

# 1 Mixture of ideal gases

Enclosed in a box of volume  $V$  are  $N_1$  molecules of species 1 with mass  $m_1$  and  $N_2$  molecules of species 2 with mass  $m_2$ . The system can be considered as an ideal gas with the total energy  $E$ .

## 1.1 Phase space volume

For a single species of an ideal gas:

$$\Omega(E) = \frac{1}{h^{3N} N!} \cdot \int \prod_{i=1}^{3N} dq_i \int \prod_{i=1}^{3N} dp_i \delta(E - H(q_i, p_i)) \quad (1)$$

For two different species with  $N_1 \gg 1$  and  $N_2 \gg 1$ , the phase space volume  $\Omega(E, V, N_1, N_2)$  is

$$\Omega(E) = \frac{V^N}{h^{3N} N_1! N_2!} \cdot \int \prod_{i=1}^{3N_1} dp_i \int \prod_{j=3N_1+1}^{3N} dp_j \delta(E - H(q_i, p_i)) \quad (2)$$

The factorials arise from the fact that we are dealing with two independent gas species and the integral over  $dq$  is carried out already and gives the volume  $V^N$  since the Hamiltonian

$$H(q_i, p_i) = \sum_{i=1}^{3N_1} \frac{p_i^2}{2m_1} + \sum_{j=3N_1+1}^{3N} \frac{p_j^2}{2m_2} \quad (3)$$

is independent of the position. At this point we can perform the momentum transformation

$$\bar{p}_i = \frac{p_i}{\sqrt{2m_1}} \quad (4)$$

$$\bar{p}_j = \frac{p_j}{\sqrt{2m_2}} \quad (5)$$

to give

$$\Omega(E) = \frac{V^N (2m_1)^{\frac{3N_1}{2}} (2m_2)^{\frac{3N_2}{2}}}{h^{3N} N_1! N_2!} \cdot \int \prod_{i=1}^{3N} d\bar{p}_i \delta\left(E - \sum_{i=1}^{3N} \bar{p}_i^2\right) \quad (6)$$

$$= \frac{V^N (2m_1)^{\frac{3N_1}{2}} (2m_2)^{\frac{3N_2}{2}}}{h^{3N} N_1! N_2!} \cdot \frac{\pi^{\frac{3N}{2}} E^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} \quad (7)$$

which was again just an integration over a  $3N$ -dimensional sphere of radius  $\sqrt{E}$  (which is a good approximation for large  $N$ ).

Introducing the reduced mass  $\mu = m_1 m_2 / (m_1 + m_2)$  one can find the following result

$$\Omega(E) = \frac{V^N \pi^{\frac{3N}{2}} (2\mu E)^{\frac{3N}{2}}}{h^{3N} N! \left(\frac{3N}{2}\right)!} \cdot \frac{N!}{N_1! N_2!} \left(\frac{m_1}{\mu}\right)^{\frac{3N_1}{2}} \left(\frac{m_2}{\mu}\right)^{\frac{3N_2}{2}} \quad (8)$$

$\alpha$   
 $1 \quad 8/8$   
 $2 \quad 4/4$   
 $3 \quad 3/3$   
 $\Sigma \quad 15/15$

## 1.2 Entropy as a function of the ratio $N_1/N_2$

The entropy of the system will be given by

$$S = k_B \ln \Omega(E) \quad (9)$$

$$= k_B \left[ \ln \left( \frac{V^N \pi^{\frac{3N}{2}} (2\mu E)^{\frac{3N}{2}}}{h^{3N} N! \left(\frac{3N}{2}\right)!} \right) + \ln \left( \frac{N!}{N_1! N_2!} \left(\frac{m_1}{\mu}\right)^{\frac{3N_1}{2}} \left(\frac{m_2}{\mu}\right)^{\frac{3N_2}{2}} \right) \right] \quad (10)$$

The first term corresponds to the standard result for an ideal gas of  $N$  identical particles with mass  $\mu$

$$S_{\text{id}} = k_B N \left\{ \ln \left[ \frac{V}{N} \left( \frac{4\pi\mu E}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} \right\} \quad (11)$$

and the second term is given by

$$S_{\text{mixed}} = k_B \left[ N \ln N - N_1 \ln N_1 - N_2 \ln N_2 + N_1 \ln \left( \frac{m_1}{\mu} \right)^{\frac{3}{2}} + N_2 \ln \left( \frac{m_2}{\mu} \right)^{\frac{3}{2}} \right] \quad (12)$$

using Stirling's approximation formula. Defining the ratio  $\eta = N_1/N_2$ , the mixed term can be rewritten to

$$S_{\text{mixed}} = k_B N \left[ \frac{\eta}{1+\eta} \left( \ln \left( \frac{m_1}{\mu} \right)^{\frac{3}{2}} - \ln \frac{\eta}{1+\eta} \right) + \frac{1}{1+\eta} \left( \ln \left( \frac{m_2}{\mu} \right)^{\frac{3}{2}} - \ln \frac{1}{1+\eta} \right) \right]. \quad (13)$$

To find the maximum entropy, we need only differentiate the mixed contribution since the identical contribution is not a function of  $\eta$

$$\frac{\partial S}{\partial \eta} = 0 \quad \longrightarrow \quad \eta_0 = \frac{N_1}{N_2} = \left( \frac{m_1}{m_2} \right)^{\frac{3}{2}}. \quad (14)$$

## 1.3 Total and partial pressures

To calculate the pressure, using the equation given, we need only differentiate  $S_{\text{id}}$  since  $S_{\text{mixed}}$  is not a function of volume

$$p = T \left( \frac{\partial S_{\text{id}}}{\partial V} \right)_{E, N_1, N_2} = \frac{N k_B T}{V} = \frac{N_1 k_B T}{V} + \frac{N_2 k_B T}{V} = p_1 + p_2 \quad (15)$$

So we can see both gases contribute to the pressure according to their number of particles.

### 1.4 Entropy of mixing

Consider a situation in which the container is separated into two volumes  $V_1$  and  $V_2$  containing only molecules of species 1 and 2, respectively. The total energy of the system is  $E$  and the two compartments are in thermal and mechanical equilibrium.

From the lecture, we know the entropy for the unmixed gas:

$$S = S_1 + S_2 \quad (16)$$

with

$$S_1 = k_B N_1 \left\{ \ln \left[ \frac{V_1}{N} \left( \frac{4\pi m_1 E}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} \right\}, \quad (17)$$

$$S_2 = k_B N_2 \left\{ \ln \left[ \frac{V_2}{N} \left( \frac{4\pi m_2 E}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} \right\}. \quad (18)$$

Rewriting it with the reduced mass  $\mu$  yields

$$S_1 = k_B N_1 \left\{ \ln \left[ \frac{V}{N} \left( \frac{4\pi \mu E}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} + \ln \left( \frac{m_1}{\mu} \right)^{\frac{3}{2}} \right\}, \quad (19)$$

$$S_2 = k_B N_2 \left\{ \ln \left[ \frac{V}{N} \left( \frac{4\pi \mu E}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} + \ln \left( \frac{m_2}{\mu} \right)^{\frac{3}{2}} \right\}. \quad (20)$$

The entropy after mixing will be higher than before, the change in entropy will be

$$\Delta S = S_{\text{id}} + S_{\text{mixed}} - S_1 - S_2 = -k_B \left( N_1 \ln \frac{N_1}{N} + N_2 \ln \frac{N_2}{N} \right). \quad (21)$$

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## 2 Thermodynamics of a black hole

We have given the following relations:

Schwarzschild radius:

$$R = \frac{2GM}{c^2} \quad (22)$$

Hawking radiation:

$$T = \frac{\hbar c^3}{8\pi GM k_B} \quad (23)$$

Einstein's mass-energy relation:

$$E = Mc^2 \quad (24)$$

### 2.1 Specific heat $c_V$

From (23):

$$\Rightarrow M = \frac{\hbar c^3}{8\pi G k_B T} \quad (25)$$

Assumption: inner energy  $U = E$ .

With (24) and  $c_V = \frac{\partial U}{\partial T}$  follows:

$$E = \frac{\hbar c^5}{8\pi G k_B T} \quad (26)$$

$$\Rightarrow c_V = \frac{\partial E}{\partial T} = -\frac{\hbar c^5}{8\pi G k_B T^2} \cdot \quad (27)$$

### 2.2 Entropy $S$

To get an expression for the entropy, we first plug (24) in (23):

$$T(E) = \frac{\hbar c^5}{8\pi G k_B E} \quad (28)$$

Next we use the definition of temperature:

$$\frac{\partial S(E)}{\partial E} := \frac{1}{T(E)} = \frac{8\pi G k_B E}{\hbar c^5} \quad (29)$$

Integration leads to

$$S(E) = \frac{4\pi G k_B E^2}{\hbar c^5} \quad (30)$$

The integration constant is set to zero to be consistent with the condition  $S(M=0) \stackrel{!}{=} 0$ .

Plugging first (24) and then (22) into this result leads to

$$S = \frac{4\pi G k_B M^2 c^4}{\hbar c^5} \quad (31)$$

$$= \frac{\pi k_B R^2 c^3}{G \hbar} \quad (32)$$

$$= \frac{1}{4} k_B \left( \frac{4\pi R^2}{L_P^2} \right) \cdot \quad (33)$$

As we can see, the entropy is directly proportional the surface area of a black hole measured in units of the Planck length  $L_P = \sqrt{\hbar G/c^3}$ .

### 2.3 Information storage

Thermodynamical entropy:

$$S_t = k_B \log \Omega \quad (34)$$

Information entropy (= number of bits):

$$S_i = \log_2(\Omega) \quad (35)$$

Combining the last two relations yields

$$S_i = \log_2 \left[ \exp \left( \frac{S_t}{k_B} \right) \right] \quad (36)$$

For a small black hole ( $R \approx 1\text{cm}$ ), one gets for the number of bits

$$S_i \approx 10^{66} . \quad (37)$$

### 3 Maxwell relations

Assume that we know the fundamental equation as

$$E = E(S, V, N) \quad (38)$$

for some well-behaved system of interest (i.e. at least  $C^2$ ). Then it should not matter in which sequence we take the partial derivatives for a second derivative like  $\frac{\partial^2 E}{\partial S \partial V}$ .

#### 3.1 Derive the Maxwell relation

We introduce the notation  $\partial_x := \frac{\partial}{\partial x}$

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S} \quad (39)$$

$$\partial_S \partial_V E = \partial_V \partial_S E \quad (40)$$

$$-\partial_S p \Big|_{V,N} = \partial_V T \Big|_{S,N} \quad (41)$$

For this, we used the fact that

$$\partial_S E \Big|_{V,N} = T \quad \text{and} \quad \partial_V E \Big|_{S,N} = -p \quad (42)$$

which can easily be verified using the fundamental equation:

$$dE = T \cdot dS - p \cdot dV + \mu \cdot dN \quad (43)$$

There are three Maxwell relations, one for each pair of the energy terms. /

### 3.2 Confirm Maxwell relation explicitly for the ideal gas

From the lecture we know that the entropy of an ideal gas is given by

$$S = k_B N \left\{ \left[ \left( \frac{V}{N} \right) \cdot \left( \frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\} \quad (44)$$

Rearrange for  $E$  and define  $C := \frac{3h^2 N}{4\pi k_B m}$

$$E = \frac{3h^2 N}{4\pi m} \cdot \left[ \frac{N}{V} \cdot \left( \frac{S}{k_B N} - \frac{5}{2} \right) \right]^{2/3} \quad (45)$$

$$= C \cdot \left[ \left( \frac{S}{V} - \frac{5}{2} N k_B \right) \right]^{2/3} \quad (46)$$

Differentiate both for volume and entropy:

$$\frac{\partial}{\partial S} \frac{\partial E}{\partial V} = \frac{\partial}{\partial S} \left[ \frac{2C}{3} \cdot \left( \frac{S}{V} - \frac{5}{2} N k_B \right)^{-1/3} \cdot \left( -\frac{S}{V^2} \right) \right] \quad (47)$$

$$= -\frac{2C}{3V^2} \cdot \frac{\partial}{\partial S} \left[ \left( \frac{S}{V} - \frac{5}{2} N k_B \right)^{-1/3} \cdot S \right] \quad (48)$$

$$= -\frac{2C}{3V^2} \cdot \frac{\partial}{\partial S} \left[ \left( \frac{S}{VS^3} - \frac{5Nk_B}{2} \frac{1}{S^3} \right)^{-1/3} \right] \quad (49)$$

$$= \frac{2C}{9V^2} \cdot \left( \frac{1}{VS^2} - \frac{5Nk_B}{2} \frac{1}{S^3} \right)^{-4/3} \cdot \left( \frac{-2}{VS^3} \right) \quad (50)$$

$$= -\frac{4C}{9V^2} \cdot \left( \frac{S}{V} - \frac{5}{2} N k_B \right)^{-4/3} \cdot S^4 \cdot \frac{1}{VS^3} \quad (51)$$

$$= -\frac{4C}{9} \cdot \frac{S}{V^3} \cdot \left( \frac{S}{V} - \frac{5}{2} N k_B \right)^{-4/3} \quad (52)$$

$$\frac{\partial}{\partial V} \frac{\partial E}{\partial S} = \frac{\partial}{\partial V} \left[ \frac{2C}{3} \cdot \left( \frac{S}{V} - \frac{5}{2} N k_B \right)^{-1/3} \cdot \frac{1}{V} \right] \quad (53)$$

$$= \frac{2C}{3} \cdot \frac{\partial}{\partial V} \left[ \left( SV^2 - \frac{5Nk_B}{2} V^3 \right)^{-1/3} \right] \quad (54)$$

$$= -\frac{4C}{9} \cdot \left( SV^2 - \frac{5Nk_B}{2} V^3 \right)^{-4/3} \cdot SV \quad (55)$$

$$= -\frac{2C}{9} \cdot \left( \frac{S}{V} - \frac{5}{2} N k_B \right)^{-4/3} \cdot \frac{1}{V^4} \cdot 2SV \quad (56)$$

$$= -\frac{4C}{9} \cdot \frac{S}{V^3} \cdot \left( \frac{S}{V} - \frac{5}{2} N k_B \right)^{-4/3} \quad (57)$$

Both leads to the same outcome, so Maxwell's relations for  $S$  and  $V$  do in fact hold for the ideal gas.