

The 2nd law of thermodynamics

Lin Hsiu hao : 热统计物理 = lecture 3

perfect heat engine  $\leftrightarrow$  perfect refrigerator

低温  $\rightarrow$  高温 automatically

你可以被冷的东西烫到

$\downarrow$  modern language

For an isolated system, its entropy

never decreases and it remains

constant during a reversible process.

That is to say,  $\Delta S \geq 0$

P240 P241, thermal physics

Understand entropy S better

熵增为何只能生热，为何不能生功？

reversible  
↓  
irreversible

I<sup>0</sup> Clausius: From Carnot's heat engine argument, he proved

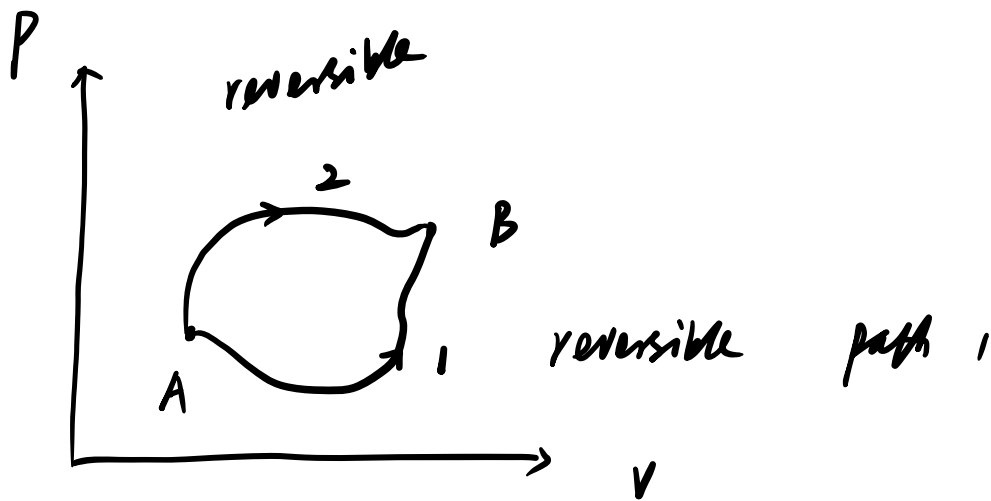
$$\oint \frac{dQ}{T} \leq 0$$

cyclic  
(apply calculus to Carnot's cycle)

"=" holds for reversible process.

Entropy is a state function

^^  
(“误解”贡献最大)



$$\oint \frac{dq}{T} = 0$$

$$\int_{\text{path 2}} \frac{dq}{T} - \int_{\text{path 1}} \frac{dq}{T} = 0$$

⇓

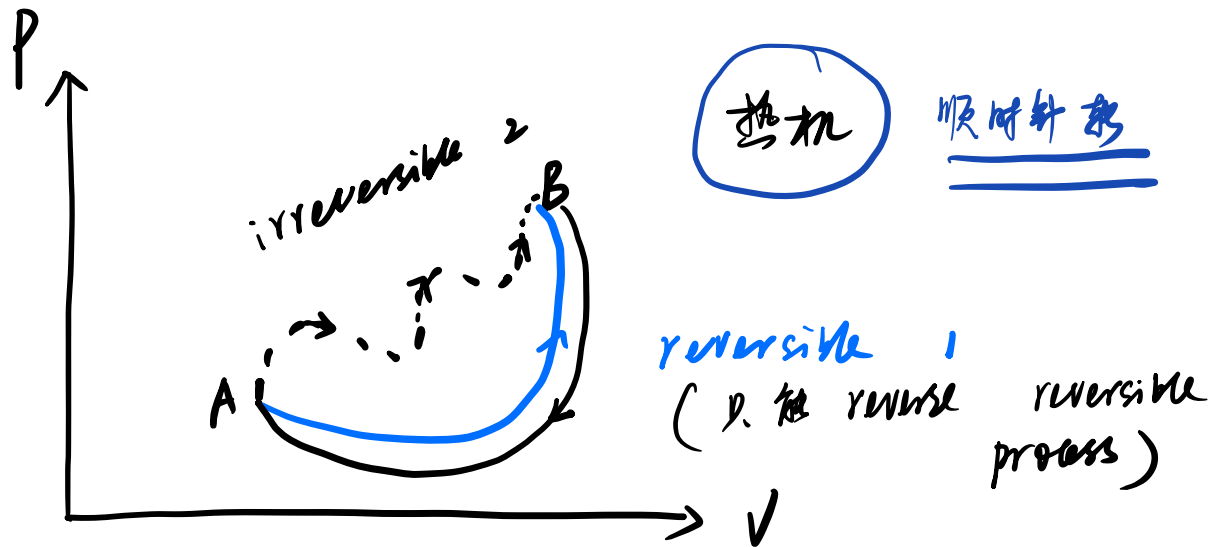
$$\begin{aligned} \int_{\text{path 2}} \frac{dq}{T} &= \int_{\text{path 1}} \frac{dq}{T} \equiv dS \\ &= S(B) - S(A) \end{aligned}$$

$\frac{dq}{T}$  : 高 + 火 (thermal ...)  
" 焓

(  $dS$  defined by reversible process )

give me a state, there is a  
value  $S$

what about irreversible process



$$\Delta S = \int_1 ds = \int_1 \frac{da}{T} = S(B) - S(A)$$

$$\oint \frac{da}{T} \leq 0$$

$$\int_{\text{IR}} \frac{da}{T} - \int_{\text{R}} \frac{da}{T} = \oint \frac{da}{T} \leq 0$$

$$\Delta S \geq \int_2 \frac{dQ}{T}$$

(如算可逆, 取 "=")

but, 怎么对公众宣讲?

For an isolated system ( $dQ = 0$ )

→  $\Delta S \geq 0$  报告给公众

(go back to the two reservoirs

$T_2, T_1$ )

吸热为正  $\Delta Q_2 = -\Delta Q_1 < 0$  ( $T_2 > T_1$ )

$$\frac{\Delta Q_2}{T_2} + \frac{\Delta Q_1}{T_1} > 0$$

not a cycle.  
direct contact

吸热, 给了能量, 也给了  $S$  (混乱度)

怎么还能步调一致地对外做功呢?

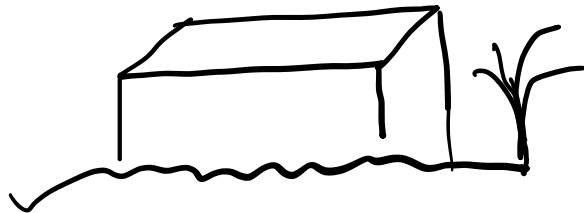
II° Boltzmann :

entropy  $\rightarrow$  state function

skip the heat, work,

(ir) reversible processes .....

Tomb :  $S = k \cdot \log W$



[ Kittel,  $\sigma = \log 2$   
(好老师知道洗脸要趁早)  
^\_^ ]

for S

Is there the microscopic explanation?

- a good question

## Entropy of mixing

consider a mixture of  $N_A$  atom A  
and  $N_B$  atom B ( $N = N_A + N_B$ )

$$\text{multiplicity: } g = \frac{N!}{N_A! N_B!}$$

$$\text{基础上的公式 } S = k \ln W = k \ln g$$
$$= k [\ln N! - \ln N_A! - \ln N_B!]$$

$$= k [N \ln N - N - (N_A \ln N_A - N_A) - (N_B \ln N_B - N_B)]$$

$$= k [N \ln N - N_A \ln N_A - N_B \ln N_B]$$

$$= k [N_A \ln \frac{N}{N_A} + N_B \ln \frac{N}{N_B}]$$

$$= -K \left[ N_A \ln \frac{N_A}{N} - N_B \ln \frac{N_B}{N} \right]$$

$$\downarrow x \equiv \frac{N_A}{N}$$

$$= K N \left[ -x \ln x - (1-x) \ln(1-x) \right]$$

$$= K N \underline{\sigma} \text{ ( Shannon entropy )}$$

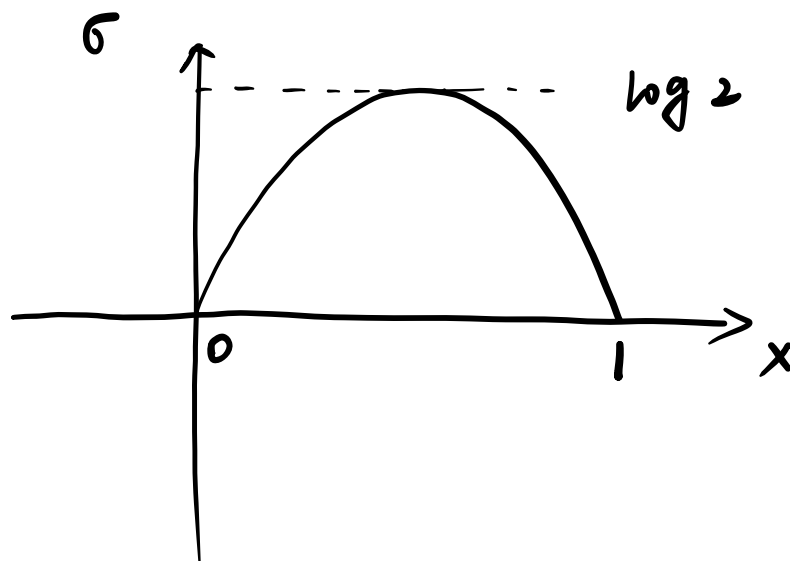
Stirling's approximation

状态数  $\rightarrow$  概率 (出类号)  
 $W \rightarrow \frac{1}{W} \rightarrow p$

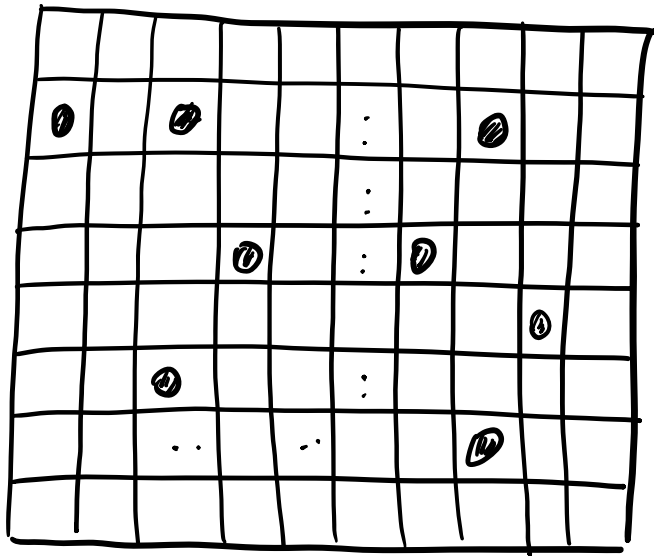
$$\sigma = - \langle \log p \rangle$$

$\downarrow$  binary

$$= - [x \log x + (1-x) \log(1-x)]$$







位置可分, 核子不可分

$C_N^{N_A}$ , 如果核子可分  
 $P_N^{N_A}$

# of  $\odot$  :  $N_A$  差  $N_A!$   
 (全排)

# of  $\square$  :  $N$

名词

Clausius : Entropy 的创造者

Energie (能量) +

trope (转换)

以此说明这是一个描述能量转换过程的等价量。