

Similar to continuous system:

for N large

↳ number of states with energy less or equal to E .

$$S = k_B \ln N(E) = k_B \ln \Omega(E)$$

↳ number of states with energy equal to E .

Given E , what is $\Omega(E)$?

$\Omega(E)$ = Number of distinguishable configurations of $\{n_{i,x}, n_{i,y}, n_{i,z}\}$

such that

$$\sum_{i=1}^N (n_{i,x}^2 + n_{i,y}^2 + n_{i,z}^2) \leq \frac{8mL^2 E}{h^2}$$

distinguishable

= Number of lattice points on a $3N$ dimensional lattice within a sphere of radius $\sqrt{\frac{8mL^2 E}{h^2}}$

$$= \frac{1}{N!} \left(\frac{8mL^2 E}{h^2} \right)^{\frac{3N}{2}} \Omega_{3N} \frac{1}{2^{3N}}$$

↳ since only positive $n_{i,x}, n_{i,y}, n_{i,z}$ occur

↑ since particles are indistinguishable

⇒ All states resulting from a permutation of the particles are actually the same state

↓ 1/6
↓ 1/8

$$S = k_B \ln \left[\left(\frac{2mL^2 E}{h^2} \right)^{\frac{3N}{2}} \frac{1}{N!} \Omega_{3N} \right]$$

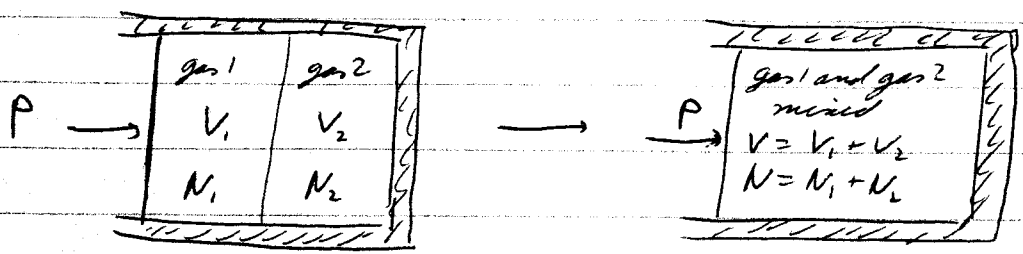
$$= k_B \ln \left[V^N (2mE)^{\frac{3N}{2}} \Omega_{3N} \frac{1}{h^{3N} N!} \right]$$

Compare to classical calculation

$$\rightarrow \boxed{C_N = h^{3N} N!}$$

V.5 The Gibbs Paradox - solution

Reminder (2 compartment version):



$$x = \frac{N_1}{N_1 + N_2}$$

$$PV_i = N_i k_B T$$

change in entropy

$$\Delta S_{mix} = -n_1 R \ln x - n_2 R \ln(1-x) = -N_1 k_B \ln x - N_2 k_B \ln(1-x)$$

$\Delta S_{mix} > 0$ even if gas 1 and gas 2 are identical!

Derive this with "new" description of ideal gas:

$$S(E, V, N) = N k_B \ln \left[V \left(\frac{2\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N k_B - k_B \ln(N!)$$

$$E = \frac{3}{2} k_B T \quad V = \frac{N k_B T}{P}$$

$$\Rightarrow S(T, P, N) = N k_B \ln \left[\frac{N k_B T}{P} (2\pi m k_B T)^{3/2} \right] + \frac{3}{2} N k_B - k_B \ln(N!)$$

before mixing:

$$S_{before}(T, P, N_1, N_2) = N_1 k_B \ln \left[\frac{N_1 k_B T}{P} (2\pi m k_B T)^{3/2} \right] + \frac{3}{2} N_1 k_B - k_B \ln(N_1!)$$

$$+ N_2 k_B \ln \left[\frac{N_2 k_B T}{P} (2\pi m k_B T)^{3/2} \right] + \frac{3}{2} N_2 k_B - k_B \ln(N_2!)$$

after mixing (different gases):

$$S_{\text{after, diff}}(T, P, N_1, N_2) = (N_1 + N_2) k_B \ln \left[\frac{(N_1 + N_2) k_B T}{P} (2\pi m k_B T)^{3/2} \right] + \frac{3}{2} (N_1 + N_2) k_B - k_B \ln[(N_1!)(N_2!)]$$

particles of type 1 and type 2 are distinguishable while all type 1 particles are indistinguishable

$$\begin{aligned} \Rightarrow \Delta S_{\text{diff}} &= S_{\text{after, diff}}(T, P, N_1, N_2) - S_{\text{before}}(T, P, N_1, N_2) \\ &= -N_1 k_B \ln N_1 - N_2 k_B \ln N_2 + (N_1 + N_2) k_B \ln(N_1 + N_2) \\ &= -N_1 k_B \ln \frac{N_1}{N_1 + N_2} - N_2 k_B \ln \frac{N_2}{N_1 + N_2} = -N_1 k_B \ln x - N_2 k_B \ln(1-x) \end{aligned}$$

after mixing (same gas):

$$S_{\text{after, same}}(T, P, N_1, N_2) = (N_1 + N_2) k_B \ln \left[\frac{(N_1 + N_2) k_B T}{P} (2\pi m k_B T)^{3/2} \right] + \frac{3}{2} (N_1 + N_2) k_B - k_B \ln[(N_1 + N_2)!]$$

all $N_1 + N_2$ particles are indistinguishable

$$\begin{aligned} \Rightarrow \Delta S_{\text{same}} &= \Delta S_{\text{after, same}}(T, P, N_1, N_2) - S_{\text{before}}(T, P, N_1, N_2) \\ &= -N_1 k_B \ln N_1 - N_2 k_B \ln N_2 + (N_1 + N_2) k_B \ln(N_1 + N_2) - k_B \ln(N_1 + N_2)! \\ &\quad + k_B \ln N_1! + k_B \ln N_2! \\ &\approx -N_1 \ln N_1 - N_2 \ln N_2 + (N_1 + N_2) \ln(N_1 + N_2) - k_B (N_1 + N_2) \ln(N_1 + N_2) \\ &\quad + k_B (N_1 + N_2) + k_B \ln N_1! - k_B N_1 + k_B \ln N_2! - k_B N_2 = 0 \end{aligned}$$

as it is to be expected since removing the wall does not change the system

∇ Canonical and grand canonical ensemble

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Reminder: microcanonical ensemble

- closed & isolated system
- $N(E)$: number of microscopic states at energy E

$$- p_i = \begin{cases} \frac{1}{N(E)} & E_i = E \\ 0 & E_i \neq E \end{cases}$$

- hard part: finding $N(E)$

then: $N(E) \rightarrow S = k_B \ln N(E) \rightarrow \text{thermodynamics}$

other ensembles:

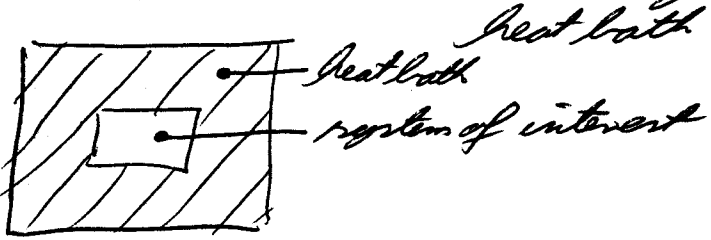
- different physical situation
- different microscopic distribution p_i
- $N(E)$ replaced by other quantities
- thermodynamics is the same! ∇

For the thermodynamics of very large systems it does not matter which ensemble is used to derive the thermodynamic quantities. However, some ensembles may be more suited than others

V.1 Canonical ensemble

V.1.1 General framework (discrete system)

Physical situation: closed system in contact with



Describe system by N states $i=1, \dots, N$ with energy of state i being E_i

- energy of system + heat bath is conserved
- energy of system by itself can fluctuate

⇒ all states can have a positive probability γ_i independent of their energy E_i

Want to find γ_i $\nabla_{\gamma_i} \rightarrow$ maximize entropy $S = -k_B \sum_{i=1}^N \gamma_i \ln \gamma_i$
 Under what conditions? ① $\sum_{i=1}^N \gamma_i = 1$ (normalization)
 ② Although energy is not conserved there has to be a well-defined average energy

$$U = \sum_{i=1}^N \gamma_i E_i$$

which is fixed by the temperature of the heat bath.

Task:

Maximize $S = -k_B \sum_{i=1}^N \gamma_i \ln \gamma_i$

under the conditions

$$\sum_{i=1}^N \gamma_i - 1 = 0$$

$$U - \sum_{i=1}^N \gamma_i E_i = 0$$

Method: Lagrange multipliers λ and μ

$$0 = \frac{\partial}{\partial \gamma_i} \left[- \sum_{i=1}^N \gamma_i \ln \gamma_i + \lambda \left(\sum_{i=1}^N \gamma_i - 1 \right) + \mu \left(U - \sum_{i=1}^N \gamma_i E_i \right) \right]$$

$$= - \ln \gamma_i - 1 + \lambda - \mu E_i$$

$$\Rightarrow \gamma_i = \underbrace{e^{\lambda-1}}_{\text{independent of } i} e^{-\mu E_i}$$

still have to find λ and μ :

Normalization $\Rightarrow \gamma_i = \frac{e^{-\mu E_i}}{\sum_{i=1}^N e^{-\mu E_i}}$

μ is a function of U determined by

$$U = \frac{\sum_{i=1}^N E_i e^{-\mu E_i}}{\sum_{i=1}^N e^{-\mu E_i}}$$

What is the physical meaning of μ ?

$$S = -k_B \sum_{i=1}^N \gamma_i \ln \gamma_i = -k_B \sum_{i=1}^N \frac{e^{-\mu E_i}}{\sum_{i=1}^N e^{-\mu E_i}} \left[-\mu E_i + \ln \sum_{i=1}^N e^{-\mu E_i} \right]$$

$$= k_B \mu \sum_{i=1}^N \gamma_i E_i + k_B \ln \sum_{i=1}^N e^{-\mu E_i}$$

$$= k_B \mu U + k_B \ln \sum_{i=1}^N e^{-\mu E_i}$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = k_B \mu + k_B U \frac{\partial \mu}{\partial U} + k_B \frac{\sum_{i=1}^N (-E_i) e^{-\mu E_i}}{\sum_{i=1}^N e^{-\mu E_i}} \frac{\partial \mu}{\partial U}$$

$$= k_B \mu + k_B U \frac{\partial \mu}{\partial U} - k_B U \frac{\partial \mu}{\partial U} = k_B \mu$$

$$\Rightarrow \mu = \frac{1}{k_B T} \equiv \beta$$

Result:

$$P_i = \frac{e^{-\beta E_i}}{\sum_{i=1}^N e^{-\beta E_i}}$$

distribution of the canonical ensemble

Features

- all states have a positive probability
- all states with the same energy have the same probability
- the probability of a state decays exponentially with its energy

Abbreviation:

$$Z(T) = \sum_{i=1}^N e^{-\frac{1}{k_B T} E_i}$$

"partition function" of the system

How do we get to thermodynamics?

$$S = k_B \frac{1}{k_B T} U + k_B \ln Z(T)$$

$$\Rightarrow U - TS = -k_B T \ln Z(T)$$

$$\Rightarrow F = -k_B T \ln Z(T) \quad \text{Helmholtz free energy}$$

Recipe:

$$\text{microscopic model} \rightarrow Z(T) = \sum_{i=1}^N e^{-\frac{1}{k_B T} E_i}$$

$$\rightarrow F = -k_B T \ln Z(T) \rightarrow \text{thermodynamics}$$