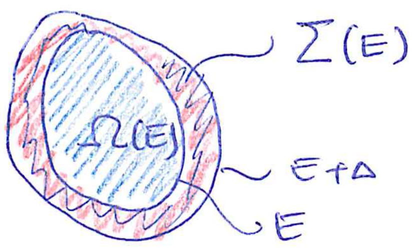


# The Entropy of a perfect gas Sakur-Tetrode

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Correct Boltzmann's Counting

thermodynamic limit

$$\ln \Gamma(E) \simeq \ln \Omega(E)$$

$$\Gamma(E) = \int d^{3N}p \, d^{3N}q \, \Delta \delta(E-H) \longrightarrow \begin{cases} = 1 & E \leq H \leq E+\Delta \\ = 0 & \text{otherwise} \end{cases}$$

$$\Omega(E) = \int d^{3N}p \, d^{3N}q \, \Theta(E-H) \longrightarrow \begin{cases} = 1 & H \leq E \\ = 0 & \text{otherwise} \end{cases}$$

Perfect gas

$H = \sum_i \frac{p_i^2}{2m}$ indep on $q$ but confinement

$$\Omega(E) = V^N \underbrace{\int d^{3N}p \, \Theta\left(E - \sum_i \frac{p_i^2}{2m}\right)}_{}$$

volume of 3N dimensional sphere of radius $R^2 = 2mE$

$$\Omega(E) = V^N \Omega_{3N} \int_0^R d\rho \, \rho^{d-1} = V^N \Omega_{3N} \frac{R^d}{d}$$

$d = 3N$

Calculation of d-dimensional solid angle

$$\int d^d x \, e^{-\sum_i x_i^2} = \left(\int dx\, e^{-x^2}\right)^d = (\sqrt{\pi})^d$$

in spherical coordinates

$$\Omega_d \int_0^\infty dx\, x^{d-1} e^{-x^2} = \frac{\Omega_d}{2}\int_0^\infty dt\, t^{\frac{d}{2}-1} e^{-t} = \frac{\Omega_d}{2}\Gamma(d/2)$$

$x^2 = t$

The $\Gamma$ function

$$\Gamma(\alpha) = \int_0^\infty dt\, t^{\alpha-1} e^{-t} = (\alpha-1)!$$

$$\boxed{\Omega_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}}$$

in large dimension the volume of a sphere is

$$\Omega_d \frac{R^d}{d} = \frac{2\pi^{d/2}}{d\,\Gamma(d/2)} R^d = \frac{\pi^{d/2}}{(d/2)!} R^d \qquad \frac{d}{2}\Gamma\left(\frac{d}{2}\right) = \frac{d}{2}!$$

$$\Omega(E) = V^N \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2}$$

large N

$$\left(\frac{3N}{2}\right)! \simeq \left(\frac{3N}{2}\right)^{\frac{3N}{2}} e^{-\frac{3N}{2}} \sqrt{2\pi \frac{3N}{2}}$$

stirling

$$\Omega(E) = V^N \left(\frac{2\pi m E}{\frac{3N}{2}} e\right)^{\frac{3N}{2}} \frac{1}{\sqrt{2\pi\frac{3N}{2}}}$$

the Boltzmann's entropy

$$S = k_B \ln \frac{\Omega(E)}{\Lambda^{3N}} = k_B \ln V^N \left(\frac{4\pi m E}{\Lambda^2 3N} e\right)^{\frac{3N}{2}}$$

$$\cancel{+ \frac{k_B}{2} \ln 2\pi \frac{3N}{2}}$$

sub extensive

$$S = \underbrace{k_B N \ln V}_{\text{super extensive}} + \underbrace{\frac{3N}{2} k_B \ln\left[\underbrace{\frac{4\pi m E}{3N\Lambda^2}}_{\text{intensive}} e\right]}_{\text{extensive}}$$

super extensive

Correct Boltzmann's Counting

$$S = k_B \ln \frac{\Omega(E)}{\Lambda^{3N} N!}$$

permutation of id particle

$$S = k_B \ln \left\{ \frac{V^N}{N!} \left[ \frac{4\pi m E}{3N \Lambda^2} \right]^{3N/2} \right\}$$

Stirling

$$\frac{V^N}{N!} = \frac{V^N}{N^N} e^N \frac{1}{\sqrt{2\pi N}}$$

subextensive in the logarithm

$$S = k_B N \ln\left[\frac{V}{N} e \left(\frac{4\pi m E}{3N h^2}\right)^{3/2}\right]$$

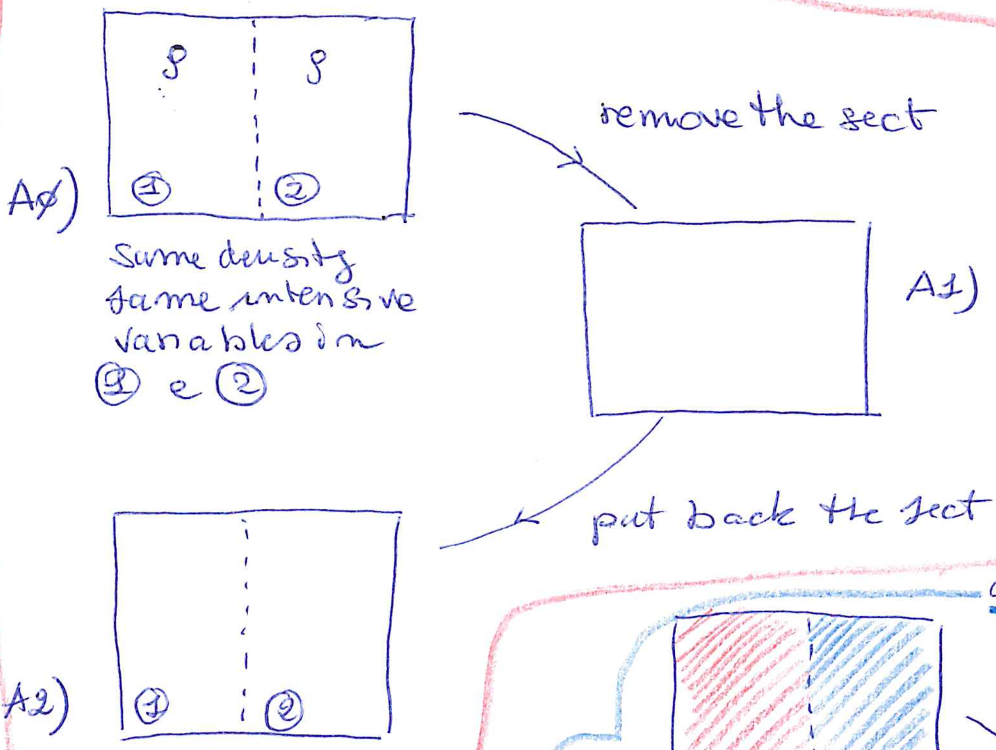
intensive

Sakur-Tetrode

## Correct Boltzmann's Counting

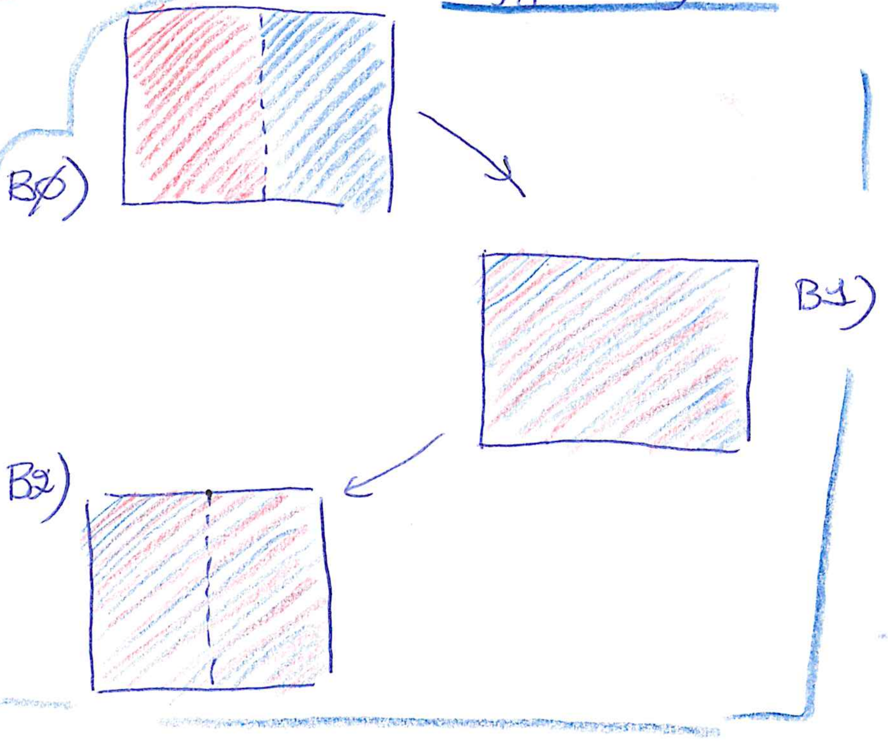
### Thermodynamic perspective

#### Same Gas




$A\emptyset \equiv A2$

#### different gases




$B\emptyset \neq B2$

Consider the entropy without CCB

$$S = k_B N \ln V + \frac{3N}{2} k_B \ln\left(\frac{4\pi m E}{3N\Lambda^2} e\right)$$

$$S = k_B N \ln V + \frac{3N}{2} k_B \ln \frac{E}{N} + \underbrace{\text{const}\ \frac{3N}{2} k \ln \frac{4\pi m e}{3N^2}}_{S'}$$

$$S(A1) = k_B N \ln V + \frac{3}{2} N \ln \frac{E}{N} + S'$$

$$N = N_1 + N_2 \qquad E = E_1 + E_2$$

but all the intensive variables are the same

$$S(A0) = k_B N_1 \ln V_1 + k_B N_2 \ln V_2 + \frac{3N_1}{2} k_B \ln \frac{E_1}{N_1} + \frac{3N_2}{2} k_B \ln \frac{E_2}{N_2}$$

$$+ S'$$

$$\frac{E}{N} = \epsilon = \frac{E_1}{N_1} = \frac{E_2}{N_2}$$

$$S(A_1) = k_B (N_1 + N_2) \ln (V_1 + V_2) + \frac{3}{2} (N_1 + N_2) \ln \epsilon + S'$$

$$S(A0) = k_B N_1 \ln V_1 + k_B N_2 \ln V_2 + \frac{3}{2} (N_1 + N_2) \ln \epsilon + S'$$

$$\Delta S = S(A1) - S(A0) = k_B N_1 \ln \frac{V_1 + V_2}{V_1} + k_B N_2 \ln \frac{V_1 + V_2}{V_2}$$

gas 1 diffuses in 1+2

gas 2 diffuses in 1+2

if $A\emptyset \equiv A2$ then

$$\boxed{A\emptyset} \xrightarrow{\Delta S'} \boxed{\cancel{A1}} \xrightarrow{-\Delta S} \boxed{A2}$$

since $A\emptyset = A2$ $S(A2) = S(A0)$

where is the negative entropy induced by the insertion of a sect from A1 to A2

?

indeed what is calculated is the MIXING ENTROPY which is correct in the B case from $B\emptyset$ to $B1$ for gas which are diffent (but with particles of equal masses)

Consider the same calculation with CCB

$$S = k_B N \ln \frac{V}{N} + k_B N \ln \frac{E}{N} + S'$$

intensive

$$S'(A\emptyset) = k_B(N_1+N_2) \ln \frac{V_1+V_2}{N_1+N_2} + k_B(N_1+N_2) \ln \frac{E_1+E_2}{N_1+N_2} + S'$$

but $\dfrac{V_1+V_2}{N_1+N_2} = \dfrac{V_1}{N_1} = \dfrac{V_2}{N_2} = v$ volume per particle

$\dfrac{E_1+E_2}{N_1+N_2} = \dfrac{E_1}{N_1} = \dfrac{E_2}{N_2} = \epsilon$ energy x particle

therefore

$$S(A\emptyset) = S_1 + S_2 = S'(A1)$$

for a system of 2 kind of particles

$$\mathcal{S} = k_B \ln \frac{\Gamma_{1+2}(E)}{N_1!\, N_2!\, \Lambda^{3N_1+3N_2}}$$

different from $(N_1+N_2)!$

$$\Gamma_{1+2}(E) = \Delta \int dp_1^{3N_1} dq_1^{3N_1} \int dp_2^{3N_2} dq_2^{3N_2}\, \delta(E - H_{1+2})$$

for a mixture of 2 perfect gases

$$\mathcal{Z} = \frac{V_1^{N_1} V_2^{N_2}}{N_1!\, N_2!} \left(\frac{4\pi m_1 E_1}{3N_1 h^2}\right)^{\frac{3N_1}{2}} \left(\frac{4\pi m_2 E_2}{3N_2 h^2}\right)^{\frac{3N_2}{2}}$$

$$\mathcal{S} = \mathcal{S}_1 + \mathcal{S}_2$$