

# OVERVIEW

- Entropy: a microscopic view

# MACROSTATES AND MICROSTATES

Consider a gas in a hermetically sealed vessel.

## MACROSTATES

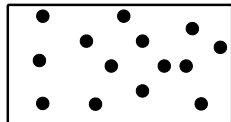
A *macrostate* is defined by a set of measurable parameters of the gas as a whole:  
temperature, pressure, density etc

(sometimes called *configuration* or *thermodynamic state*)



## MICROSTATES

A *microstate* is defined by a set of velocities and positions of all individual molecules.

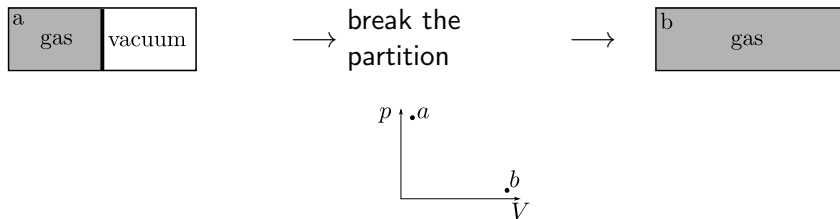


Entropy: provides a link between *macro-* and *microstates*.

# FREE EXPANSION OF AN IDEAL GAS

Consider a thermally insulated vessel, separated into two parts: one contains an ideal gas, the other is empty.

## IRREVERSIBLE EXPANSION:



**Q:** What is the temperature change of the gas during the free expansion?

**Q:** What is the change of entropy?

# FREE EXPANSION OF AN IDEAL GAS

First law of thermodynamics:

$$Q = \Delta U + W$$

The vessel is insulated  $\Rightarrow Q = 0$

The right-hand part of the vessel is evacuated  $\Rightarrow W = 0$

Therefore,  $\Delta U = 0$

For the ideal gas,  $U = \nu C_V T$ , hence  $T = \text{const}$  during the free expansion.

NB: This only holds for an ideal gas. For real gases,  $T$  will change.

# FREE EXPANSION OF AN IDEAL GAS

Calculating the entropy change during the free expansion: connect the initial and final states by a reversible process, then use the definition of entropy  $dS = \delta Q/T$  — *for this reversible process*

First law of thermodynamics (reversible processes only)

$$T dS = dU + p dV$$

Since  $T = \text{const}$ , use a reversible isothermal expansion. Then for the ideal gas  $U = \nu C_V T$ , hence  $dU = 0$ .

# FREE EXPANSION OF AN IDEAL GAS

First law of thermodynamics for a reversible isothermal expansion

$$T dS = p dV$$

Ideal gas law:  $pV = \nu RT$ , hence  $p = \nu RT/V$

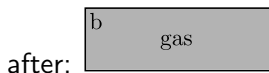
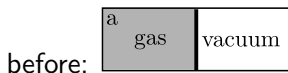
$$dS = \nu R \frac{dV}{V}$$

Integrate:

$$\Delta S = \nu R \int_{V_a}^{V_b} \frac{dV}{V} = \nu R \ln V \Big|_{V_a}^{V_b} = \nu R \ln \frac{V_b}{V_a}$$

# FREE EXPANSION OF AN IDEAL GAS

A special case: suppose originally the gas occupied the half of the volume:  $V_b = 2V_a$



$$\Delta T = T_b - T_a = 0$$

$$\Delta S = S_b - S_a = \nu R \ln \frac{V_b}{V_a} = \nu R \ln 2$$

NB: entropy is not conserved (while internal energy is).

Using  $\nu = N/N_A$  and  $R = k_B N_A$ , find that

$$\Delta S = N k_B \ln 2$$

i.e.: entropy change *per particle* is  $k_B \ln 2$

# MICROSCOPIC CALCULATION OF THE ENTROPY

Start with an empty vessel, and add particles one by one. We add particles at random positions, hence probability of a particle to end up in the right-hand or left-hand half of the container is  $1/2$  — which is equivalent to a coin flip (heads is right-hand side, tails is left-hand side)

To define a *macrostate*, we only need to specify how many particles are in each half of the container: state  $a$  is  $N$  particles in the left-hand part, state  $b$  is each of the halves have  $N/2$  particles. Coin flip analogy: “there are  $N$  tails” and “there are  $N/2$  heads and  $N/2$  tails”

*Microstates* track each individual particle (heads-heads-tails-... etc).

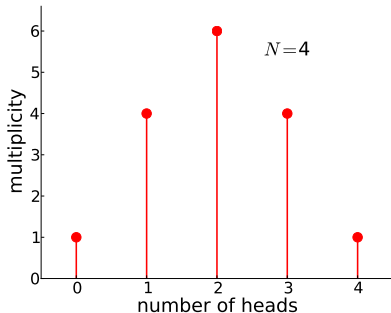







# TOSSING COINS

Start with  $N = 4$

There are 5 possible *macrostates*.

Each coin flip outcome is equiprobable,  
but macrostates have different  
*multiplicity*



Macroscopic state	Corresponding microscopic states
Four heads	
Three heads, one tails	
Two heads, two tails	
One heads, three tails	
Four tails	

# TOSSING COINS

**Q:** What is the multiplicity  $W$  of the macrostate with  $n_1$  heads and  $n_2$  tails out of  $N$  trials ( $n_1 + n_2 = N$ )?

**A:** The number of combinations (aka *binomial coefficient*)

$$W = \frac{N!}{n_1! n_2!}$$

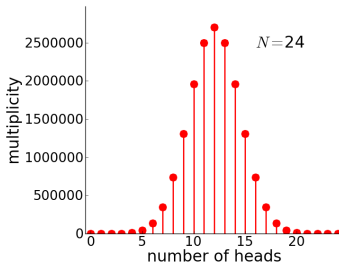
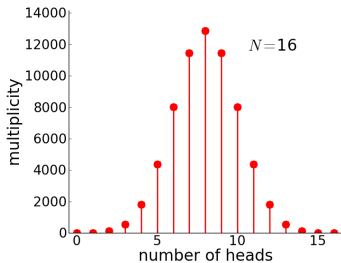
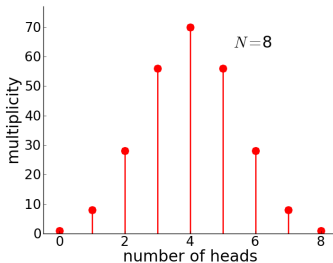
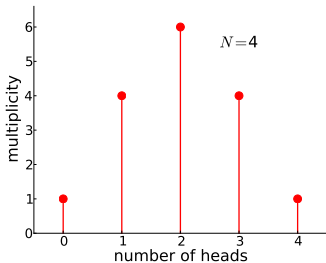
Here “ $N$  factorial” is  $N! = N \times (N - 1) \times (N - 2) \times \cdots \times 1$  and, by definition,  $0! = 1$

For  $N = 4$ :

$n_1$	0	1	2	3	4
$n_2$	4	3	2	1	0
$W$	1	4	6	4	1

# TOSSING COINS

As  $N \rightarrow \infty$ ,  $W$  develops a very narrow peak:



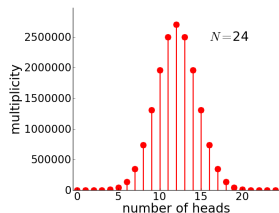
# BACK TO MOLECULES

**Q:** So good for coin flips, what about molecules?

**A:** A basic postulate of statistical mechanics:

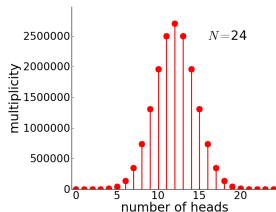
In thermal equilibrium, all *microstates* (having the same energy) are equally probable.

But then, *macrostates* are definitely not equiprobable!



NB: Largest multiplicity means largest degree of disorder  
( $n_1 \approx n_2 \approx N/2 \Rightarrow$  least information about individual molecules)

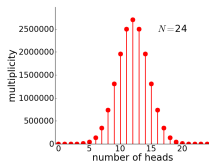
# BACK TO MOLECULES



In thermal equilibrium, all *microstates* (having the same energy) are equally probable.

- Any system left to its own devices evolves towards the *macrostate* with the largest multiplicity (cf: The arrow of time)
- What we observe as a thermal equilibrium, is the state with the largest multiplicity (in fact, the other way around: we observe it *because* it has the largest multiplicity)
- Largest multiplicity  $\Longleftrightarrow$  largest degree of disorder.

# ENTROPY



Entropy: a convenient way of quantifying “large multiplicity”

Multiplicity  $W = \frac{N!}{n_1! n_2!}$ . It is simply not convenient to deal with ratios of huge numbers.

## ENTROPY

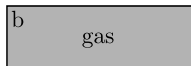
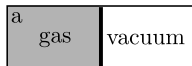
$$S = k_B \ln W$$

Hence the entropy difference

$$\Delta S = k_B \ln \frac{W_2}{W_1}$$

# ENTROPY

Apply this definition to the two *macrostates*:



Only take into account the location of each molecule (left-hand or right-hand part)

State *a*:

$$n_1 = N \quad n_2 = 0$$

hence

$$W_a = \frac{N!}{n_1! n_2!} = 1$$

State *b*:

$$n_1 = N/2 \quad n_2 = N/2$$

hence

$$W_b = \frac{N!}{n_1! n_2!} = \frac{N!}{(N/2)! (N/2)!}$$

# ENTROPY

For  $N \gg 1$  use the *Stirling formula*:  $N! \approx \left(\frac{N}{e}\right)^N$

$$W_b = \frac{N!}{(N/2)! (N/2)!} = \frac{(N/e)^N}{(N/2e)^{(N/2+N/2)}} = 2^N$$

Finally,

$$\begin{aligned} S_b - S_a &= k_B \ln(2^N) - k_B \ln 1 \\ &= Nk_B \ln 2 \end{aligned}$$

(In agreement with the thermodynamic calculation)



# WHY DOES THE AIR IN THIS LECTURE HALL NOT COMPRESS SPONTANEOUSLY?

**Q:** “Free compression”: What is the probability of the air to occupy only one half of this lecture hall?

**A:** The volume of the hall is  $\sim 10\text{ m} \times 10\text{ m} \times 10\text{ m}$  Thus there is

$$\sim \frac{10^3\text{ m}^3}{22.4\text{ L/mol}} = 4.4 \cdot 10^4 \text{ moles of air}$$

$$\Delta S/k_B = -4.4 \cdot 10^4 \times 6.0 \cdot 10^{23} \ln 2 \sim -2 \cdot 10^{28}$$

hence

$$\text{Probability} \sim 2^{\Delta S/k_B} \sim 2^{-2 \cdot 10^{28}}$$

So the expectation time of such an event is quite a bit longer than the lifetime of the universe ( $\sim 15$  billion years)