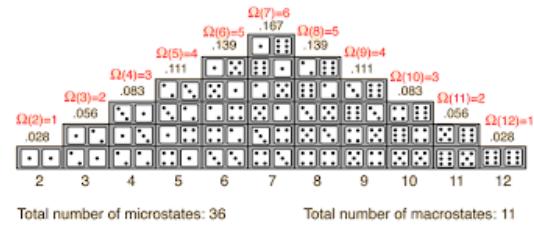


General Physics II: Thermodynamics

Prof. M. Hirschmann

Spring semester 2024



Content of this course – today's lecture

- Chapter 1. Introduction
- Chapter 2. Temperature and zeroth law of thermodynamics
- Chapter 3. Gas laws
- Chapter 4. Statistical thermodynamics I: Kinetic theory of gas
- Mathematical Excursion — Preparation for Chapter 5.
- **Chapter 5. Statistical thermodynamics II (Boltzmann factor, Maxwell-Boltzmann distr.)**
- Chapter 6. Energy, heat and heat capacity
- Chapter 7. First law of thermodynamics and thermal processes
- Lecture 7: Mock Exam I, *led by Dr. Tress*
- Chapter 8. Entropy and the second and third law of thermodynamics
- Chapter 9. Thermal machines
- Chapter 10. Thermodynamic potentials and equilibria
- Lecture 12: Mock Exam II, *led by Dr. Tress*
- Chapter 11. Heat transfer (Conduction, Convection, Radiation)
- Lecture 14: Final review and open questions

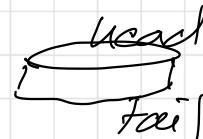
5. Statistical nature of Thermodynamics II

- 5.1 Microstates and Macrostates
- 5.2 Microstates and thermal equilibrium
- 5.3 Boltzmann factor
- 5.4 Probability distribution of gas speeds
- 5.5 Maxwell-Boltzmann distribution of absolute speeds

So much enlightened in this class!

5.1 Microstates and Macrostates

Imagine a system with 1, 2, 3 coins



Now at 100s: 2, 4, 8 possibilities

1 coin

H $\frac{1}{2}$

T $\frac{1}{2}$

2 coins

HH $\frac{1}{4}$

TH $\frac{1}{4}$

HT $\frac{1}{4}$

TT $\frac{1}{4}$

3 coins

HHH

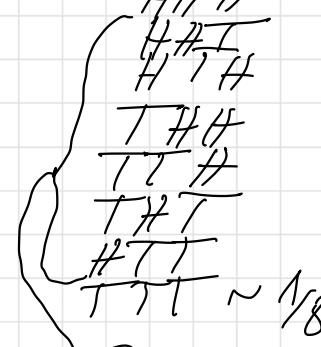
HHT

HTH

THH

HTT

TTT



Each individual state has same probability

"Microstates"

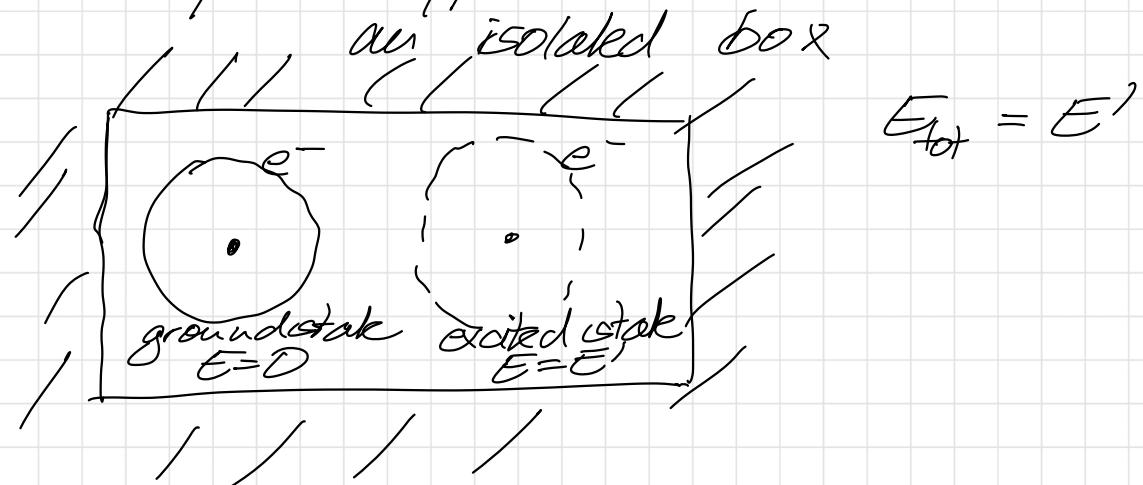
mixed states $\frac{3}{4}$
(both T & H)

are more likely than pure states
(only T or only H)

Groups of microstates (like pure, mixed states) are called macrostates

- more likely than individual microstates
- needs to be defined, can vary from system to system

Physical example: Suppose we have two atoms in



Energy in box is fixed to $E_{\text{tot}} = E'$, what are the possible microstates?

All possible microstates:

~~O+O~~ ~~O+E'~~ ~~E'+O~~ ~~2E'~~
✓ ✓

The macrostate $E_{\text{tot}} = E'$ permits 2 microstates.

Example in TD:

Microstates of gas: position, velocity, kinetic energy of each gas molecule

Macrostates of gas: global, macroscopic quantities like $\bar{O}, \bar{P}, \bar{T}, \dots$

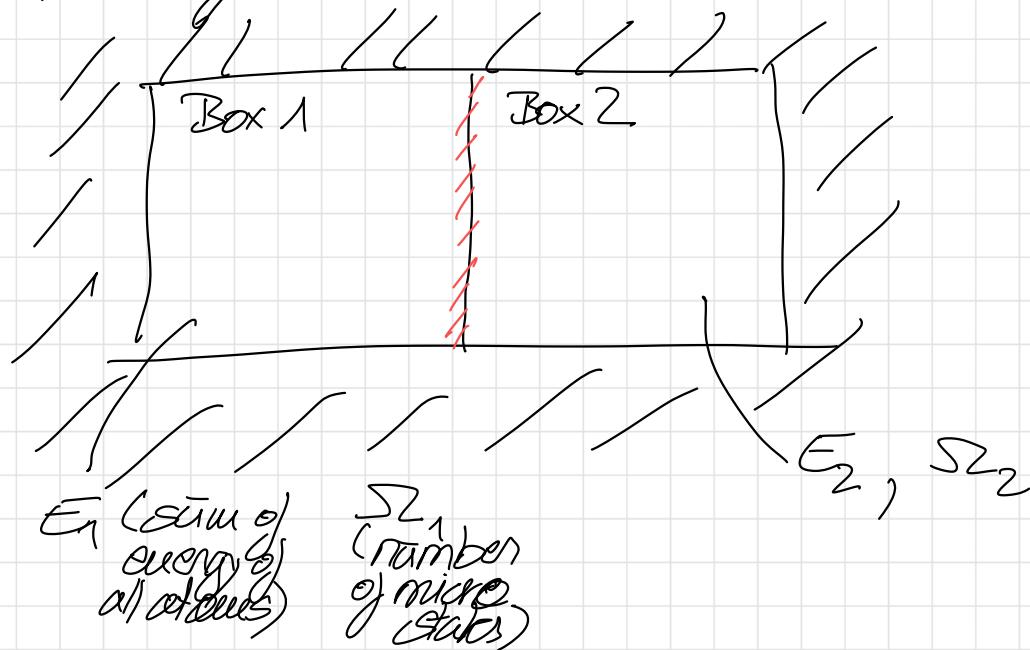
Set of diff. microstates may lead to same macrostate.

All microstates have the same probability

Probability of macrostate \sim total probability of those microstates leading to that macrostate

5.2 Microstates and thermal equilibrium

Let's now consider two large boxes (with billions of atoms) isolated from the environment



Note: allow for thermal contact between box 1 & 2
(exchange of energy) *What happens?*

What is the total # of microstates (in Box 1+2) as a fct of total energy ($E = E_1 + E_2$)?

Sum up over all microstates: $\Omega(E) = \underline{\sum_1(O) \cdot \sum_2(E_1 + E_2) +}$

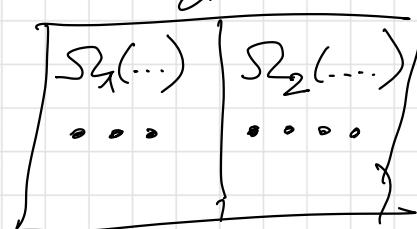
$\sum_1(dE) \cdot \sum_2(E_1 + E_2 - dE) + \dots$ many possibilities - -

$\sum_1(E_1 + E_2) \sum_2(O)$

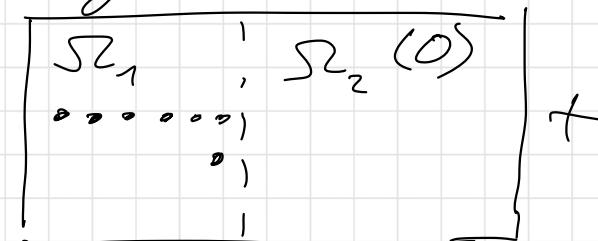
most extreme cases for energy distribution

Example: energy is discrete in form of balls

Initially:



open wall \rightarrow



$$\left[\begin{array}{cccc|cc} S_{2_1} & & & S_{2_2} & & & \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \\ & & & & & & \\ & & & & & & \\ & & & & & & \end{array} \right]$$

$$+ \dots$$

Just counting, only physics is deicto Energy per box & related # of microstates.

$S_2(E)$: Total # of microstates in box 1 & box 2

Now: which groups of them are more likely to have?

Example: Two boxes, each with only 3 atoms, either in groundstate or in excited state

$$E_1 := 2E'$$

$$S_1(2E') = \begin{Bmatrix} E'E'0 & | & 00E' \\ E'0E' & | & 0E'0 \\ 0E'E' & | & E'00 \end{Bmatrix}$$

$$E_2 := E'$$

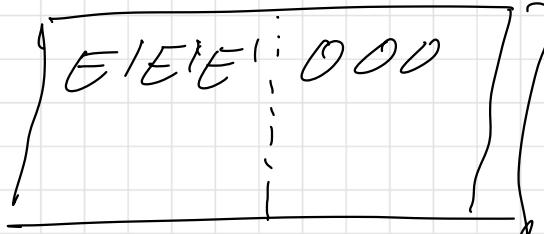
$$S_2(E') = 3$$

Make wall dia-
thermal (energy
exchange)

What are the most likely configurations of microstates?

$3E'$ can be distributed over the two boxes

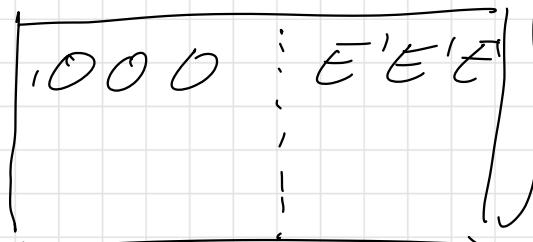
* All $3E'$ on the left



1 microstate

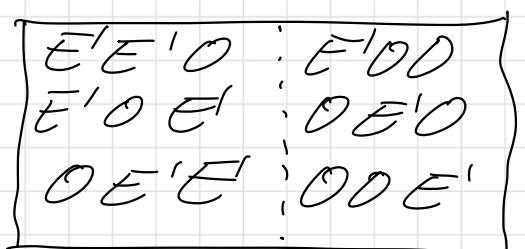
not most likely
cases

* All $3E'$ on the right



1 microstate

* 2 E' on the left,
 E' on the right
(or vice versa)



mixed stack
is much more
likely

3 x 3 = 9 microstates

In reality, many more microstates possible (not only 3 but billions of atoms)

- extremely unlikely that all energy is is just on the left or on the right
- Energy is somehow distributed over the box
- System is taking on a macroscopic configuration that maximises the # of microstates, since this corresponds to the highest probability

Mathematical formulation:

$$\Omega = \underbrace{\frac{\partial}{\partial E_1} S_{E_1}(E_1) S_{E_2}(E_2)}_{\text{Maximise of the number of microstates}} \quad \text{where } E_2 = E - E_1$$

Use product rule:

$$0 = \frac{dS_1(E_1)}{dE_1} S_2(E_2) + S_1(E_1) \cdot \frac{dS_2(E_2)}{dE_1}$$

$$0 = \frac{dS_1(E_1)}{dE_1} S_2(E_2) + S_1(E_1) \cdot \frac{dS_2(E_2)}{dE_2} \cdot \frac{dE_2}{dE_1}$$

From side: $\frac{dE_2}{dE_1} \quad E_1 + E_2 = E_{\text{tot}} \stackrel{\text{const.}}{\quad} \left| \frac{d}{dE_1} \right.$

$$1 + \frac{dE_2}{dE_1} = 0 \Rightarrow \frac{dE_2}{dE_1} = -1$$

$$\Rightarrow 0 = \frac{dS_1(E_1)}{dE_1} S_2(E_2) - S_1(E_1) \frac{dS_2(E_2)}{dE_2}$$

$$\Rightarrow S_1(E_1) \frac{dS_2(E_2)}{dE_2} = \frac{dS_1(E_1)}{dE_1} S_2(E_2) \Big|_{S_2}^{S_1}$$

$$\Rightarrow \frac{1}{S_2(E_2)} \cdot \frac{dS_2(E_2)}{dE_2} = \frac{1}{S_1(E_1)} \frac{dS_1(E_1)}{dE_1}$$

$$\Rightarrow \frac{d}{dE_2} \log(S_2(E_2)) = \frac{d}{dE_1} \log(S_1(E_1)) \stackrel{?}{=} \frac{1}{k_B T}$$

Most likely distribution of energies is that if derivatives of the log of # of microstates in Box 1 & 2 are equal

Relax to TD: the most likely state should be thermal equilibrium

$$\frac{d}{dE} \log S(E) \stackrel{?}{=} \frac{1}{k_B T}$$

our assumption, which will be checked later

Summary 5.1, 5.2 Microstates, macrostates and thermal equilibrium

- Microstates of gas:
 - Properties, such as position and velocity, of individual gas particles
 - Every microstate is equally probable
- Macrostates of gas:
 - Described by global quantities, such as T, V, P, etc.
 - Set of different microstates that lead to the same macrostate
 - Probability of macrostate: sum of probabilities of microstates leading that macrostate
- A system takes on that macroscopic configuration which maximises the number of microstates (highest probability)
- We think that most likely macrostate may be thermal equilibrium, i.e. two systems in contact have the same T ("Boltzmann argument")

$$\frac{1}{kT} = \frac{d \ln \Omega}{dE}$$

*our assumption
don't believe until proven*

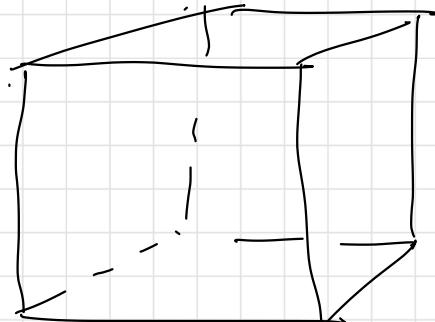
5.3 Boltzmann factor

What is the probability that box 1 has Energy E_1 ?

$$P_1(E_1) = \frac{\Omega_1(E_1) \Omega_2(E_2)}{\sum_E (\Omega_1(E) \Omega_2(E_{\text{tot}} - E))}$$

Ω = # of microstates to have E in box 1

$E_{\text{tot}} = E_1 + E_2$



"main system"
Box 1

Box: Universe,
heat bath
atmosphere
"extremely big"
in thermal contact

sum of microstates of all possible energy distributions

$$\log P_1(E_1) = \log (\Omega_1(E_1) + \log (\Omega_2(E_2) - \log \sum_E (\Omega_1(E) \Omega_2(E_{\text{tot}} - E)))$$

independent of E_1
→ const

$$\log P_1(E_1) = \log S_1(E_1) + \log S_2(E_2) + C$$

↪ # of microstates in the Universe, $E_2 = E_{\text{tot}} - E_1$

$$\log S_2(E_2) = \log S_2(\underbrace{E_{\text{tot}}}_{\text{huge}} - \underbrace{E_1}_{\text{small}}) \approx \cancel{x}$$

Aside: Taylor approximation: $F(x) = \log(S_2(x))$, $a = E_{\text{tot}}$

$$= F(E_{\text{tot}}) + \left. \frac{dF}{dx} \right|_{E_{\text{tot}}} \underbrace{(x - E_{\text{tot}})}_{E_{\text{tot}} - E_1 - E_{\text{tot}} = -E_1}$$

$\cancel{x} \approx \underbrace{\log(S_2(E_{\text{tot}}))}_{\text{gigantic form}} - E_1 \underbrace{\left. \frac{d}{dE_2} \log(S_2(E_2)) \right|_{E_{\text{tot}}}}_{\cong \frac{1}{k_B T} \text{ "our assumption"}}$

total # of microstates in Universe

$$\Rightarrow \log S_2(E_2) = \log (S_2(E_{\text{tot}})) - \frac{E_1}{k_B T}$$

$$\Rightarrow \log P_1(E_1) = \log S_1(E_1) + \underbrace{\log (S_2(E_{\text{tot}}))}_{\substack{\text{ind. of } E_1 \\ + C}} - \frac{E_1}{k_B T}$$

$$= \log S_1(E_1) - \frac{E_1}{k_B T} + C \quad | \exp$$

$$\Rightarrow P_1(E_1) = \underbrace{e^{C'}}_K S_1(E_1) \cdot e^{-E_1/k_B T}$$

: Boltzmann factor

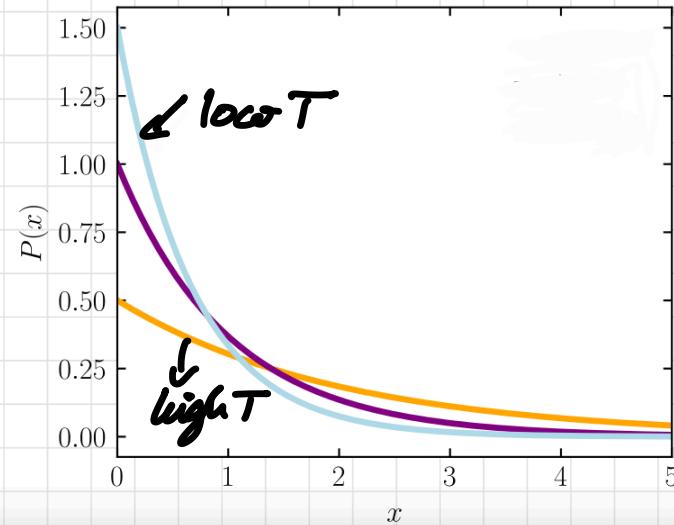
Probability that my system open to universe, has an energy E_1 scaling with Boltzmann factor $\#$ of microstates allowing for E_1 in our system.

Notes to the Boltzmann factor:

accounts for the influence of taking E_1 from the Universe on the total number of microstates in Universe

The more energy you take out, the less likely it is to have that much energy in the main system.

$$P(E) = k \mathcal{S}(E) e^{-\frac{E}{k_B T}}$$



5.4 Probability distribution of ^{velocities} speeds of gas particles

Kinetic energy of a gas molecule: $E = \frac{mv^2}{2} = \frac{m(v_x^2 + v_y^2 + v_z^2)}{2}$

Probability of one gas particle to have E :

$$P(E) \sim \mathcal{Z}(E) e^{-E/k_B T}$$

Compute P that a ^{ideal} gas particle has a velocity vector:

$$P(v_x, v_y, v_z) \sim \mathcal{Z}(v_x, v_y, v_z) e^{-\frac{m}{2k_B T} (v_x^2 + v_y^2 + v_z^2)}$$

$\mathcal{Z} = 1$, either particle goes in this direction or not.

\rightarrow compute normalization \mathcal{Z}

- \rightarrow Integrate over all directions a gas particle can have
- \rightarrow Total probability = 1

$$1 = \int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y \int_{-\infty}^{+\infty} dv_z K e^{-\frac{mv^2}{2k_B T}} = \sigma_x^2 + \sigma_y^2 + \sigma_z^2$$

$$1 = K \int_{-\infty}^{+\infty} dv_x e^{-\frac{mv_x^2}{2k_B T}} \int_{-\infty}^{+\infty} dv_y e^{-\frac{mv_y^2}{2k_B T}} \int_{-\infty}^{+\infty} dv_z e^{-\frac{mv_z^2}{2k_B T}}$$

Math notes: $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$

$$1 = K \left(\frac{2 \cdot \frac{1}{2} \sqrt{\frac{\pi}{a}}}{2 \sqrt{\frac{m}{2k_B T}}} \right)^3$$

due to integration from $-\infty - +\infty$ (and not just from $0 - +\infty$)

$$\Rightarrow K = \sqrt{\frac{m}{2\pi k_B T}}^3$$

P that a gas particle has a velocity v_x, v_y, v_z

$$P(v_x, v_y, v_z) = \sqrt{\frac{m}{2\pi k_B T}}^3 e^{-\frac{m}{2k_B T} (v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z$$

Prob. (density) to have a velocity between v & $v+dv$

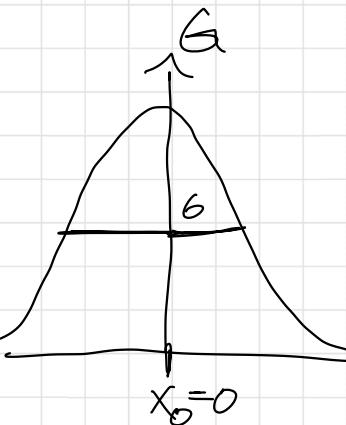
Probability distribution fct.

$$P(v) dv = \sqrt{\frac{m}{2\pi k_B T}}^3 e^{-\frac{m}{2k_B T} v^2} dv = v_x^2 v_y^2 v_z^2$$

In one direction (x-dir):

$$P(v_x) dv_x = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m}{2k_B T} v_x^2} dv_x$$

This is a Gaussian Jct:



$$G_{\sigma, x_0}(x) = \frac{1}{\sigma \sqrt{2\pi}} \cdot \exp \left[-\frac{(x - x_0)^2}{2\sigma^2} \right]$$

* x_0 is the mean

$$\langle x \rangle = \int_{-\infty}^{+\infty} x G(x) dx = x_0$$

$$\text{In our case: } \langle x \rangle = 0 \quad (x_0 = 0)$$

$$\sigma^2 (\text{STD}^2) = \text{Var}(x) = \langle (x - x_0)^2 \rangle = \frac{kT}{m}$$

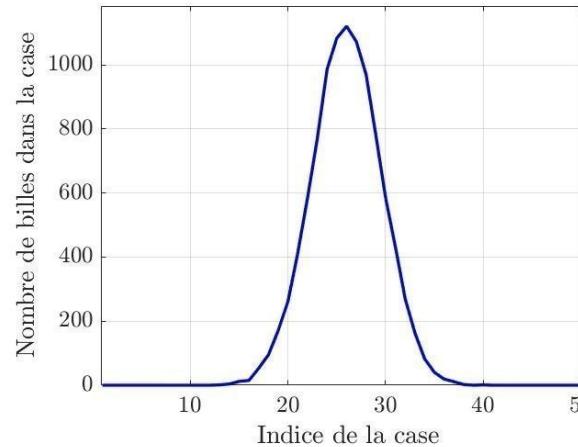


Experiment 391 Planche de Galton (Gaussian distr.)

Statement of the Phenomenon: The Galton Board is a system invented by Sir Francis Galton in the 19th century. It is constructed in three parts:

- a compartment containing metal balls,
- a series of rows of obstacles (horizontal nails),
- wooden compartments at the bottom where the balls can settle.

Observation: When the balls are released from the upper compartment, they fall onto the nails and land in the compartments. Each time the experiment is repeated, a bell-shaped (Gaussian) distribution of the balls in the compartments is observed.





Experiment 391: Planche de Galton (Gaussian distr.)

<https://www.youtube.com/watch?v=Ej0xlqr-Rcl>

Why do we always arrive at the same distribution?

—>In probability theory, there is a well-known theorem about the sum of a sequence of N random variables. This is the central limit theorem. It states that this sum of random variables converges towards a normal/Gaussian distribution for a sufficiently large number of random variables . Thus, this law demonstrates a kind of “intrinsic organization in randomness”.

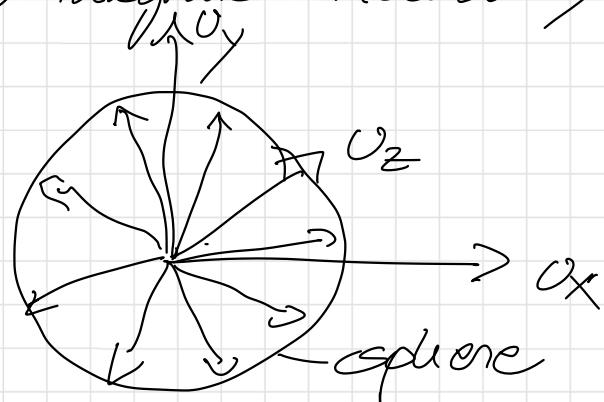
In the case of our experiment, the random variables are the directions taken by the balls after hitting a nail. As a first approximation, we can say that these random variables are binomial laws whose two possible outcomes are "going left" and "going right."

The same can be applied for the probability that a gas particle/molecule has a certain velocity, also described by a Gaussian distribution.

5.5 Maxwell-Boltzmann distribution of absolute speeds

Compute $F(v)$ the probability that a gas particle has an absolute speed $|v|$

↳ Integrate Probability dist. for v over $|v|$



$$\text{recall: } v^2 = v_x^2 + v_y^2 + v_z^2$$

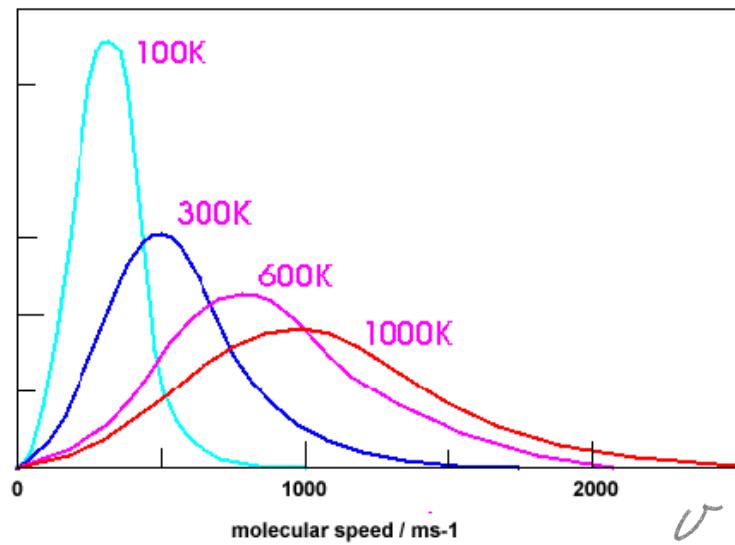
$$dv_x dv_y dv_z = v^2 dv_x dv_y dv_z$$

$$\Rightarrow F(v)dv = \sqrt{\frac{m}{2\pi k_B T}}^3 v^2 e^{-\frac{mv^2}{2k_B T}} dv \int_0^{\pi} \int_0^{2\pi} \sin\theta d\theta d\phi$$
$$= \frac{4\pi}{3}$$

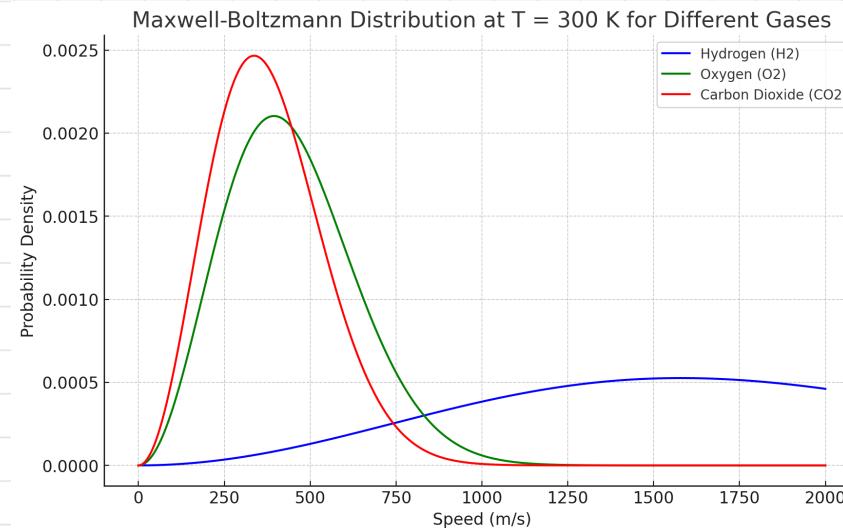
$$f(v) dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} v^2 dv$$

Maxwell-Boltzmann distribution

number of particles



v



v



Experiment 167:

Apparatus for the study of the kinetic theory of gases

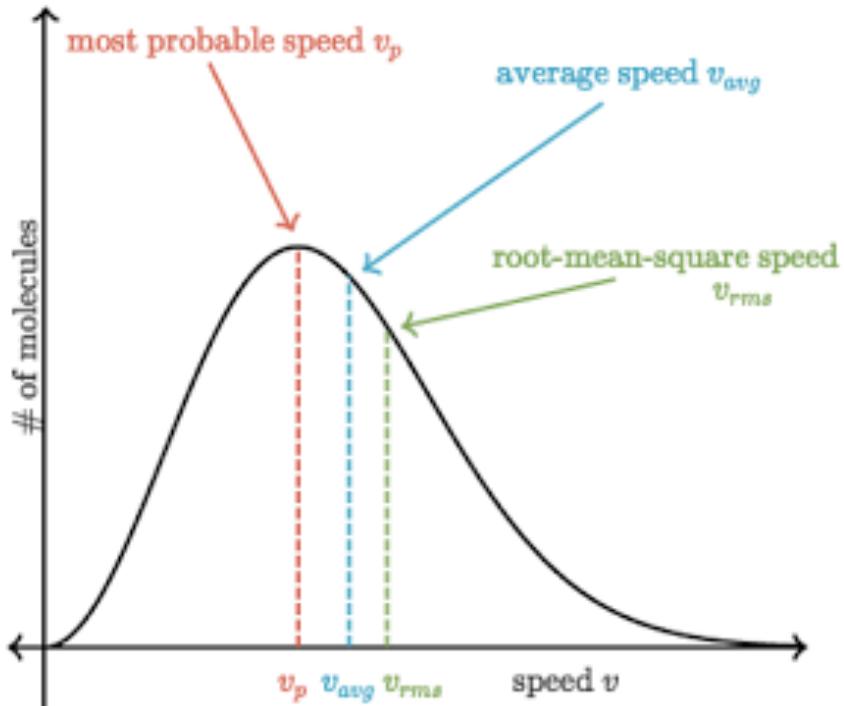
<https://www.youtube.com/embed/4KFSmWcXcH8>

Set-up: tiny balls are brought into movement in a cylinder with a hole towards a device with different compartments

Observation: depending on the velocity of the different balls, they fall into different compartments in the device on the left, showing a Maxwell-Boltzmann distribution.

Each time the experiment is repeated, a Maxwell-Boltzmann distribution of the balls in the compartments is observed.





MB dist

$$\langle \sigma \rangle = \int_0^{\infty} \sigma f(\sigma) d\sigma$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\int_0^{\infty} v^2 f(v) dv}$$

$$v_{mp}: \frac{d}{dv} F(v) = 0$$

① v_{rms}

$$v_{rms}^2 = \int_0^\infty v^2 f(v) dv$$

$$= \int_0^\infty 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^4 e^{-\frac{mv^2}{2kT}} dv \quad a := \frac{m}{2kT}$$
$$= 4\pi \sqrt{\frac{a}{\pi}}^3 \int_0^\infty v^4 e^{-av^2} dv$$

Solve integral via a trick:
Replace $v^4 e^{-av^2}$ with $\frac{\partial^2}{\partial a^2} e^{-av^2}$

$$\Rightarrow v_{rms}^2 = 4\pi \sqrt{\frac{a}{\pi}}^3 \frac{\partial^2}{\partial a^2} \int_0^\infty dv e^{-av^2}$$
$$= \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

$$\Rightarrow v_{rms}^2 = 4\pi \sqrt{\frac{a^3}{\pi}} \frac{\partial^2}{\partial a^2} \left(\frac{1}{2} \sqrt{\frac{\pi}{a}} \right)$$

$$= 4\pi \sqrt{\frac{a^3}{\pi}} \frac{\partial^2}{\partial a^2} \left(-\frac{1}{2} \frac{1}{\sqrt{a^3}} \right)$$

$$= -\sqrt{a^3} \left(-\frac{3}{2} \right) \frac{1}{\sqrt{a^5}} = \frac{3}{2} \frac{1}{a}$$

$$= \frac{3}{2} \frac{2k_B T}{m} = \frac{3k_B T}{m}$$

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

same result as in Chapter 4
derived from M-B distribution

\Rightarrow Postulak $\frac{d}{dE} \log S(E) = \frac{1}{k_B T}$ is confirmed!

$$\langle 2Kv \rangle = \int_0^\infty v F(v) dv$$

$$= 4\pi \sqrt{\frac{a}{\pi}}^3 \int_0^\infty v^3 e^{-av^2} dv$$

Aside : $\int_0^\infty x^3 e^{-ax^2} = -\frac{\partial}{\partial a} \int_0^\infty x e^{-ax^2} dx =$

$$-\underbrace{\frac{\partial}{\partial a} x e^{-ax^2}}_0 \Big|_0^\infty + \underbrace{\frac{1}{2a}}_0$$

$$= -\frac{\partial}{\partial a} \frac{1}{2a} = \frac{1}{2a^2}$$

$$\langle 2v \rangle = 4\pi \sqrt{\frac{a}{\pi}}^3 \frac{1}{2a^2} = \frac{2}{\sqrt{\pi}} \frac{1}{\sqrt{a}} = 2 \sqrt{\frac{2k_B T}{\pi m}} =$$

$$= \sqrt{\frac{8k_B T}{\pi m}}$$

③ Most probable speed

$$\frac{d}{dv} f(v) = 0$$

$$\frac{d}{dv} f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2}$$

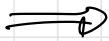
$$\frac{d}{dv} \left(v^2 e^{-\frac{m}{2kT} v^2} \right)$$

$$= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \left[2v e^{-\frac{m}{2kT} v^2} + v^2 \left(-\frac{m}{2kT} \right) \cdot 2v \cdot e^{-\frac{m}{2kT} v^2} \right]$$

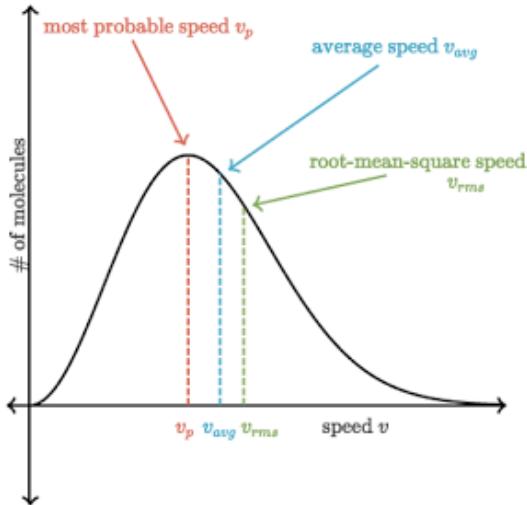
$$= 8\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \cdot e^{-\frac{m}{2kT} v^2} \left(v - \frac{mv^3}{2kT} \right) \stackrel{?}{=} 0$$

maximum

$$\Rightarrow v_{mp} - m \frac{v_{mp}^3}{2kT} = 0 \Rightarrow \frac{mv_{mp}^2}{2kT} = 1$$



$$v_{mp} = \sqrt{\frac{2kT}{m}}$$



$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} = \frac{2}{\sqrt{\pi}} \cdot v_{mp}$$

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3}{2}} \cdot v_{mp}$$

$$v_{mp} < \langle v \rangle < v_{rms}$$

Summary 5.3, 5.4, 5.5 Boltzmann factor and Maxwell distribution

- Boltzmann factor: Probability that a system, open to the Universe, has an energy E:

$$P_r(E_r) \propto e^{-E_r/kT}$$

- Probability that one gas particle has a velocity vector v_x, v_y, v_z

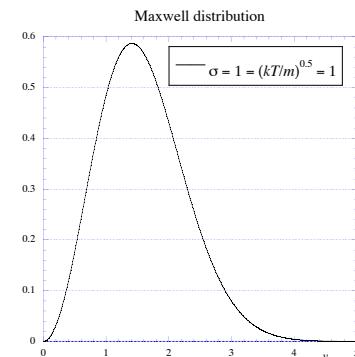
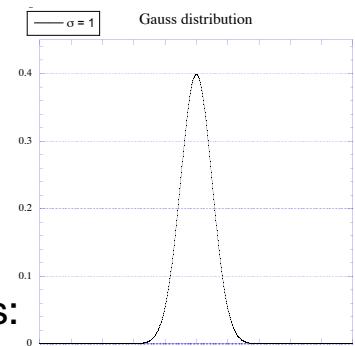
$$P(v) = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m}{2kT} (v_x^2 + v_y^2 + v_z^2) \right] dv_x dv_y dv_z$$

- Maxwell-Boltzmann distribution of absolute velocity of gas particles:

$$F(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp \left(-\frac{m}{2kT} v^2 \right)$$

- Boltzmann argument right, as we confirm result from last week:

$$v_{\text{rms}}^2 = \frac{3kT}{m}$$



WATCH: Boltzmann distribution: <https://www.youtube.com/watch?v=BdjLEHM6-t4&t=4s>

Conceptual Questions:

- Imagine you have 4 coins and you toss them. What is the probability that there will be at least two heads?
a) 1/2 b) 1/16 c) 1/8 d) 3/8 e) 11/16; What are micro and macro states in this context?
- What is the probability that a system (in thermal equilibrium) takes on energy E_1 given the number of microstates Ω_1 ? What is in this context the meaning of the Boltzmann factor?

Conceptual Questions:

- What is the Maxwell distribution of gas, and what does it depend on?
- What is correct? The rms speed of the molecules of an ideal gas
 - a) is the same as the most probable speed of the molecules.
 - b) is always equal to square root of 2 times the maximum molecular speed.
 - c) will increase as the T of a gas increases
 - d) is not equal to the average speed of a gas.
 - e) all of the above

Up next:

- Chapter 1. Introduction
- Chapter 2. Temperature and zeroth law of thermodynamics
- Chapter 3. Gas laws
- Chapter 4. Statistical thermodynamics I: Kinetic theory of gas
- Mathematical Excursion — Preparation for Chapter 5.
- Chapter 5. Statistical thermodynamics II (Boltzmann factor, Maxwell-Boltzmann distr.)
- **Chapter 6. Energy, heat and heat capacity**
- Chapter 7. First law of thermodynamics and thermal processes
- Lecture 7: Mock Exam I, *led by Dr. Tress*
- Chapter 8. Entropy and the second and third law of thermodynamics
- Chapter 9. Thermal machines
- Chapter 10. Thermodynamic potentials and equilibria
- Lecture 12: Mock Exam II, *led by Dr. Tress*
- Chapter 11. Heat transfer (Conduction, Convection, Radiation)
- Lecture 14: Final review and open questions