

# Statistical Mechanics: Lecture 3

## Classical Ideal Gas

Now that we have the expression for the entropy in microcanonical ensemble, let us use it to calculate the entropy of an ideal gas of classical particles. Let there be  $N$  particles of mass  $m$  each, enclosed in a box of volume  $V$ . The Hamiltonian is given by

$$H = \sum_i \frac{p_i^2}{2m}, \quad (1)$$

where sum over  $i$  represents sum over all particles and the three components. Let the total energy of the gas be  $E$ . Total number of microstates can then be written as

$$\Omega(E, N, V) = \int_V \prod_i dx_i dy_i dz_i \frac{1}{h^{3N}} \int_E \prod_i dp_{xi} dp_{yi} dp_{zi} \quad (2)$$

The integral over space can be carried out straightaway, giving the volume,

$$\Omega(E, N, V) = \frac{V^N}{h^{3N}} \int_E \prod_i dp_{xi} dp_{yi} dp_{zi} \quad (3)$$

Momenta are constrained by the relation

$$\sum_i \left( \frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \right) = E \quad (4)$$

If the summation over  $i$  were not there, this would be the equation of a sphere with radius  $\sqrt{2mE}$ . With the summation, it is the equation of a  $3N$ -dimensional hypersphere of radius  $\sqrt{2mE}$ . We assume that the energy is not exactly constant, but can vary by an amount  $\Delta E$ .  $\Delta E$  is chosen to satisfy

$$\frac{E}{N} < \Delta E \ll E. \quad (5)$$

The momentum space volume accessible to the gas is a thin shell of a  $3N$ -dimensional hypersphere of radius  $\sqrt{2mE}$ , and thickness  $\sqrt{\frac{m}{2E}} \Delta E$ . Here we have used the fact that  $R = \sqrt{2mE}$ , and hence  $dR = \sqrt{\frac{m}{2E}} dE$ . Clearly our thermodynamic results should not depend on this arbitrary  $\Delta E$ . Volume in the momentum space accessible to the system is equal to (surface area of a  $3N$ -dimensional hypersphere of radius  $\sqrt{2mE}$ )  $\times \sqrt{\frac{m}{2E}} \Delta E$ . Volume and surface area of a  $n$ -dimensional hypersphere are given by

$$V_n(R) = \frac{\pi^{n/2}}{(n/2)!} R^n, \quad S_n(R) = \frac{2\pi^{n/2}}{\Gamma(n/2)} R^{n-1} \quad (6)$$

So, the surface area of a  $3N$ -dimensional hypersphere of radius  $\sqrt{2mE}$  is given by

$$S_{3N}(\sqrt{2mE}) = \frac{2\pi^{3N/2}}{\Gamma(3N/2)} (2mE)^{(3N-1)/2} \quad (7)$$

Total number of microstates can now be written as

$$\begin{aligned}\Omega(E, N, V) &= \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(3N/2 - 1)!} (2mE)^{(3N-1)/2} \sqrt{\frac{m}{2E}} \Delta E \\ &= \frac{V^N}{h^{3N}} \frac{(2\pi mE)^{3N/2}}{(3N/2 - 1)!} \frac{\Delta E}{E}\end{aligned}\quad (8)$$

Entropy of the gas can now be written as

$$\begin{aligned}S(E, V, N) &= k \log \Omega \\ &= k \log \left( \frac{V^N}{h^{3N}} \frac{(2\pi mE)^{3N/2}}{(3N/2 - 1)!} \frac{\Delta E}{E} \right) \\ &= Nk \log \left( \frac{V}{h^3} (2\pi mE)^{3/2} \right) - k \log \{(3N/2 - 1)!\} + k \log \left( \frac{\Delta E}{E} \right)\end{aligned}\quad (9)$$

For a macroscopic gas,  $N$  is very large, of the order of  $10^{23}$ , and it makes sense to use the Stirling formula  $\log(n!) \approx n \log(n) - n$ . So we get

$$\begin{aligned}\log \{(3N/2 - 1)!\} &\approx (3N/2 - 1) \log(3N/2 - 1) - 3N/2 + 1 \\ &\approx (3N/2 - 1) \log(3N/2) - 3N/2 + 1\end{aligned}\quad (10)$$

Entropy of the gas now takes the form

$$\begin{aligned}S(E, V, N) &= Nk \log \left( \frac{V}{h^3} (2\pi mE)^{3/2} \right) - k \left( \frac{3N}{2} - 1 \right) \log \left( \frac{3N}{2} \right) + \frac{3Nk}{2} - k + k \log \left( \frac{\Delta E}{E} \right) \\ &= Nk \log \left( \frac{V}{h^3} (2\pi mE)^{3/2} \right) + \frac{3Nk}{2} + \left\{ k \log \left( \frac{3N}{2} \right) - k + k \log \left( \frac{\Delta E}{E} \right) \right\}\end{aligned}\quad (11)$$

In the equation above, the terms in the curly brackets are all much smaller than the other terms, which are at least of order  $N$ , and hence can be neglected to yield

$$S = Nk \log \left( V \left[ \frac{4\pi mE}{3N\hbar^2} \right]^{3/2} \right) + \frac{3Nk}{2}\quad (12)$$

## Entropy of Mixing: Gibbs Paradox

Mixing of two different gases is an irreversible process. It should thus lead to an increase in entropy. Let us check that out in our expression for entropy of an ideal gas. Let there be a box of volume  $V$ , which is partitioned as shown in the figure. Let there be two different, but similar, gases in the two partitions, *at the same temperature and pressure*. We remove the partition, and allow the gases to mix.

Before mixing, the initial entropy of the combined system, before mixing, is just the sum of the entropies of the two gases:

$$S_I = N_1 k \log \left( V_1 \left[ \frac{4\pi m_1 E_1}{3N_1 \hbar^2} \right]^{3/2} \right) + \frac{3N_1 k}{2} + N_2 k \log \left( V_2 \left[ \frac{4\pi m_2 E_2}{3N_2 \hbar^2} \right]^{3/2} \right) + \frac{3N_2 k}{2}\quad (13)$$

After the partition is removed, the energy, pressure, temperature of the gases will not change, as they were already at same temperature and pressure. The only difference is that now volume  $V$  is available to both the gases. The final entropy, after mixing, looks like

$$S_F = N_1 k \log \left( V \left[ \frac{4\pi m_1 E_1}{3N_1 \hbar^2} \right]^{3/2} \right) + \frac{3N_1 k}{2} + N_2 k \log \left( V \left[ \frac{4\pi m_2 E_2}{3N_2 \hbar^2} \right]^{3/2} \right) + \frac{3N_2 k}{2} \quad (14)$$

The change in entropy is given by

$$\Delta S = S_F - S_I = N_1 k \log \left( \frac{V}{V_1} \right) + N_2 k \log \left( \frac{V}{V_2} \right) \quad (15)$$

Clearly, the entropy increases after mixing of the two gases, which is what one would expect.  $\Delta S$  is called the *entropy of mixing*. However, there is a problem. If the two gases were identical, removing the partition should not have any effect. But our expression for entropy given by (12), yields the same change in entropy (15) even if the two gases are identical! One can verify that for

$E_1 \quad N_1 \quad V_1$	$E_2 \quad N_2 \quad V_2$
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same gas in the two partitions, the expression (14) reduces to the expression (12) of entropy of a gas of  $N$  particles in a volume  $V$ . In this case  $E_1/N_1 = E_2/N_2 = E/N$ . The final entropy in the case of identical gases, is given by

$$\begin{aligned} S_F &= N_1 k \log \left( V \left[ \frac{4\pi m E}{3N \hbar^2} \right]^{3/2} \right) + \frac{3N_1 k}{2} + N_2 k \log \left( V \left[ \frac{4\pi m E}{3N \hbar^2} \right]^{3/2} \right) + \frac{3N_2 k}{2} \\ &= (N_1 + N_2) k \log \left( V \left[ \frac{4\pi m E}{3N \hbar^2} \right]^{3/2} \right) + \frac{3(N_1 + N_2) k}{2} \\ &= N k \log \left( V \left[ \frac{4\pi m E}{3N \hbar^2} \right]^{3/2} \right) + \frac{3N k}{2} \end{aligned} \quad (16)$$

For the case of same gas in the two parts, removing the partition is a reversible process, because one can reinsert the partition later, and one will not be able to make out if the partition was removed before. Hence, the change in entropy on removing the partition should be zero. The fact that expression (12) for entropy yields a non-zero entropy of mixing for identical gases, is called *Gibbs paradox*.

Gibbs empirically realized that while counting the number of microstates, if one divides the number of microstates by  $N!$ , the paradox disappears. He concluded that our counting of microstates must be thus wrong. The way we have counted the microstates, interchanging two particles gives one a new microstate. However, from quantum mechanics we know that elementary particles and atoms should be treated as identical particles. So, the way we have counted the microstates, we have done an overcounting by assuming the particles to distinguishable. So, we must divide by  $N!$  to correct for it. Equation (8) will thus take the following form

$$\Omega(E, N, V) = \frac{1}{N!} \frac{V^N (2\pi m E)^{3N/2} \Delta E}{\hbar^{3N} (3N/2 - 1)! E} \quad (17)$$

Using Stirling's approximation for  $N!$ , we have to subtract  $k(N \log(N) - N)$  from (12) to obtain the correct expression for entropy

$$S(E, N, V) = Nk \log \left( \frac{V}{N} \left[ \frac{4\pi m E}{3N\hbar^2} \right]^{3/2} \right) + \frac{5Nk}{2} \quad (18)$$

This is called the *Sackur-Tetrode equation*, and describes the entropy of a classical (monoatomic) ideal gas. It is named for Hugo Martin Tetrode (1895-1931) and Otto Sackur (1880-1914), who developed it independently as a solution of Boltzmann's gas statistics and entropy equations, at about the same time in 1912.

The entropy of two gases before mixing is now given by

$$S_I = N_1 k \log \left( \frac{V_1}{N_1} \left[ \frac{4\pi m_1 E_1}{3N_1 \hbar^2} \right]^{3/2} \right) + \frac{5N_1 k}{2} + N_2 k \log \left( \frac{V_2}{N_2} \left[ \frac{4\pi m_2 E_2}{3N_2 \hbar^2} \right]^{3/2} \right) + \frac{5N_2 k}{2} \quad (19)$$

If the two gases are the same,  $V_1/N_1 = V_2/N_2 = V/N$  and energy per particle is also same, if they are at the same temperature and pressure,  $E_1/N_1 = E_2/N_2 = E/N$ . So, the above equation reduces to

$$\begin{aligned} S_I &= N_1 k \log \left( \frac{V}{N} \left[ \frac{4\pi m_1 E}{3N\hbar^2} \right]^{3/2} \right) + \frac{5N_1 k}{2} + N_2 k \log \left( \frac{V}{N} \left[ \frac{4\pi m_2 E}{3N\hbar^2} \right]^{3/2} \right) + \frac{5N_2 k}{2} \\ &= (N_1 + N_2) k \log \left( \frac{V}{N} \left[ \frac{4\pi m_1 E}{3N\hbar^2} \right]^{3/2} \right) + \frac{5(N_1 + N_2)k}{2} \\ &= Nk \log \left( \frac{V}{N} \left[ \frac{4\pi m_1 E}{3N\hbar^2} \right]^{3/2} \right) + \frac{5Nk}{2} \end{aligned} \quad (20)$$

which is the equation for the entropy of the gas of  $N$  particles in a volume  $V$ , that is, the gas after mixing. So, for the case of same gas, mixing has no effect.

One can verify that for the case of different gases, the Sackur-Tetrode equation leads the same expression for the entropy of mixing, as given by (15).

## Equation of state

In thermodynamics, the pressure of a gas is defined as

$$P \equiv T \left( \frac{\partial S}{\partial V} \right)_E \quad (21)$$

We plugin the expression for entropy from (18) in the equation to obtain the pressure of our classical ideal gas.

$$\begin{aligned} P &= NkT \frac{\partial}{\partial V} \log \left( \frac{V}{N} \left[ \frac{4\pi m E}{3N\hbar^2} \right]^{3/2} \right) \\ &= NkT \frac{1}{V} \\ &\boxed{PV = NkT} \end{aligned} \quad (22)$$

This is the familiar equation of state for an ideal gas.

