

The 2nd law of thermodynamics

Lin Hsiu hao : 热统计物理 = lecture 3

perfect heat engine \leftrightarrow perfect refrigerator

if 低温 \rightarrow 高温 automatically

你将被冷的东西烫到

\downarrow modern language

For an isolated system, its entropy

never decreases and it remains

constant during a reversible process.

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

Prado P166, thermal physics (Kittel)

Understand entropy S better

摩擦为何只能生热，为何不能生功？

reversible
↓
irreversible

I⁰ Clausius: From Carnot's heat engine argument, he proved

对于循环而言

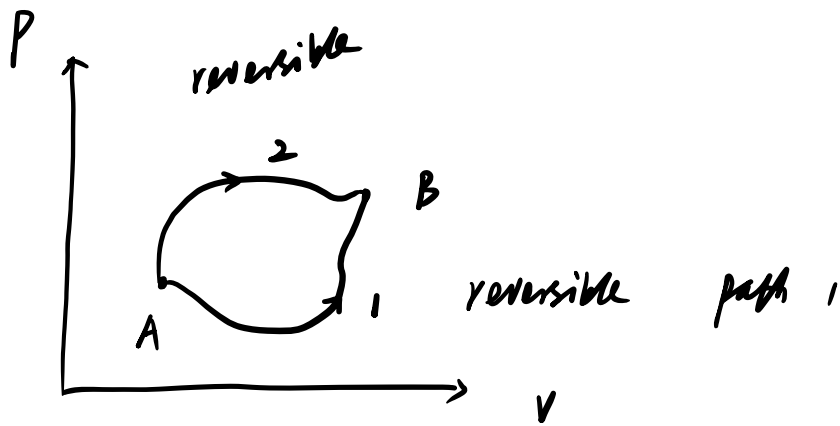
$$\oint \frac{dq}{T} \leq 0$$

cyclic
(apply calculus to Carnot's cycle)

"=" holds for reversible process.

Entropy is a state function

😊
("误解"贡献最大)



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

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

\Downarrow

$$\int_{\text{path 2}} \frac{dq}{T} = \int_{\text{path 1}} \frac{dq}{T} \equiv dS$$

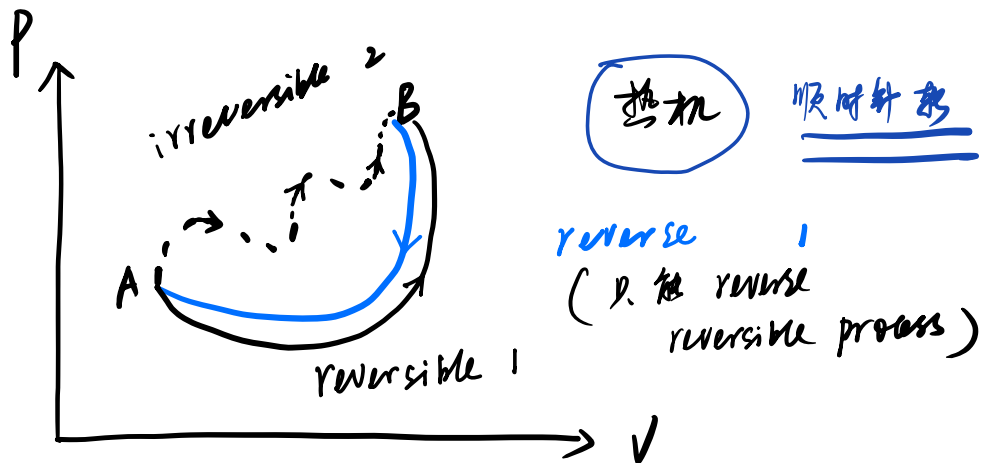
$$= S(B) - S(A)$$

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

(dS defined by reversible process)

give me a state, there is a
value S

what about irreversible process



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

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

$$\int_{\text{IR}} \frac{dq}{T} - \left[\int_{\text{R}} \frac{dq}{T} \right] = \oint \frac{dq}{T} \leq 0$$

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

(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) 高温自动向低温放热

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

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

这里, 两个热源
合在一起看孤立系
熵增。

not a cycle
direct contact

吸热, 给了热量, 也给了 S (混乱度)

怎么还能步调一致地对外做功呢?

the state variable S , review Carnot cycle

$$W = Q = Q_H + Q_L$$

the "working fluid" absorbs heat from reservoir T_H

releases heat to $\sim T_L$

For a **real heat engine**:

there is a temperature differential **dT**

between the reservoir and the fluid while the heat exchange takes place.

$$\Delta S_H = \int_{Q_{in}} \frac{dQ_H}{T} > \frac{Q_H}{T_H}$$

$$0 > \Delta S_L > \frac{Q_L}{T_L}$$

$$\Delta S_H + \Delta S_L = \Delta S_{cycle} = 0$$

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} < 0 \Rightarrow \frac{Q_H}{T_H} < -\frac{Q_L}{T_L} \Rightarrow -\frac{T_L}{T_H} > \frac{-Q_L}{Q_H}$$

$$\eta = \frac{W}{Q_H} = \frac{Q_H + Q_L}{Q_H} < 1 - \frac{T_L}{T_H} = \eta_I$$

" = " for the **ideal** heat engine

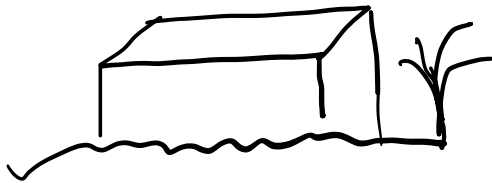
II° Boltzmann :

entropy \rightarrow state function

skip the heat, work,

(ir) reversible processes

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



问: S 是广延量
还是强度量?

[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 ($N = N_A + N_B$)

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

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

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

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

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

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

$$\downarrow x \equiv \frac{N_A}{N} = k N [-x \ln x - (1-x) \ln (1-x)]$$

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

Stirling's approximation

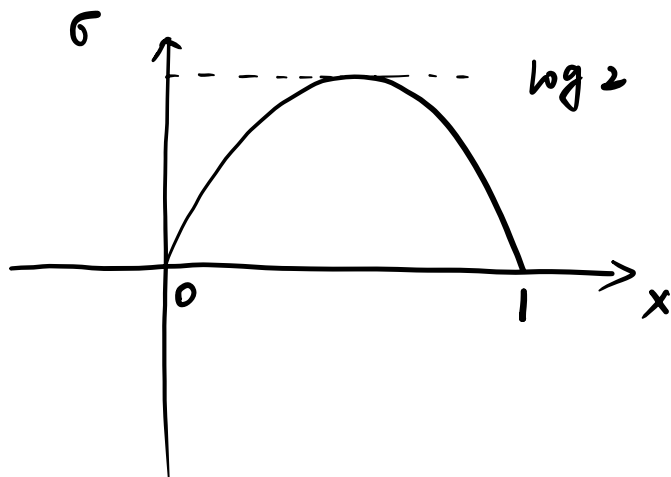
$$\ln N! = N \ln N - N$$

状态数 \rightarrow 几率 (出负号)
 $W \rightarrow \frac{1}{W} \rightarrow p$

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

\downarrow binary

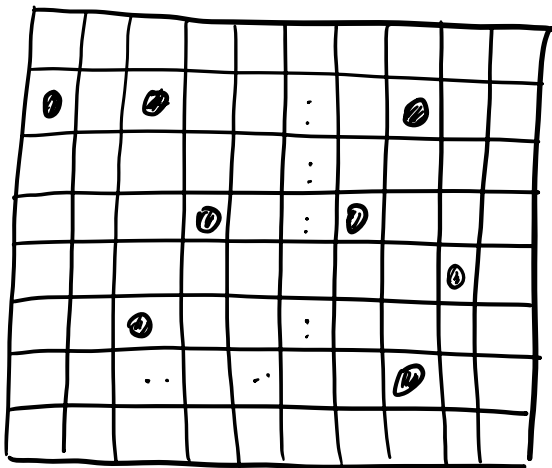
$$- [x \log x + (1-x) \log (1-x)]$$



问：你想着一场怎样的比赛？

什么叫势均力敌？什么叫精彩？

illustration of configuration :



位置可分, 粒子不可分

$C_N^{N_A}$, 如果粒子可分 $P_N^{N_A}$

of ● : N_A 差 $N_A!$
(全排)

of □ : 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。

辨析 完美热机
理想热机
实际热机

$$\sigma = - \sum_i p_i \ln p_i$$

$$S = k_B \ln W$$

讨论在不确定度的意义上,

为什么有符号差异

微观状态数与几率的关系