Right way

$$\int_{U(0,0,0)}^{U(x,y,z)} dU = U(x,y,z) - \underbrace{U(0,0,0)}_{\text{constant}} = y + x^3y^3 - x^2z^2$$

Any path

$$= \int_{(0,0,0)}^{(x,0,0)} (3x^2\cancel{y^3}^{\to 0} - 2x\cancel{z^2}^{\to 0})\,dx \rightarrow 0$$

$dy = 0$
$dz = 0$
$y = 0$
$z = 0$

$$+ \int_{(x,0,0)}^{(x,y,0)} (1 + 3x^3y^2)\,dy \rightarrow y + x^3y^3$$

$dx = 0$
$dz = 0$
$z = 0$

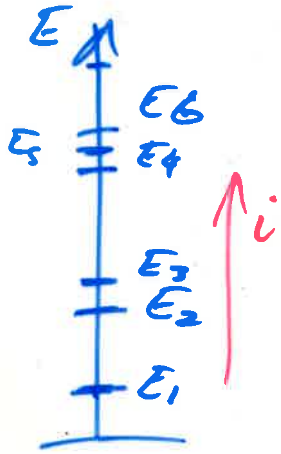
$$+ \int_{(x,y,0)}^{(x,y,z)} (-2x^2z)\,dz \rightarrow -x^2z^2$$

$dx = 0$
$dy = 0$

$$U(x,y,z) = y + x^3y^3 - x^2z^2 + \text{constant}$$

$đQ$ – not exact / $\frac{đQ}{T} = dS$ – exact
$S(x,y,z)$

Imagine a system with discrete energy levels (e.g. Einstein solid)



Create an ensemble of N copies of the system
↑ Large

put boxes in thermal contact
can exchange energy.

Let n_1 be the number of boxes with energy E_1
n_i E_i

i labels the energy states, not the boxes
$i = 1, 2, \dots, \infty$

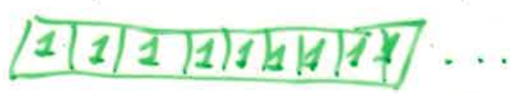
$$n_i = 0, 1, 2, \dots, N$$

Constraint #1: $\sum_{i=1}^{\infty} n_i = N$

How many ways are there to arrange the energies?

$$\Omega = \frac{N!}{n_1!\,n_2!\cdots} = \frac{N!}{\prod_{i=1}^{\infty}(n_i!)}$$

e.g. How many ways are there to put all the boxes in state E_1? 1 ✓



$n_1 = N$

$$\frac{N!}{N!\,0!\,0!\cdots} = 1 \checkmark$$

e.g. How many ways to fill $5 = N$ boxes, 3 in state E_2, 2 in state E_4? 10

2	2	2	4	4

2	2	4	2	4

2	4	4	2	2

cf postnet. $n_1 = 0,\ n_2 = 3,\ n_3 = 0,\ n_4 = 2 \ldots$

$$\sum_{i=1}^{\infty} n_i = 2 + 3 = 5 = N \checkmark$$

Constraint #2 Fix the total Energy of the N systems $\Longleftrightarrow$ Fix Average energy

$$E_{TOT} = N\, E_{AVG} = NU = N\bar{E} = N\langle E \rangle$$

Probability that a random box has Energy E_i is $P_i = \dfrac{n_i}{N}$

Constraint #1 $\quad \dfrac{\sum_i n_i}{N} = \dfrac{N}{N} \Longrightarrow \sum_i P_i = 1$

Constraint #2 $\quad \dfrac{\sum_{i=1}^{\infty} n_i E_i}{N} = \dfrac{E_{tot}}{N} \Longrightarrow \sum_i P_i E_i = \bar{E} = U$

Maximize Ω, but subject to both constraints

multiplicity of microstates

by varying $\{n_i\}$ or equivalently $\{p_i\}$

$$\frac{S}{k_B} = \ln \Omega - \lambda\left(\sum_i p_i - 1\right) - \beta\left(\sum_i p_i E_i - U\right)$$

could have been *any* monotonically increasing function