

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

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

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

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

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

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 μ

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

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 η

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

1.3 Total and partial pressures

To calculate the pressure, using the equation given, we need only differentiate S_{id} since S_{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 μ 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

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

2 Thermodynamics of a black hole

We have given the following relations:

Schwarzschild radius:

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

Hawking radiation:

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

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:

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

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

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

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

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

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

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:

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

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

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

Addition: One can also think about this in the following way:

The thermodynamical entropy for a bit (two-state system) is given by

$$S_{\text{bit}} = k_B \ln 2 . \quad (38)$$

Thus, the number of bits is given by

$$\#\text{bits} = \frac{S_t}{S_{\text{bit}}} = \frac{\ln \Omega}{\ln 2} \approx 10^{66} . \quad (39)$$

3 Maxwell relations

Assume that we know the fundamental equation as

$$E = E(S, V, N) \quad (40)$$

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 $\partial_x := \frac{\partial}{\partial x}$

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S} \quad (41)$$

$$\partial_S \partial_V E = \partial_V \partial_S E \quad (42)$$

$$-\partial_S p \Big|_{V,N} = \partial_V T \Big|_{S,N} \quad (43)$$

For this, we used the fact that

$$\partial_S E \Big|_{V,N} = T \quad \text{and} \quad \partial_V E \Big|_{S,N} = -p \quad (44)$$

which can easily be verified using the fundamental equation:

$$dE = T \cdot dS - p \cdot dV + \mu \cdot dN \quad (45)$$

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

$$S = k_B N \left\{ \left[\left(\frac{V}{N} \right) \cdot \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\} \quad (46)$$

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

$$E = \frac{3h^2 N}{4\pi m} \cdot \left[\frac{N}{V} \cdot \left(\frac{S}{k_B N} - \frac{5}{2} \right) \right]^{2/3} \quad (47)$$

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

Differentiate both for volume and entropy:

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

$$= -\frac{2C}{3V^2} \cdot \frac{\partial}{\partial S} \left[\left(\frac{S}{V} - \frac{5}{2} N k_B \right)^{-1/3} \cdot S \right] \quad (50)$$

$$= -\frac{2C}{3V^2} \cdot \frac{\partial}{\partial S} \left[\left(\frac{S}{VS^3} - \frac{5Nk_B}{2} \frac{1}{S^3} \right)^{-1/3} \right] \quad (51)$$

$$= \frac{2C}{9V^2} \cdot \left(\frac{1}{VS^2} - \frac{5Nk_B}{2} \frac{1}{S^3} \right)^{-4/3} \cdot \left(\frac{-2}{VS^3} \right) \quad (52)$$

$$= -\frac{4C}{9V^2} \cdot \left(\frac{S}{V} - \frac{5}{2} N k_B \right)^{-4/3} \cdot S^4 \cdot \frac{1}{VS^3} \quad (53)$$

$$= -\frac{4C}{9} \cdot \frac{S}{V^3} \cdot \left(\frac{S}{V} - \frac{5}{2} N k_B \right)^{-4/3} \quad (54)$$

$$\frac{\partial}{\partial V} \frac{\partial E}{\partial S} = \frac{\partial}{\partial V} \left[\frac{2C}{3} \cdot \left(\frac{S}{V} - \frac{5}{2} N k_B \right)^{-1/3} \cdot \frac{1}{V} \right] \quad (55)$$

$$= \frac{2C}{3} \cdot \frac{\partial}{\partial V} \left[\left(SV^2 - \frac{5Nk_B}{2} V^3 \right)^{-1/3} \right] \quad (56)$$

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

$$= -\frac{2C}{9} \cdot \left(\frac{S}{V} - \frac{5}{2} N k_B \right)^{-4/3} \cdot \frac{1}{V^4} \cdot 2SV \quad (58)$$

$$= -\frac{4C}{9} \cdot \frac{S}{V^3} \cdot \left(\frac{S}{V} - \frac{5}{2} N k_B \right)^{-4/3} \quad (59)$$

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