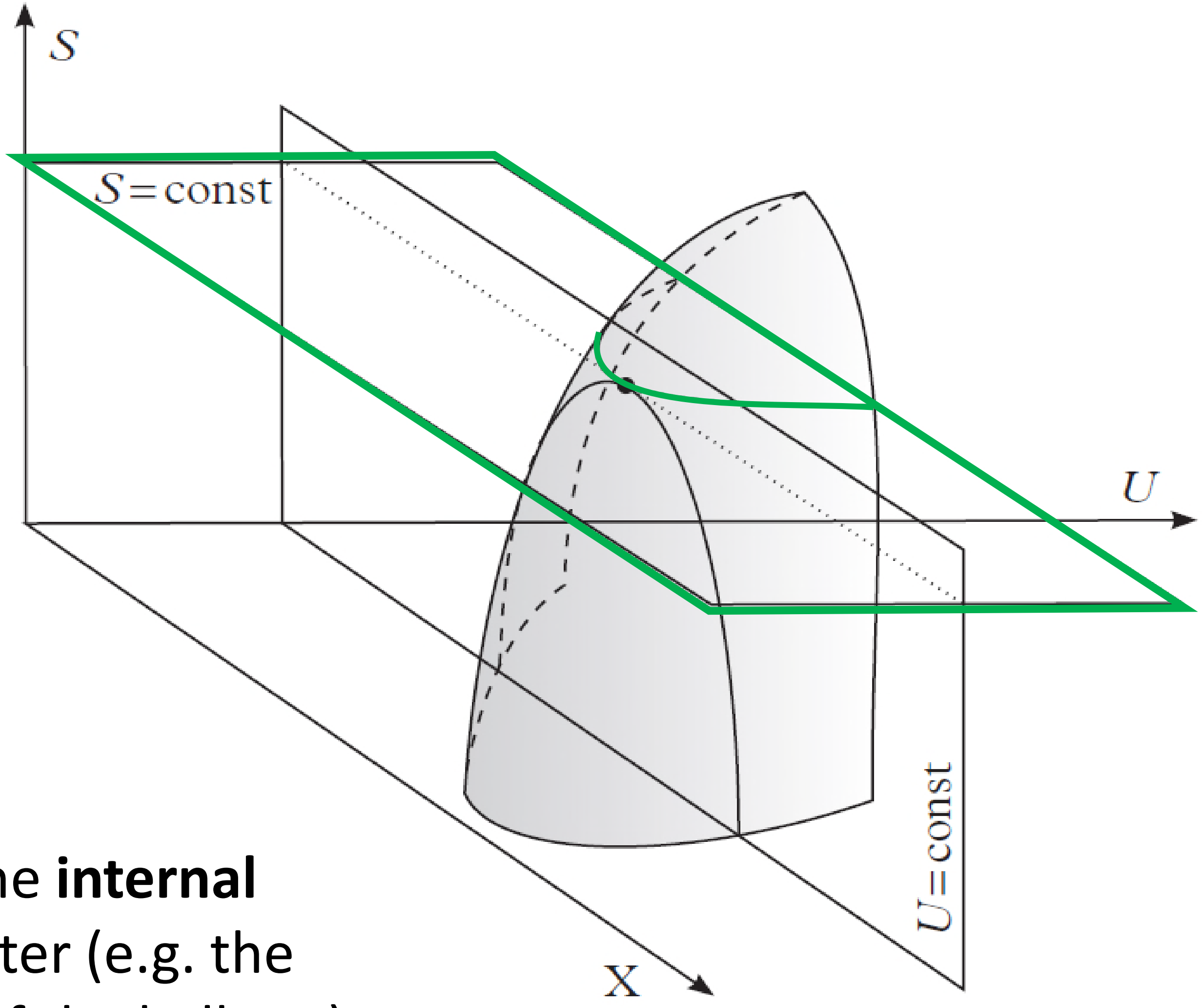
From the outside perspective this is a simple pV system with $p = p_2$.

p_1 and r (the radius of the balloon) are **internal parameters** whose values are, in equilibrium, such the total entropy is maximised.



Finding the state at maximum S subject to the constraint of fixed U.

X is some **internal** parameter (e.g. the radius of the balloon)



The diagram has been drawn so as to suggest that the equilibrium state is also the one at minimum U for given S.

We will now prove this.

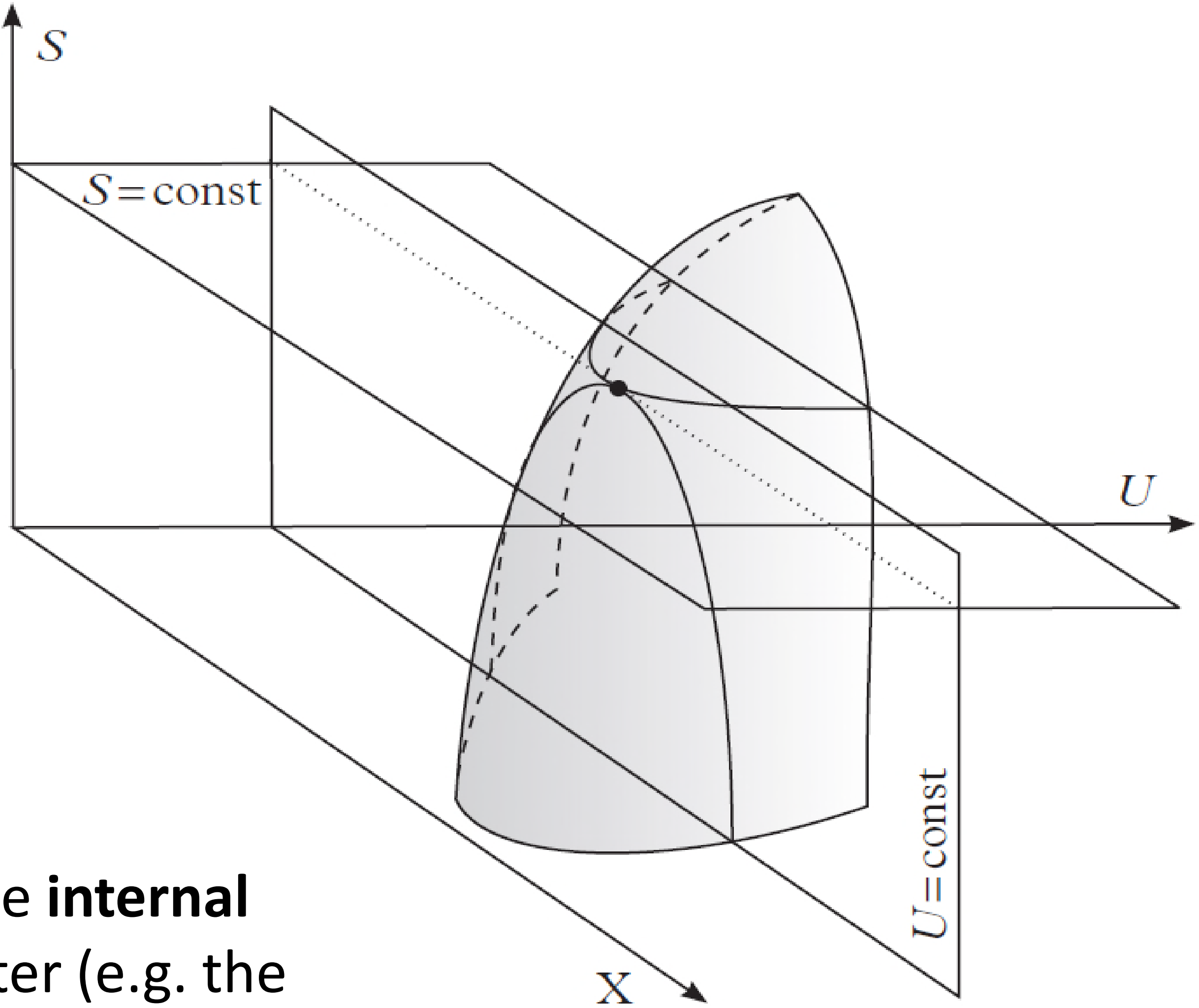
X is some **internal** parameter (e.g. the radius of the balloon)

Proof of the minimum energy principle

Theorem: for an isolated system, the state of maximum entropy at given U (i.e. the equilibrium state) is also the state of minimum U at given S.

Proof.

1. Suppose the contrary. Then at $(S_0\,, V)$ the equilibrium state has
$$U > U_{min}(S_0\,, V)$$
2. Allow X to change and thus withdraw energy W at fixed S (i.e. energy extracted in the form of work), with system volume V still fixed.
3. Send the energy back to the system in the form of heat.
4. Now we have $S_{final} > S_0$ with V fixed and U also fixed (X has changed)
5. But that means the starting state did not have maximum S for the given (U,V) after all, so it cannot have been the equilibrium state.
6. Q.E.D.



The diagram has been drawn ~~so as to suggest that~~

correctly.

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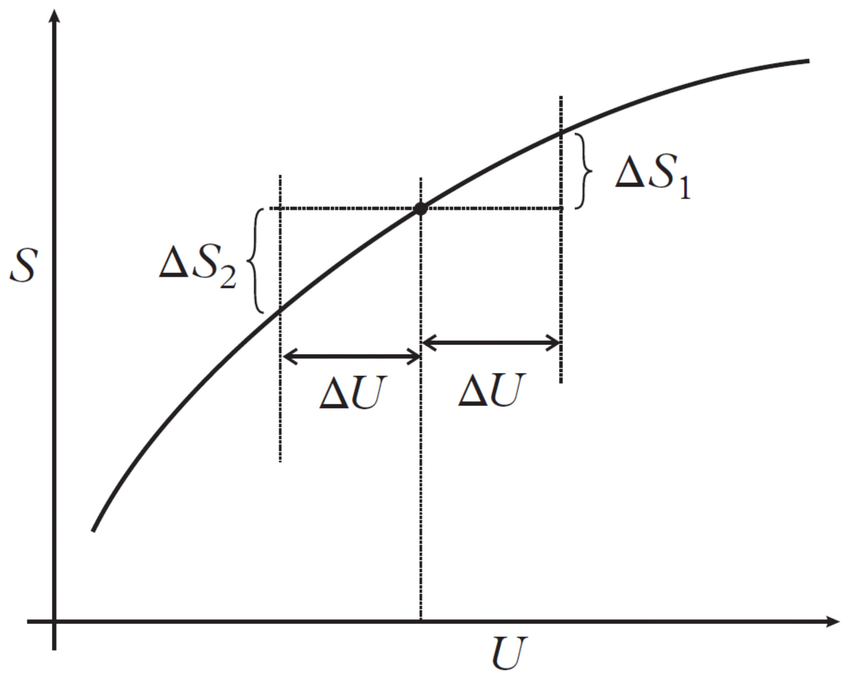
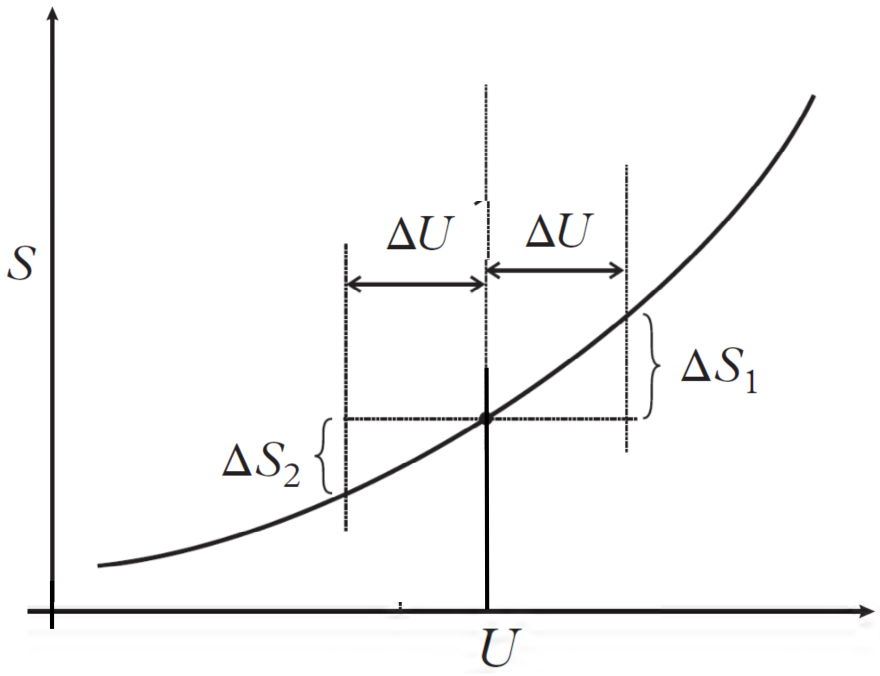
Stability of thermal equilibrium



$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} < 0$$

STABLE



$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} > 0$$

UNSTABLE

Le Chatelier's Principle

If a system is in stable equilibrium, any perturbation produces processes which tend to restore the system to its original equilibrium state.

Example consequences:

$$C_V \geq 0$$

$$\kappa_S \geq 0.$$

But in lecture 6 we proved

$$C_p \geq C_V$$

$$\kappa_T \geq \kappa_S$$

So in summary,

$$C_p \geq C_V \geq 0$$

$$\kappa_T \geq \kappa_S \geq 0.$$

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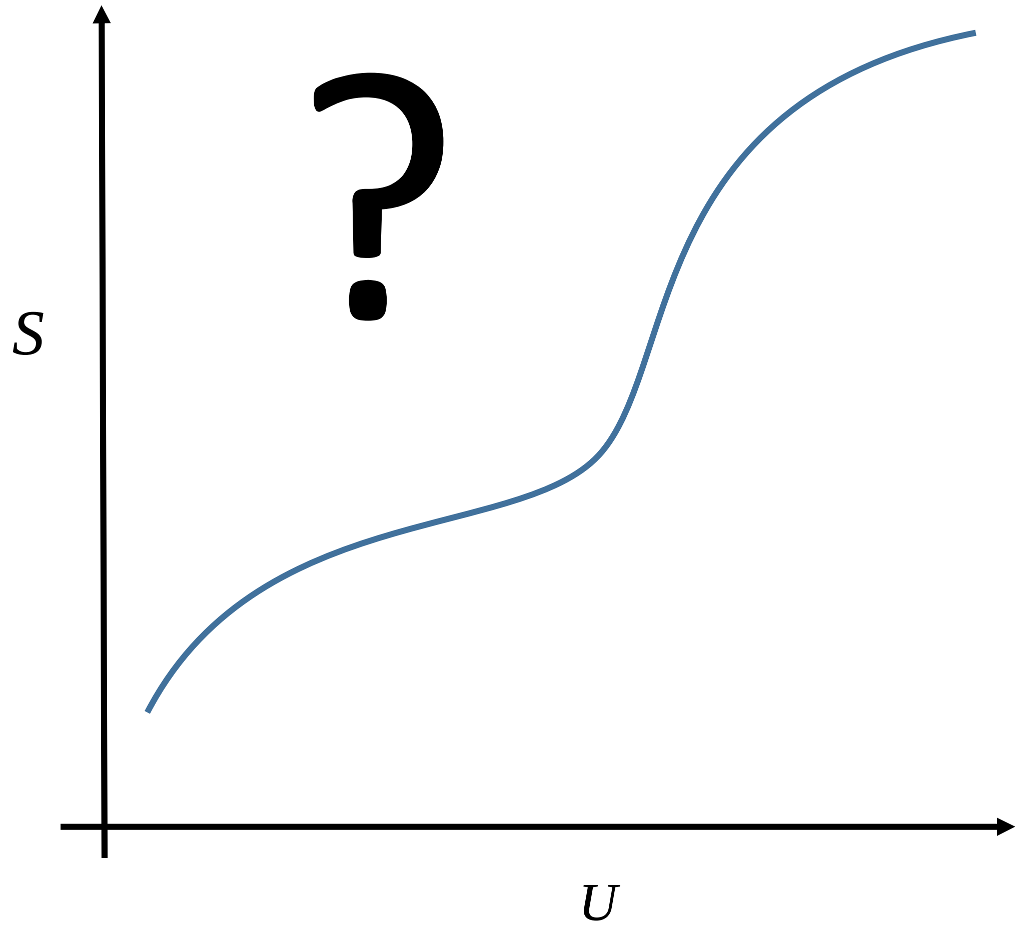
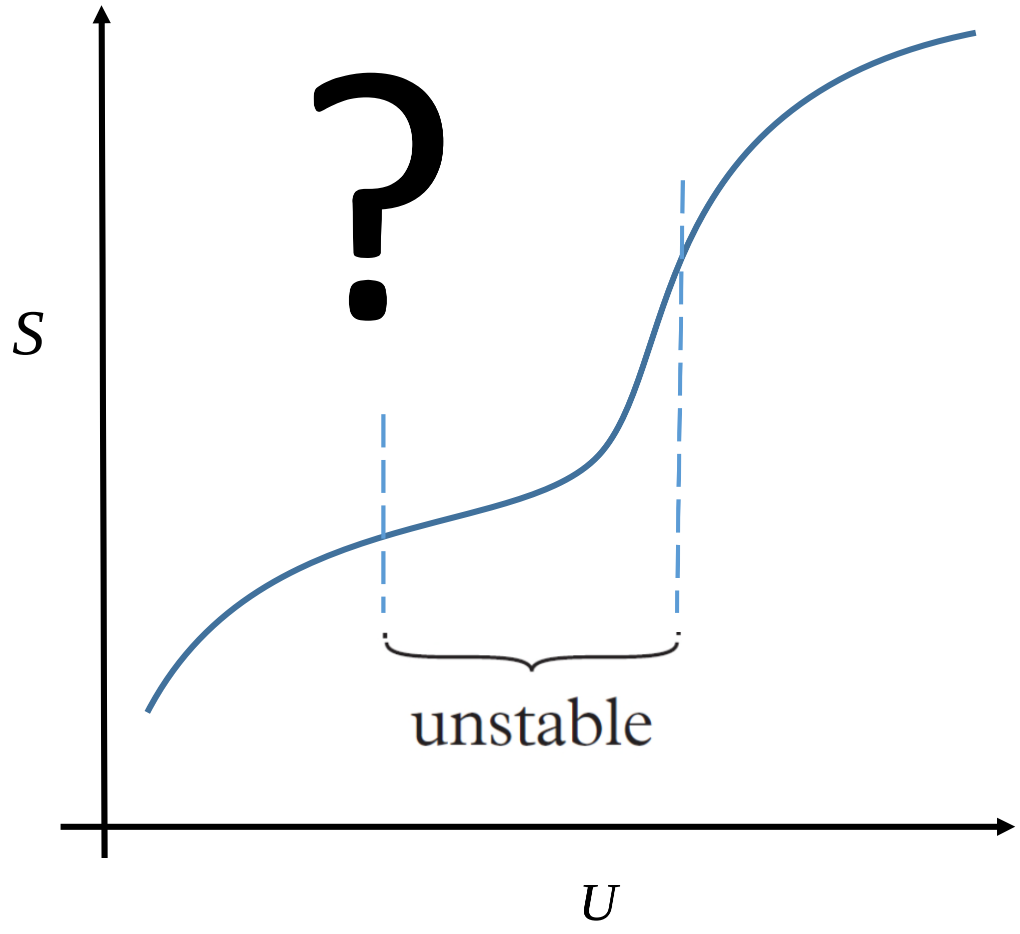
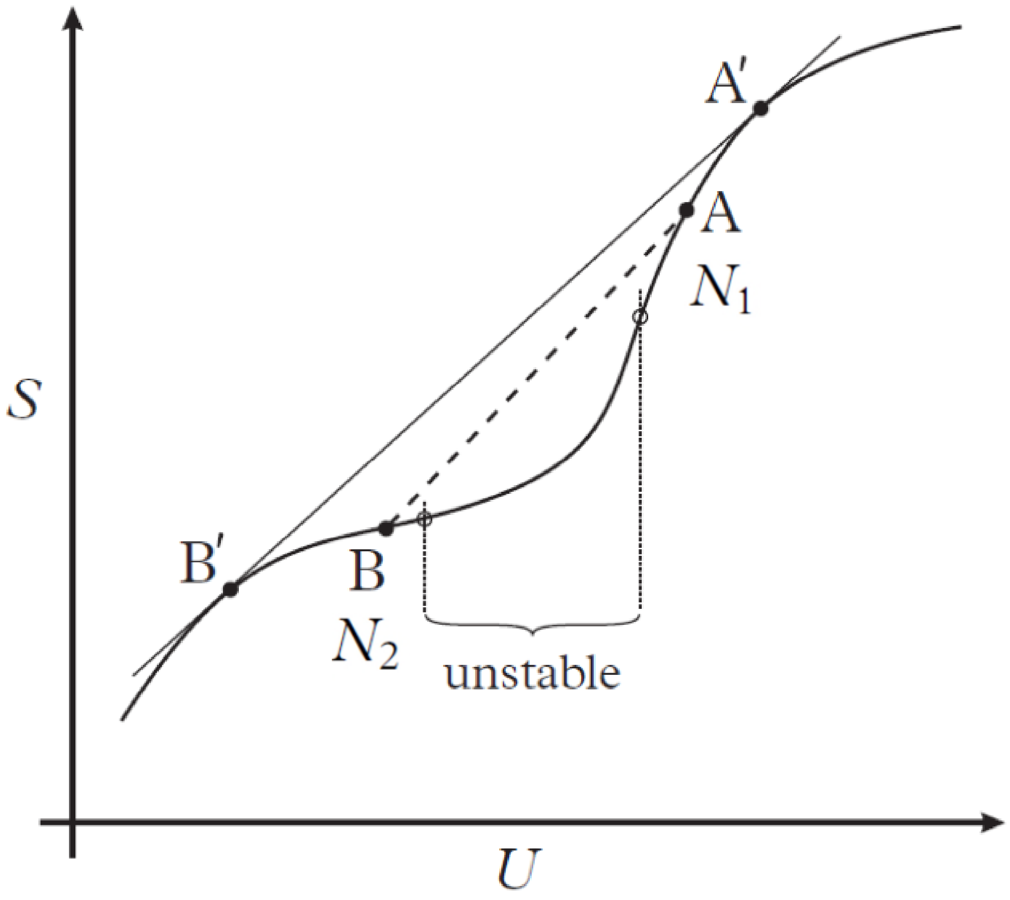
But what if the entropy (as a function of U for a isolated system) does this:



But what if the entropy (as a function of U for a system at fixed V, N) does this:



Send N_1 particles to state A and N_2 particles to state B



$$\left.\begin{aligned} U &= N_1 u_A + N_2 u_B \\ N &= N_1 + N_2 \end{aligned}\right\}$$

(conservation of U and N)

Solve for N_1 , N_2 in terms of U_A , U_B :

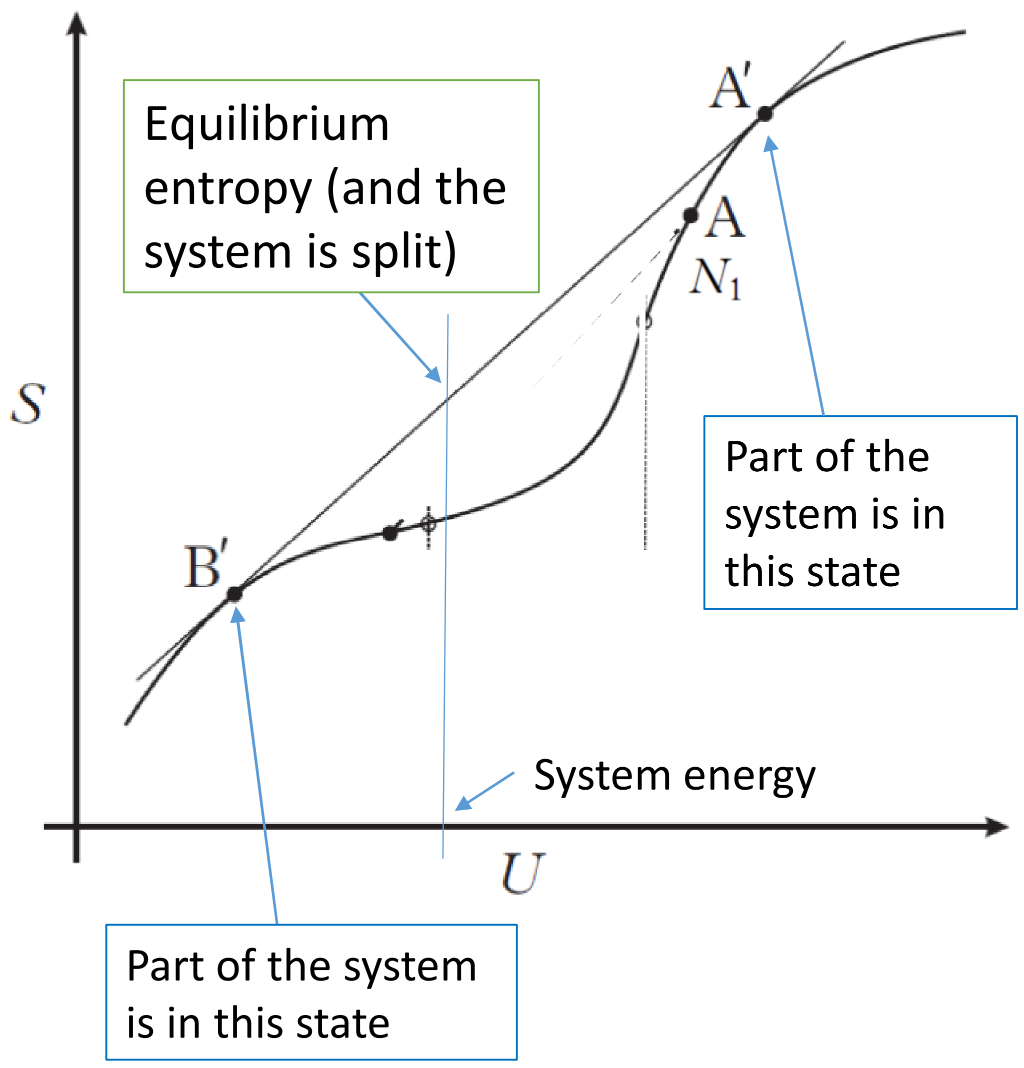
$$\frac{N_1}{N} = \frac{U - U_B}{U_A - U_B}, \qquad \frac{N_2}{N} = \frac{U_A - U}{U_A - U_B}.$$

Hence entropy of the system in the new (split) state is

$$S = N_1 s_A + N_2 s_B = \frac{(U - U_B)S_A + (U_A - U)S_B}{U_A - U_B}$$

= on a straight line from A to B

Overall result: max entropy is on the line from A' to B'



$$U = N_1 u_A + N_2 u_B$$
$$N = N_1 + N_2$$

(conservation of U and N)

Solve for N_1, N_2 in terms of U_A, U_B:

$$\frac{N_1}{N} = \frac{U - U_B}{U_A - U_B}, \qquad \frac{N_2}{N} = \frac{U_A - U}{U_A - U_B}.$$

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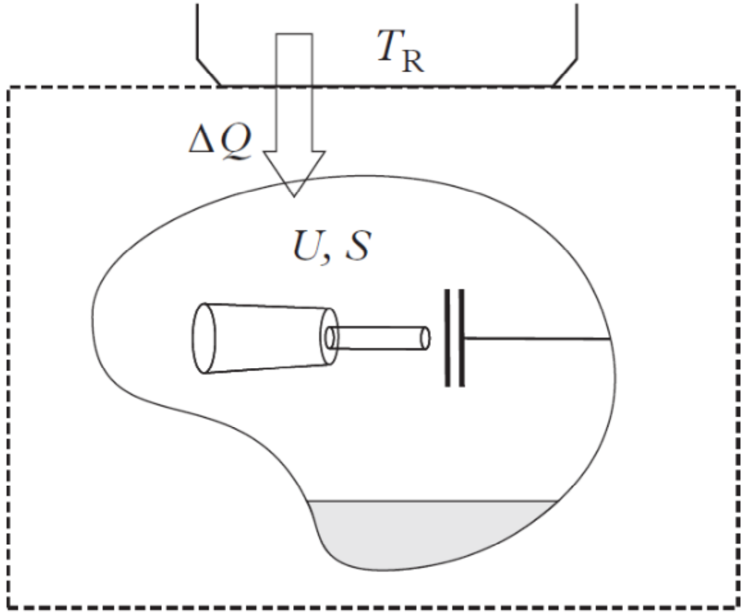
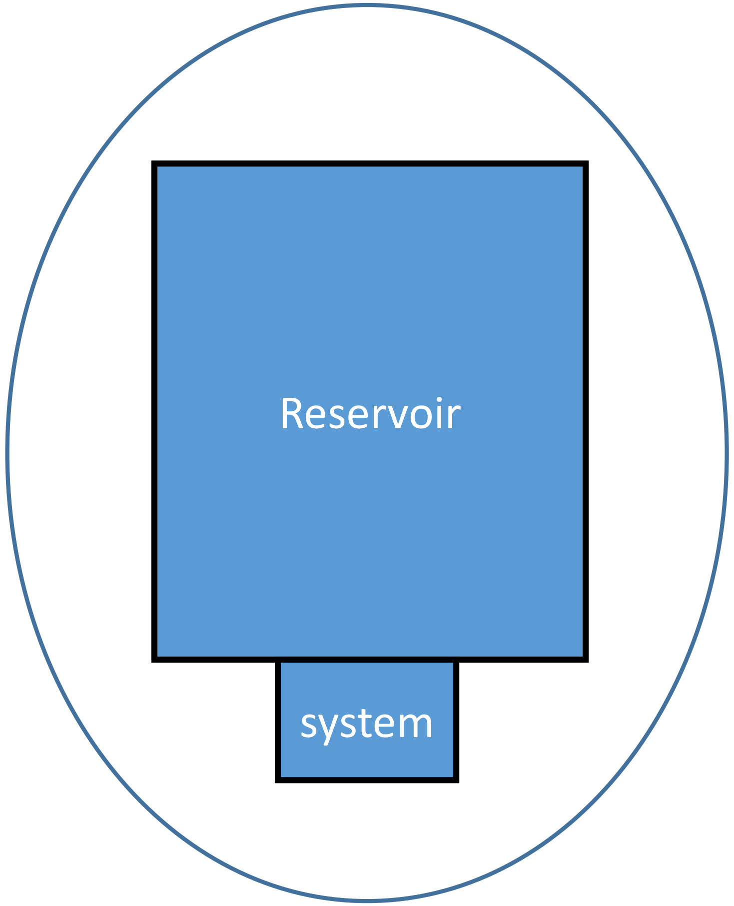
So far we discussed an ISOLATED system (fixed U, V).

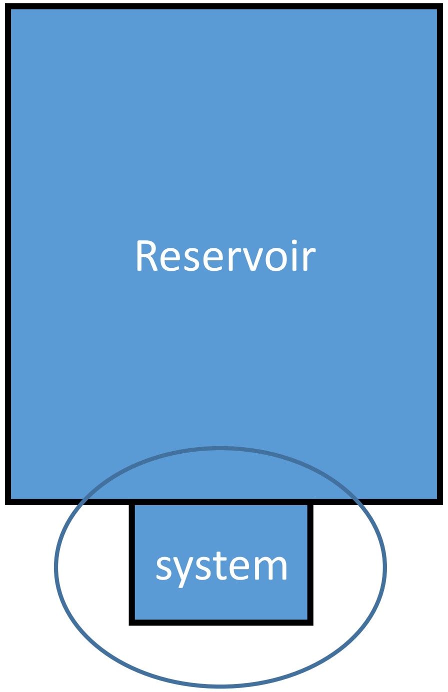
Now we want to discuss a system at fixed (T, V)



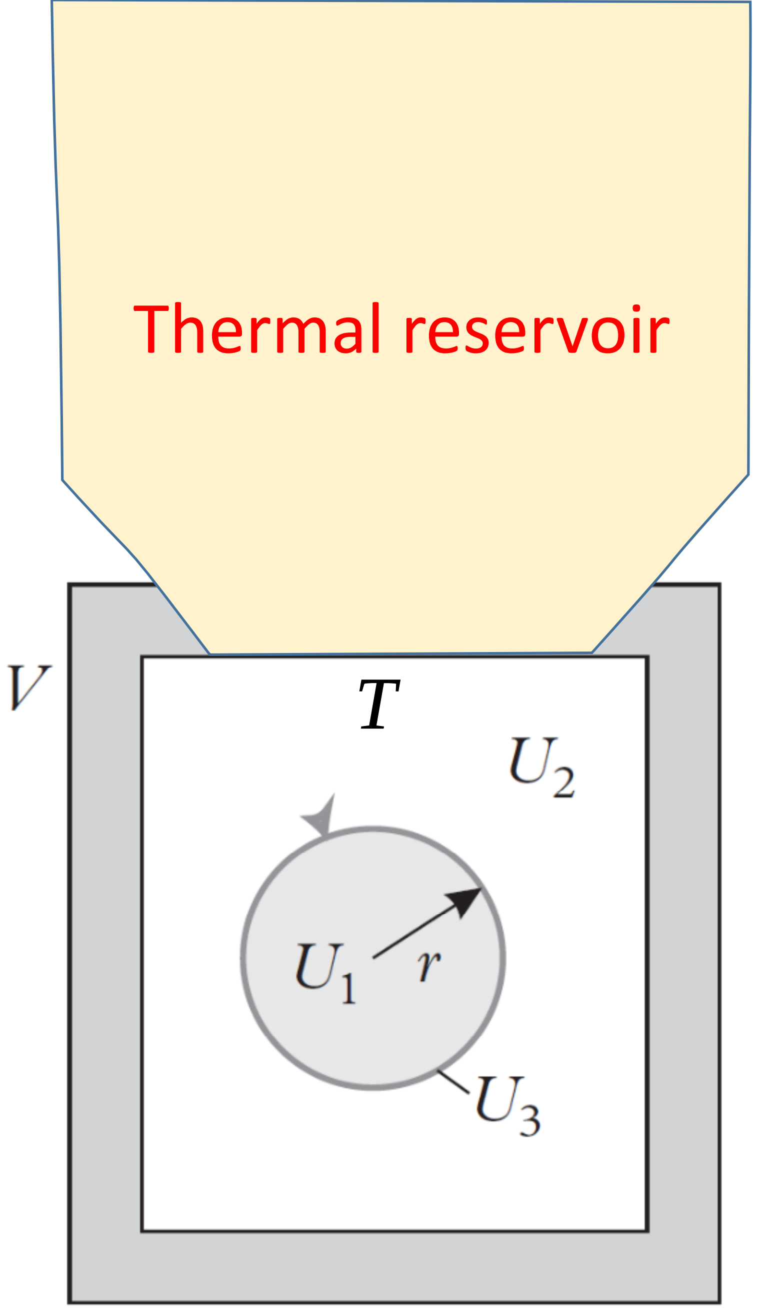
A generic system
(with whatever internal structure)
maintained at some given
temperature through heat
exchange (at constant volume)
with a reservoir.

The big idea





Max entropy of (system + reservoir) is at **min free energy of system alone**



Fixed V and T: Equilibrium size of balloon is now when F of the system is minimised.

Of all states the system can reach, which is the thermal equilibrium state?

(1) Isolated system: fixed U, V, N: maximum entropy.

$$\mathrm{d}\tilde{S} = 0.$$

(2) Rigid system in thermal contact with a reservoir: fixed T, V, N: minimum Helmholtz function.

$$d\tilde{F} = 0.$$

(3) Flexible system in thermal and mechanical contact with a reservoir: fixed T, p, N: minimum Gibbs function.

$$d\tilde{G} = 0.$$