

# 1) Classical ideal gas

noninteracting particles

$$\Omega(N, E, V) \propto V^N$$

$$\frac{P}{T} = k_B \left. \frac{\partial \ln \Omega}{\partial V} \right|_{N, E} = \frac{N k_B}{V}$$

$$\Rightarrow PV = N k_B T = n R T$$

$$k_B = \frac{R}{N_A} \quad \text{Boltzmann const.}$$

How to calculate  $\Omega$  explicitly?

$$\sum_{i=1}^N \epsilon_i = E$$

$$\epsilon(n_x, n_y, n_z) = \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) \quad (2)$$

( $N$  particles in a cube of edge  $L$  and  $V = L^3$ ).

$$\epsilon = \frac{\hbar^2}{8m V^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$

$$\epsilon^* = \frac{8m V^{2/3}}{\hbar^2} \epsilon = n_x^2 + n_y^2 + n_z^2$$

$$\sum_{r=1}^{3N} n_r^2 = \frac{8m V^{2/3}}{\hbar^2} E \equiv E^*$$

$$S(N, V, E) = S(N, V^{2/3} E)$$

$V^{2/3} E = \text{const.}$  for a reversible adiabatic process

$$P = T \left. \frac{\partial S}{\partial V} \right|_{N, E} = \frac{\left. \frac{\partial S}{\partial V} \right|_{N, E}}{\left. \frac{\partial S}{\partial E} \right|_{N, V}}$$

$$= - \left. \frac{\partial E}{\partial V} \right|_{N, S}$$

$$\left( \text{cf. } dE = T ds - p dV + \mu dN \right)$$

$$E = \text{const.} \cdot V^{-2/3} \quad \text{for } N, S = \text{const.}$$

$$\text{so } P = \frac{2}{3} \frac{E}{V} \quad \text{Combining this}$$

$$\text{with } PV = N k_B T \quad \text{gives}$$

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

$$\text{Def. } \Sigma(N, V, E) = \sum \Omega(N, V, E')$$

related to  $\Xi(E)$ , Eq. (3.25)  $E' \leq E$

$$\Sigma(1, V, E) \approx \frac{1}{8} \frac{4\pi}{3} (E^*)^{3/2}$$

volume of positive octant of a sphere in  $n_x, n_y, n_z$  space.

$$\Sigma(1, V, E) \approx \frac{\pi}{6} \left( \frac{8mV^{2/3}}{h^2} E \right)^{3/2} = \frac{\pi}{6} \frac{V}{h^3} (8mE)^{3/2}$$

A better approximation is

$$\Sigma_1(E^*) \approx \frac{\pi}{6} (E^*)^{3/2} \mp \frac{3\pi}{8} E^*$$

where  $-$  holds for Dirichlet b.c.  
and  $+$  holds for Neumann b.c.

[see Fig. 1.2 on page 13]

$\Sigma(N, V, E)$  is the hypervolume of 5  
the positive sector of a  $3N$ -dim.  
hypersphere of radius  $\sqrt{E^*}$ :

$$\Sigma_N(E^*) \simeq \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} (E^*)^{3N/2}$$

$$\Sigma(N, V, E) \simeq \left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{3N/2}}{(3N/2)!}$$

Say we know the energy of the  
system lies in the interval

$$E \pm \frac{\Delta}{2} \quad \text{then}$$

$$\Omega(N, V, E) \simeq \frac{\partial \Sigma(N, V, E)}{\partial E} \Delta$$

$$= \left(\frac{V}{h^3}\right)^N \frac{3N}{2} \frac{(2\pi m E)^{3N/2}}{(3N/2)!} \frac{\Delta}{E}$$

$$\ln \Omega(N, V, E) \approx N \ln \left[ \frac{V}{h^3} (2\pi m E)^{3/2} \right]$$

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$$+ \ln \frac{\Delta}{E} + \ln \frac{3N}{2} - \ln \left( \frac{3N}{2} \right)!$$

$\ln n! \approx n \ln n - n$ , so

$$\ln \Omega(N, V, E) \approx N \ln \left[ \frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right]$$

$$+ \frac{3N}{2} + \left\{ \ln \left( \frac{3N}{2} \right) + \ln \frac{\Delta}{E} \right\}$$

The last two terms in  $\{ \}$  are negligible compared to the first two terms for  $N \gg 1$ . Thus  $\ln \Omega$  is effectively independent of  $\Delta$ !

$$\ln \Omega(N, V, E) \approx N \ln \left[ \frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3N}{2}$$

## 2) Entropy of mixing and the Gibbs paradox [7]

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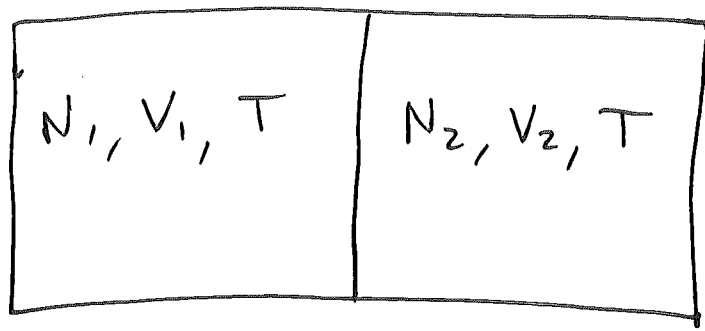
$$S = k_B \ln \Omega$$

Experimentally,  $S$  is an extensive quantity. That is

$$S(N, V, E) = N s\left(\frac{V}{N}, \frac{E}{N}\right)$$

for a large system, where surface effects, etc. can be neglected (as we have done by dropping corrections to  $\Sigma(N, V, E)$ ). However, our result for  $\Omega(N, V, E)$  does not satisfy this principle due to the  $\ln V$  term.

To highlight this effect, let's consider the entropy of mixing:



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$$N = N_1 + N_2 \quad V = V_1 + V_2$$

When partition is removed, the two gases mix, and  $S = S(N, V, E)$ .

$$\Delta S = S(N, V, E) - S_1(N_1, V_1, E_1) - S_2(N_2, V_2, E_2)$$

$$E = \frac{3}{2} N k_B T, \quad E_i = \frac{3}{2} N_i k_B T$$

$$S_i = N_i k_B \ln V_i + \frac{3}{2} N_i k_B \left\{ 1 + \ln \left( \frac{2\pi m_i k_B T}{h^2} \right) \right\}$$

$$\Delta S = N \ln V - N_1 \ln V_1 - N_2 \ln V_2$$

$$= N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \geq 0$$



This is true even if

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$$P_1 = \frac{N_1 k_B T}{V_1} = P_2 = \frac{N_2 k_B T}{V_2},$$

in which case

$$\Delta S_{P_1=P_2} = N_1 \ln \frac{N_1+N_2}{N_1} + N_2 \ln \frac{N_1+N_2}{N_2}$$

$$= N \ln N - N - (N_1 \ln N_1 - N_1) - (N_2 \ln N_2 - N_2)$$

$$= \ln N! - \ln N_1! - \ln N_2!$$

This is the entropy of mixing. After removing the partition, all  $N$  molecules can be on either side, while beforehand they were each confined to one side or the other.

However, a problem arises if 10  
the two gases are the same.  
For then we can reinsert the  
partition and return to the  
macrostate we started with;  
The process is reversible for  
identical gases, so  $\Delta S_{P_1=P_2} = 0$ .

This paradox can be resolved,  
following Gibbs, by dividing  $\Omega_N$   
by  $N!$  :

$$\Omega_{\text{Gibbs}}(N, V, E) = \frac{\Omega_{\text{P.S.}}(N, V, E)}{N!}$$

The division by  $N!$  reflects the  
fact that interchanging two identical

molecules in the gas does not lead to a distinct quantum state of the system. In QM, it is not possible, even in principle, to keep track of the individual particles making up the gas, so our enumeration of the  $N$ -particle states must reflect this fact. With Gibbs' correction, we have

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

which is truly extensive.

$$\mu = -T \left. \frac{\partial S}{\partial N} \right|_{V, E} = k_B T \ln \left\{ \frac{N}{V} \left( \frac{h^2}{2\pi m k_B T} \right)^{3/2} \right\}$$

where I used  $E = \frac{3}{2} N k_B T$ . (12)

It should be pointed out that although Gibbs' ansatz has solved the paradox of mixing identical gases, and rendered the entropy of a classical ideal gas extensive, it does not represent an exact result for a system of noninteracting quantum molecules, but only holds in the low-density, high-temperature limit.