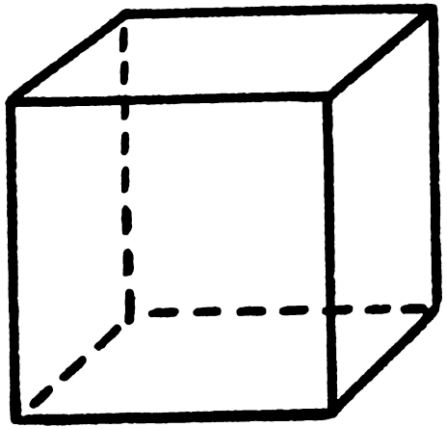
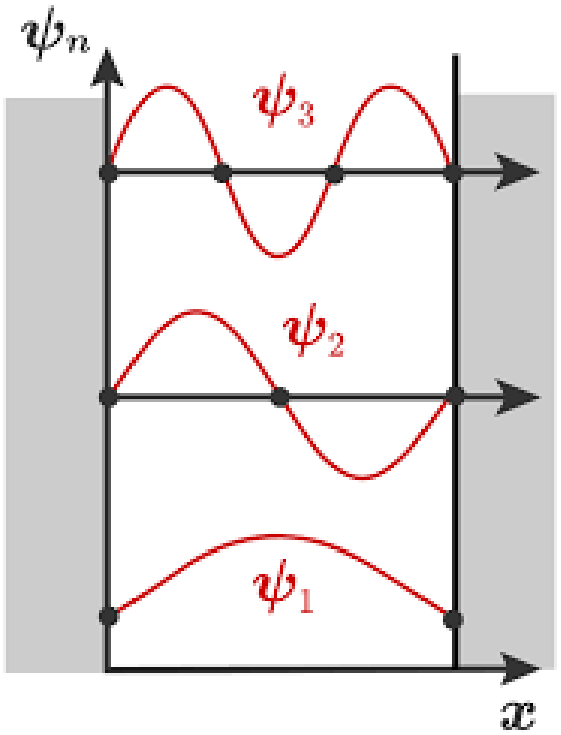
Some further points on statistical mechanics

1. **The method of periodic boundary conditions**
2. **Gas in 2, 1 (and 0) dimensions**
3. Intrinsic spin of atoms and molecules → (2J+1) factor
4. identical nuclei → reduced set of states
5. **Stability of thermal equilibrium**
6. Negative temperature in spin system
7. Ferro-magnetic phase transition (brief remarks)

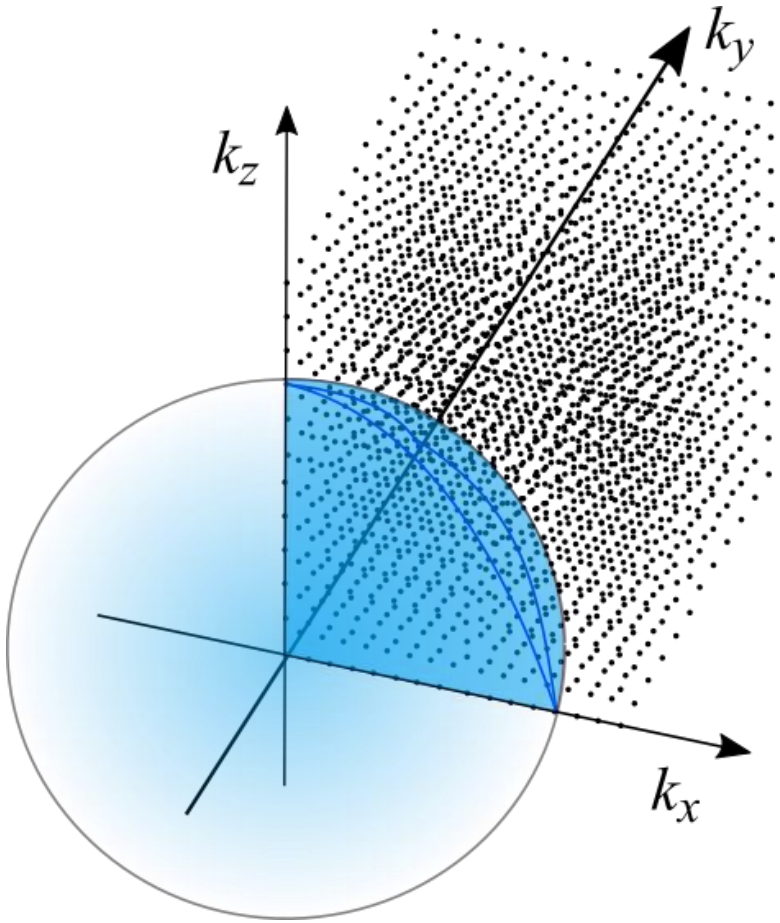
Gas in a box





Potential well with

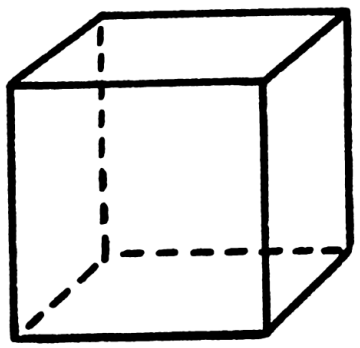
energy
eigenstates
(in one dimension)



States in k space

The method of periodic boundary conditions

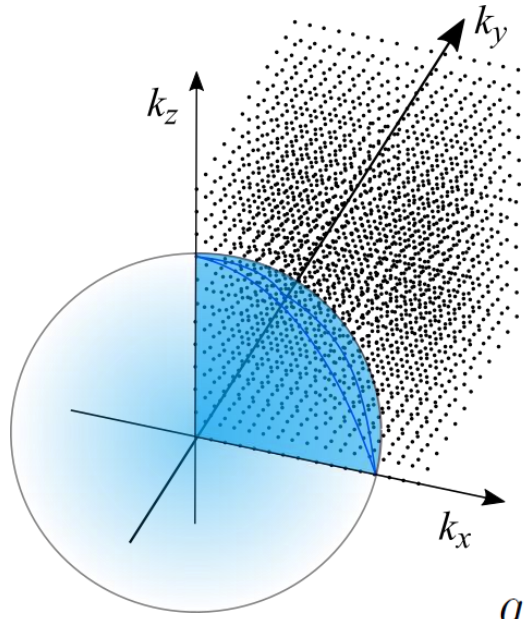
Particles confined in a box



Standing waves,

$$\sin(k_x\, x)\, \sin(k_y\, y)\, \sin(k_z\, z)$$

$$\Delta k_x = \frac{\pi}{L}$$



$$k_x, k_y, k_z > 0$$

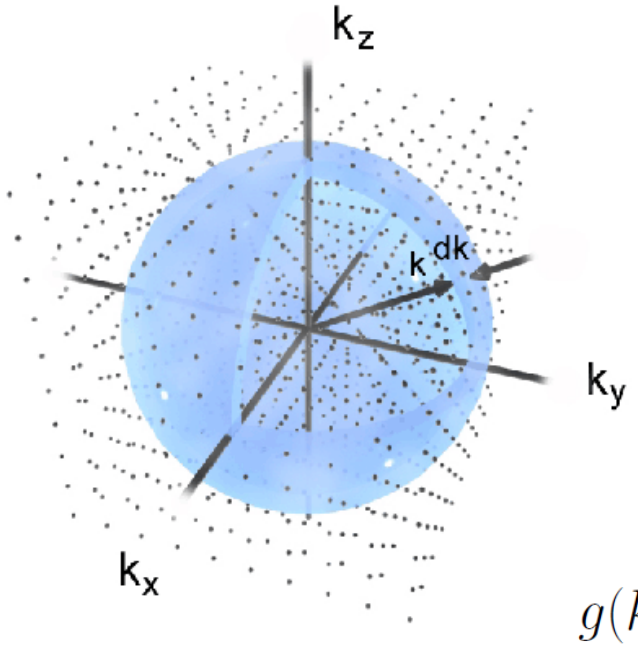
$$g(k)\mathrm{dk} = \frac{1}{8} 4\pi \mathrm{k}^2 \frac{\mathrm{V}}{\pi^3} \mathrm{dk}$$

Free particles with a *mathematical constraint*: wavefunctions must have period L.

Travelling waves,

$$e^{ik_x x}\, e^{ik_y y}\, e^{ik_z z}$$

$$\Delta k_x = \frac{2\pi}{L}$$

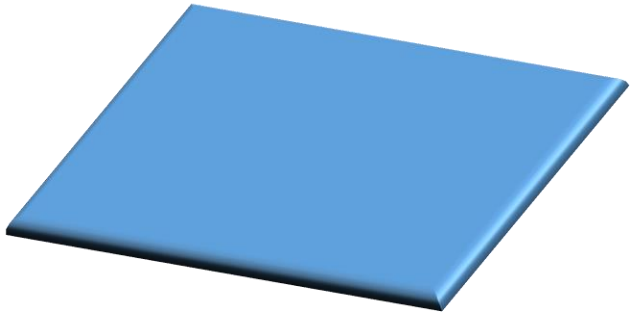


$$k_x, k_y, k_z$$

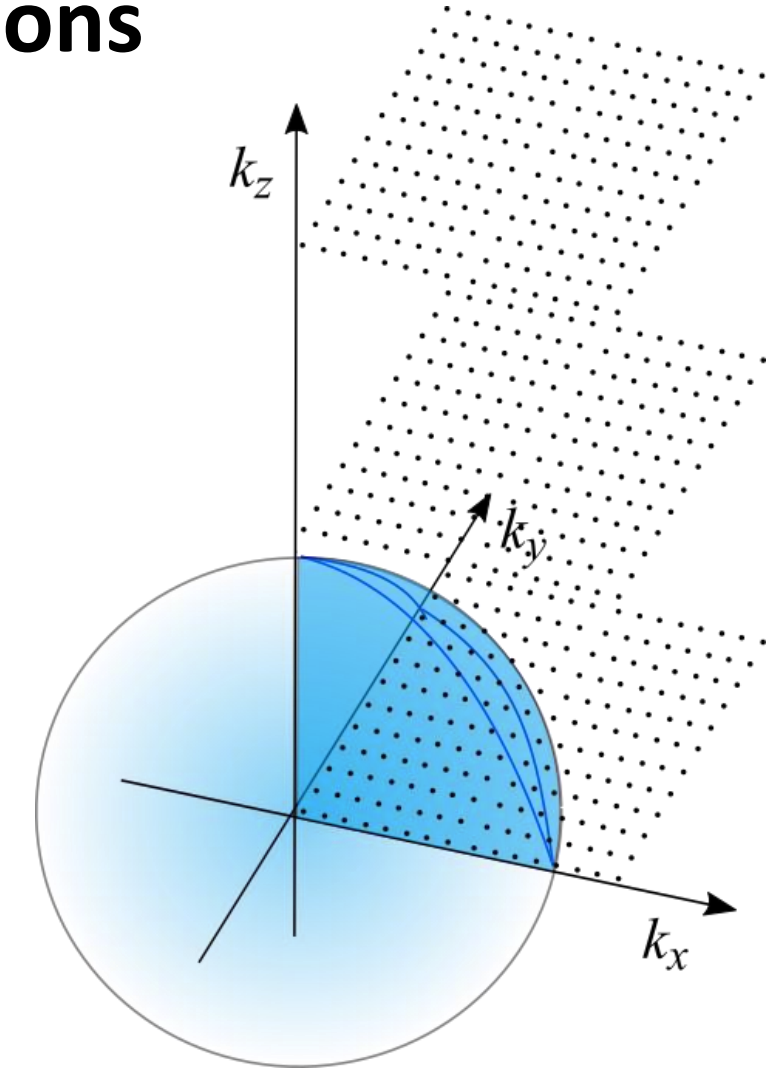
+ve or -ve

$$g(k)\mathrm{dk} = 4\pi \mathrm{k}^2 \frac{\mathrm{V}}{(2\pi)^3} \mathrm{dk}$$

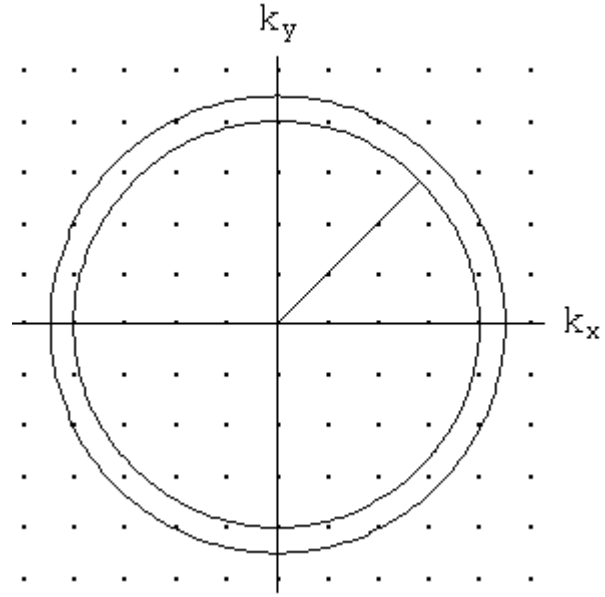
Gas in 2 dimensions



Thin box,
area A



k space: for lowish T, only 1st layer of states are excited → z part of the motion is in its ground state and stays there

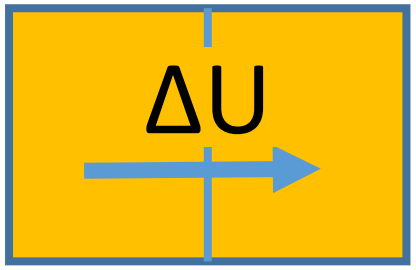


Hence we say we have a "2-dimensional gas".

Adopt $\boldsymbol{k} \equiv (k_x, k_y)$

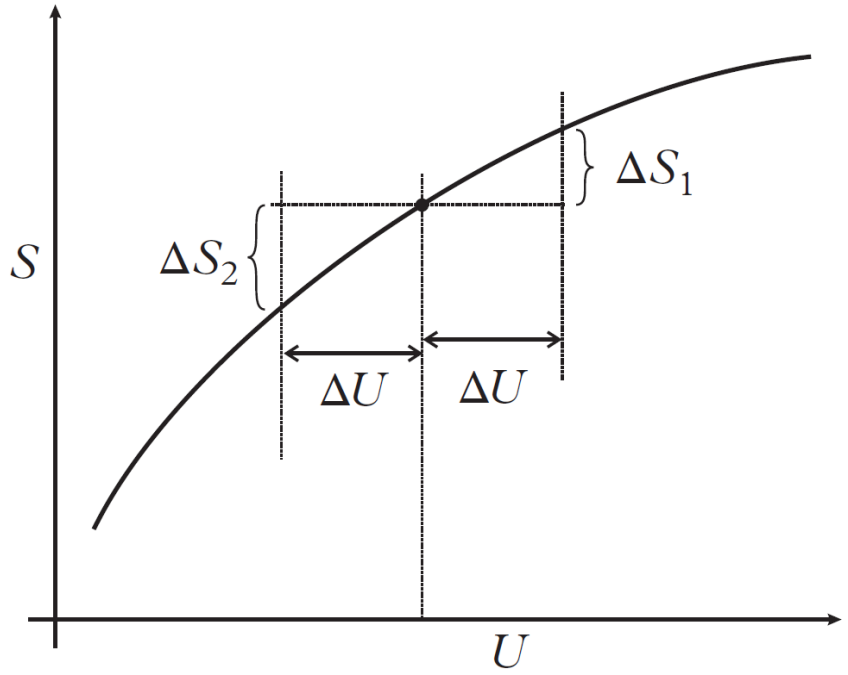
$$g(k)\mathrm{dk} = \frac{\mathrm{A}}{(2\pi)^2} 2\pi \mathrm{k dk}$$

Stability of thermal equilibrium

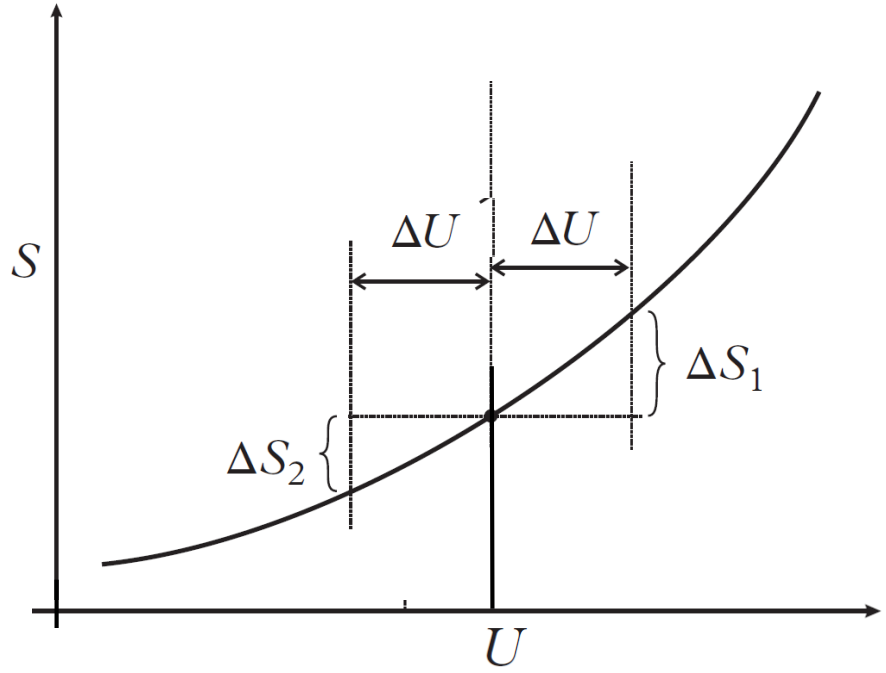


We consider an isolated thermodynamic system with an internal movement of energy

It concerns how the entropy varies with the internal energy:

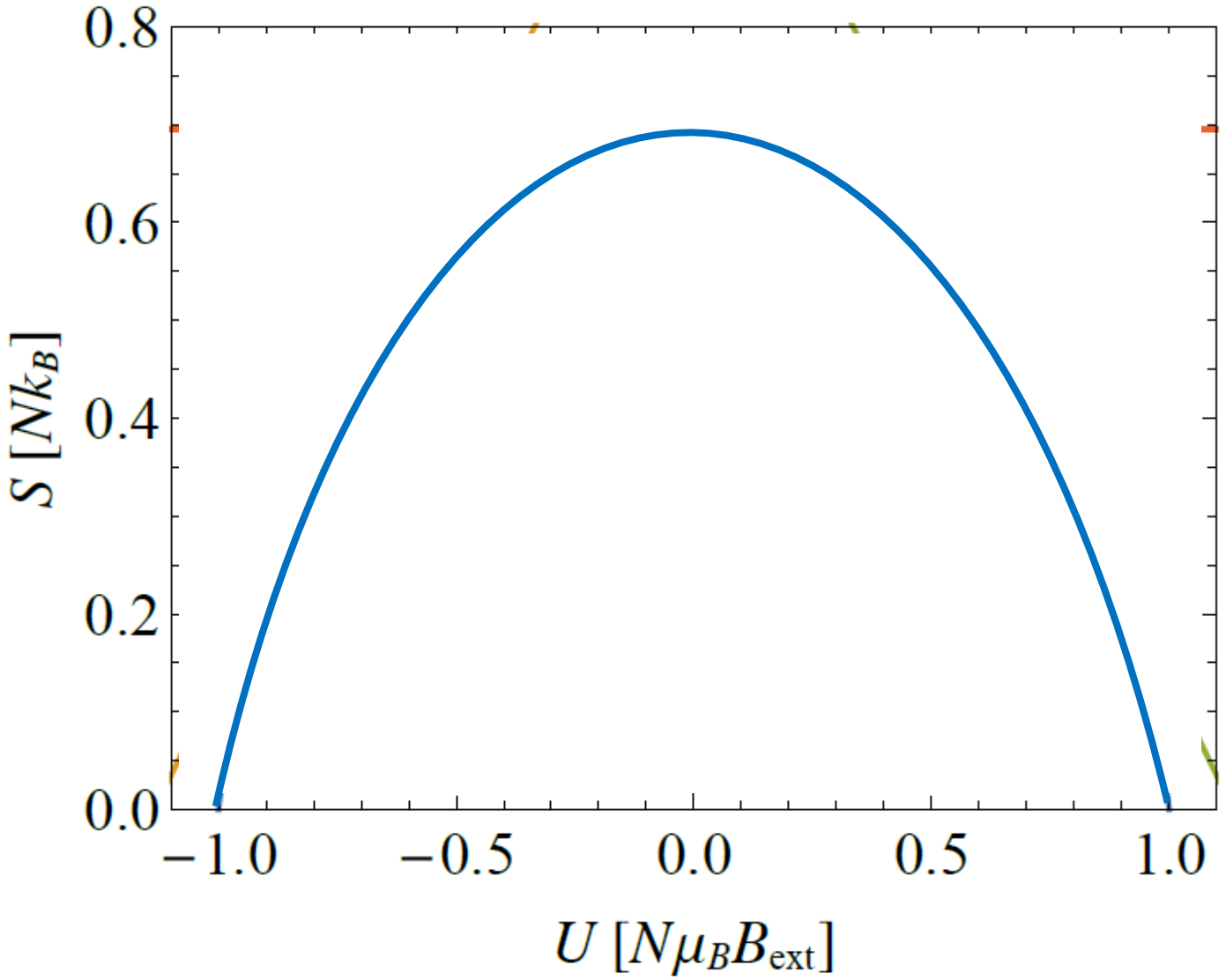


$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} < 0$$ STABLE

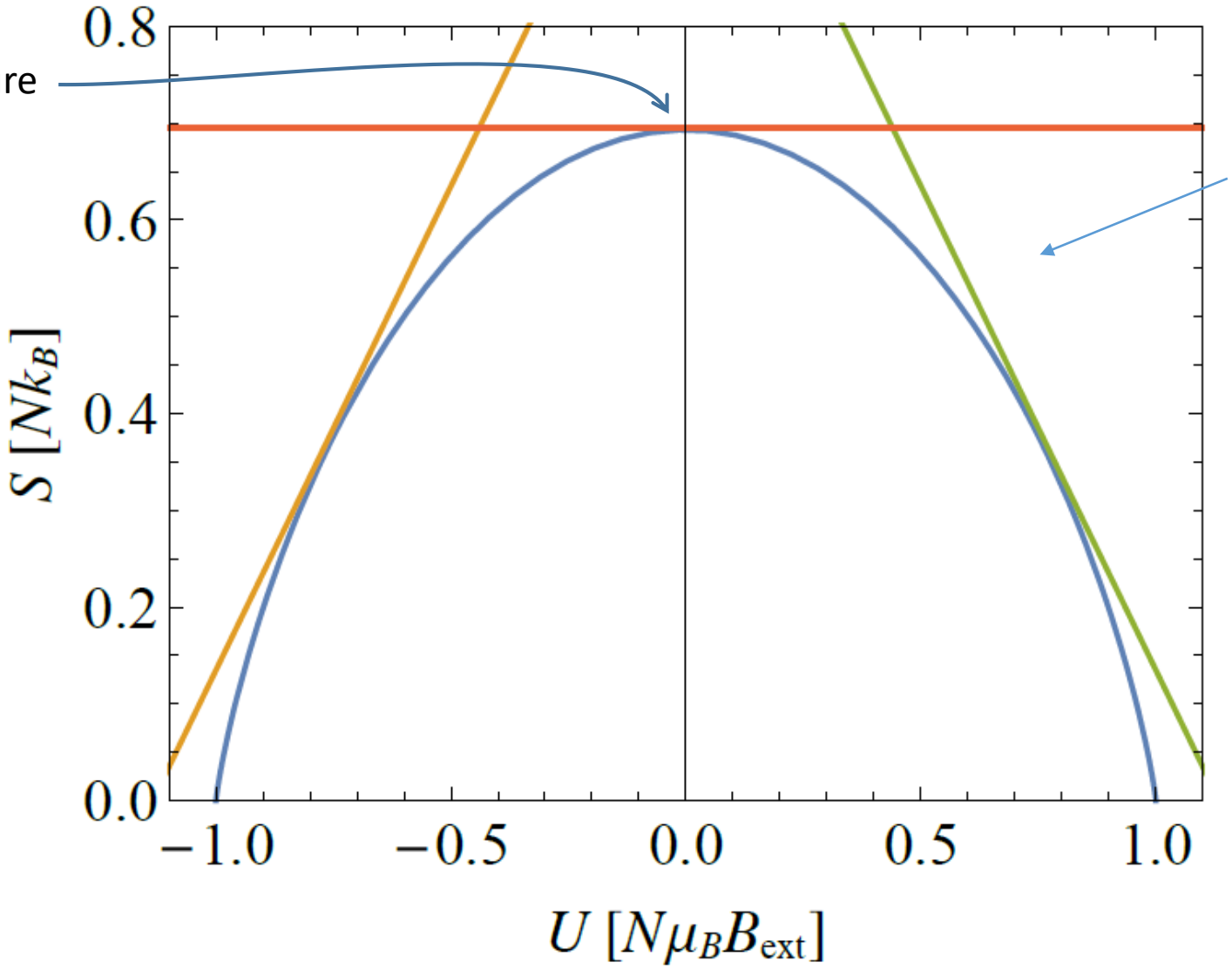


$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} > 0$$ UNSTABLE

Entropy of a paramagnet as a function of internal energy.



Entropy of a paramagnet as a function of internal energy.

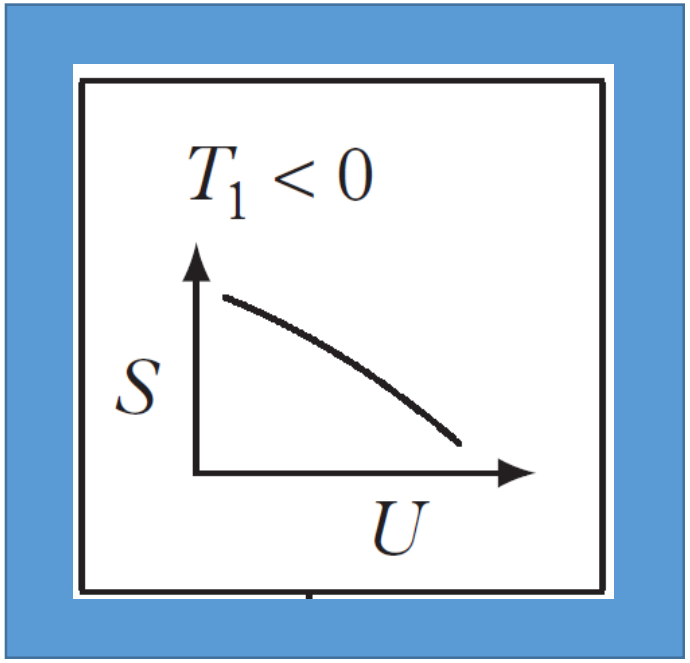


Negative temperature regime.

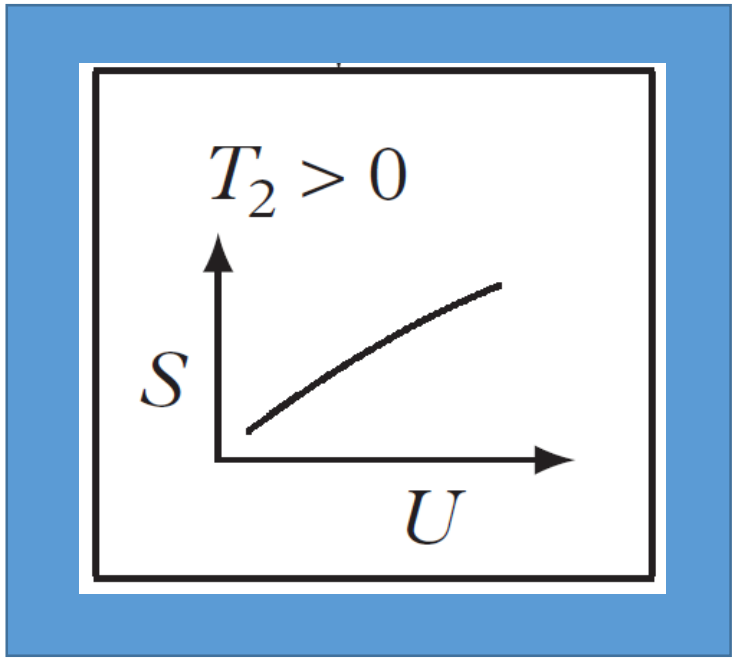
It can be accessed by abruptly reversing the B field.

The straight lines give three examples of the slope (dS/dU).

Which way will the heat flow?

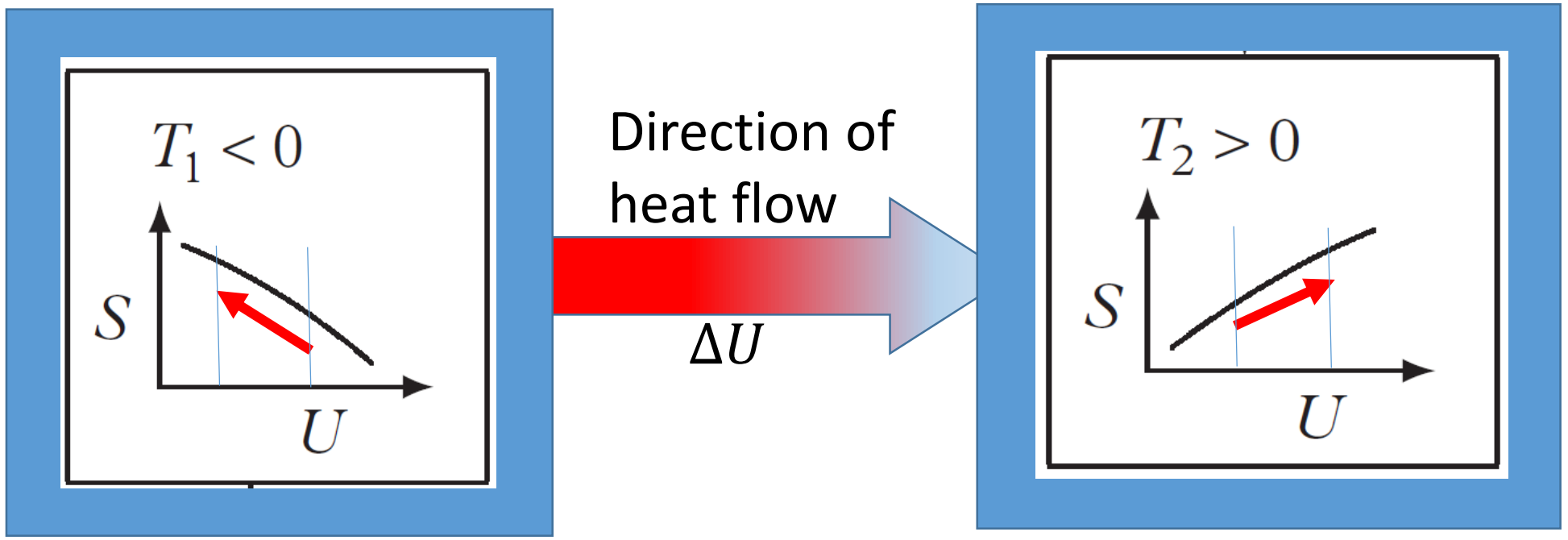


A system at negative temperature



A system at positive temperature

Negative temperature means the system is extremely **hot**



A system at negative temperature

A system at positive temperature

It follows that negative temperature is always at most metastable, not fully stable.

Ferromagnetic phase transition

At low temperatures the interactions between the magnetic dipoles become significant.

For ferromagnets the dipoles tend to line up even with no applied B field.

Hence at temperatures below the magnetic phase transition there is a non-zero magnetization M at B=0.