

Exam 3 averages

Multiple choice : 67.7%

Hand-graded part: 45%

Overall : 60.7%

FINAL EXAM – next Tuesday (May 1)

- Comprehensive
- 20 multiple choice questions *only*.
- Equation sheet will be posted later this week, please familiarize with it – one like that will be attached to your final exam.

If you have Final Exam conflict:

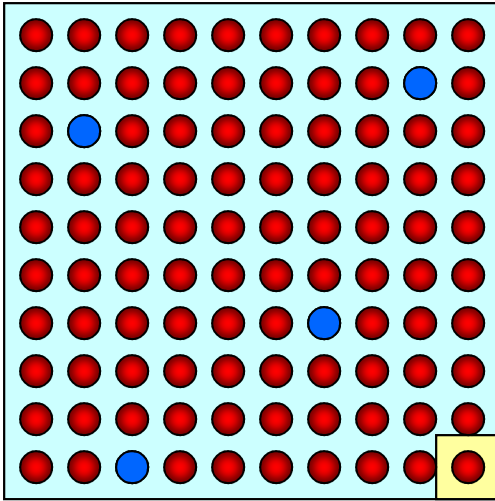
- Notify us immediately (TODAY IS LAST DAY!).

Indicate your exam schedule for Tuesday through Saturday.

- Depending on your schedule, the makeup exam will be scheduled, most likely, for Friday or Saturday.

The Boltzmann distribution

N=100 oscillators,
q=4 quanta



What is the probability to find an atom in a solid at certain energy level?

The Boltzmann distribution

The probability of finding a microscopic system to be in a state with energy E above ground state is proportional to

$$\Omega(E) e^{-\frac{E}{kT}}$$

For large systems!

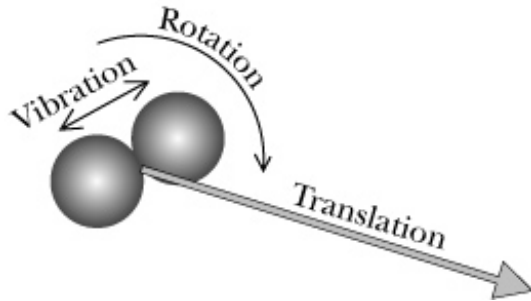
Boltzmann factor

Number of microstates
corresponding to energy E

See pages 394-395 for derivation

Application: The Boltzmann distribution in a gas

Ideal gas: molecules do not interact with each other (low density)



Energy of a molecule of mass M :

$$K_{trans} + E_{vib} + E_{rot} + Mgy_{cm}$$

Notes:

Omit rest energy, nuclear and electronic energies

Omit y_{cm} for brevity

Measure E_{vib} and E_{rot} with respect to ground state

Probability to find a molecule at energy E : $P(E) \propto e^{-\frac{K_{trans} + E_{vib} + E_{rot} + Mgy_{cm}}{kT}}$

Translational and gravitational energies are quantized, but if $kT \gg$ quantum, probability to find a molecule at certain location with certain velocity is:

$$P(E) \propto e^{-\frac{K_{trans} + E_{vib} + E_{rot} + Mgy_{cm}}{kT}} dx dy dz dv_x dv_y dv_z$$

Application: The Boltzmann distribution in a gas

$$P(E) \propto e^{-\frac{K_{trans} + E_{vib} + E_{rot} + Mgy_{cm}}{kT}} dx dy dz dv_x dv_y dv_z$$

$$P(E) \propto \left(e^{-\frac{K_{trans}}{kT}} dv_x dv_y dv_z \right) \left(e^{-\frac{Mgy_{cm}}{kT}} dx dy dz \right) \left(e^{-\frac{E_{vib}}{kT}} \right) \left(e^{-\frac{E_{rot}}{kT}} \right)$$

Velocity
distribution

Height
distribution

Vib. and Rot.
Energy distribution

Height distribution in a gas

$$P(E) \propto \left(e^{-\frac{K_{trans}}{kT}} dv_x dv_y dv_z \right) \left(e^{-\frac{Mgy}{kT}} dx dy dz \right) \left(e^{-\frac{E_{vib}}{kT}} \right) \left(e^{-\frac{E_{rot}}{kT}} \right)$$

$$P(y) \propto e^{-\frac{Mgy}{kT}} \underbrace{dx dy dz}_{\text{Volume}}$$

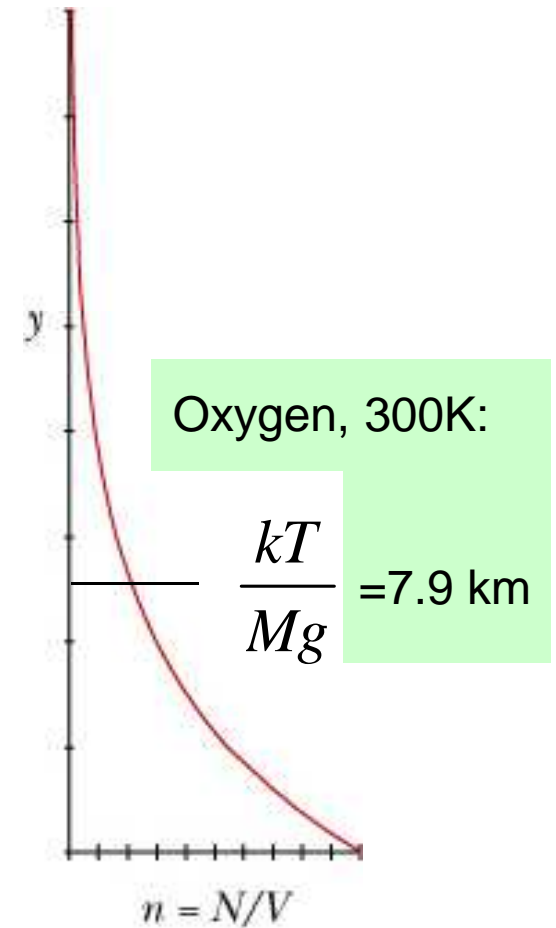
↑
density

Important factor: kT

Height 0: $P(0) \propto 1 \cdot dx dy dz$

Height $y = \frac{kT}{Mg}$: $P(y) \propto e^{-1} \cdot dx dy dz = 0.38P(0)$

Example exercises: 11.X.12-11.X.14

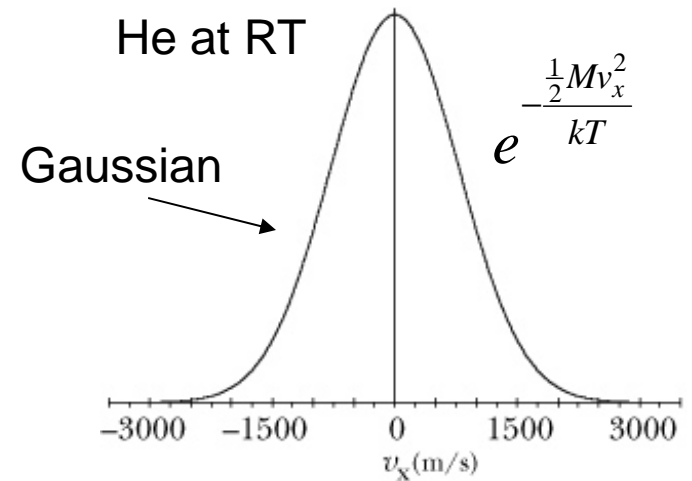


Distribution of velocities in a gas

$$P(E) \propto \left(e^{-\frac{K_{trans}}{kT}} dv_x dv_y dv_z \right) \left(e^{-\frac{Mgy}{kT}} dx dy dz \right) \left(e^{-\frac{E_{vib}}{kT}} \right) \left(e^{-\frac{E_{rot}}{kT}} \right)$$

$$P(v) \propto e^{-\frac{K_{trans}}{kT}} dv_x dv_y dv_z \quad K_{trans} = \frac{1}{2} Mv^2 = \frac{1}{2} Mv_x^2 + \frac{1}{2} Mv_y^2 + \frac{1}{2} Mv_z^2$$

$$P(v_x, v_y, v_z) \propto \left(e^{-\frac{\frac{1}{2} Mv_x^2}{kT}} dv_x \right) \left(e^{-\frac{\frac{1}{2} Mv_y^2}{kT}} dv_y \right) \left(e^{-\frac{\frac{1}{2} Mv_z^2}{kT}} dv_z \right)$$



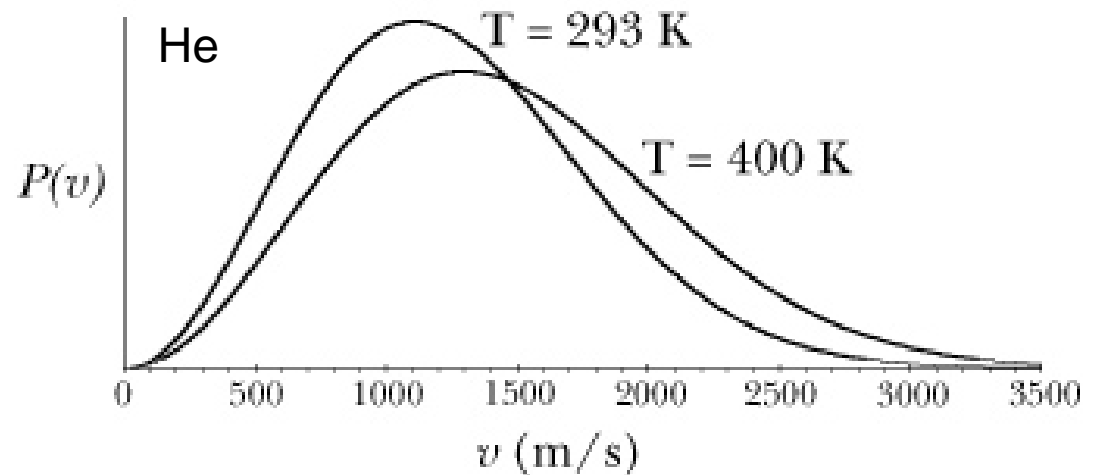
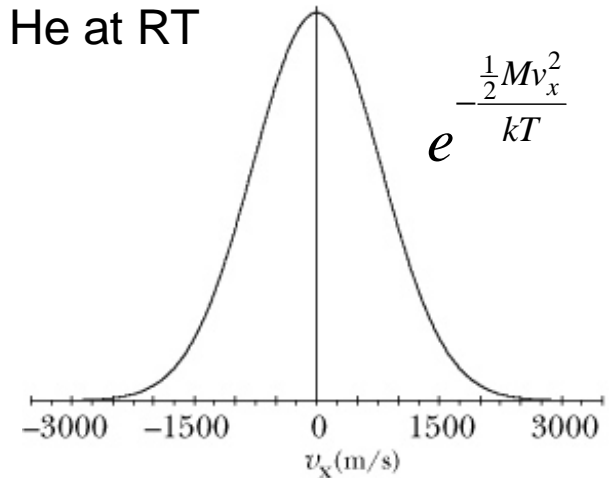
Distribution of speeds in a gas

See 11.8 for details

Maxwell-Boltzmann speed distribution
(low-density gas)

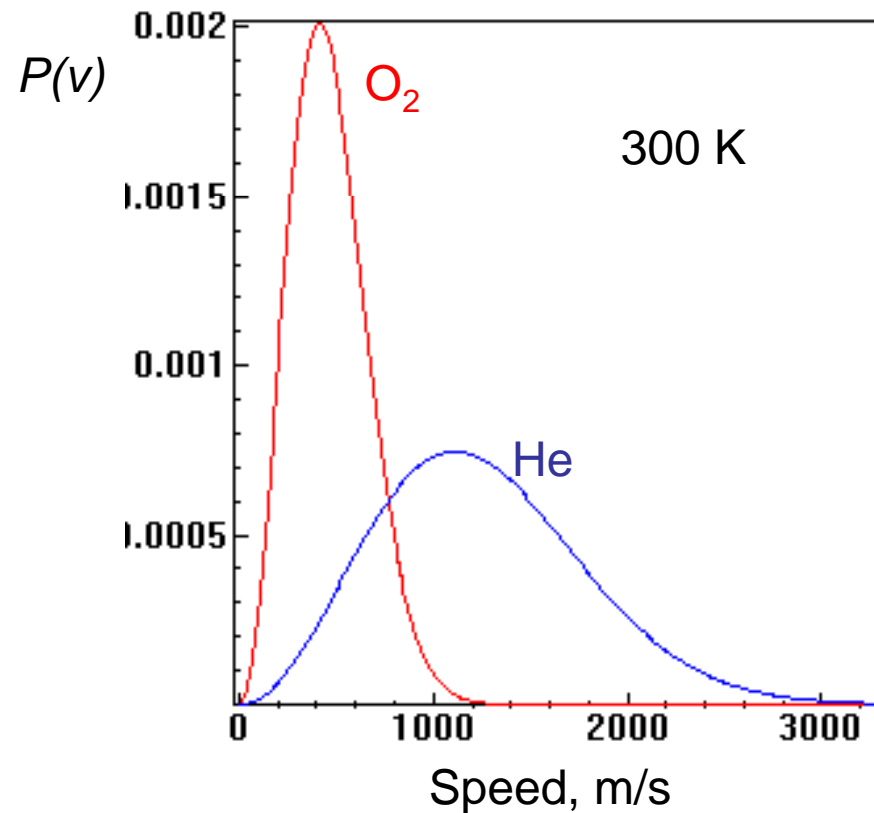
$$P(v) = 4\pi \left(\frac{M}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{\frac{1}{2}Mv^2}{kT}}$$

He at RT



Retaining a gas in the atmosphere

$$P(v) = 4\pi \left(\frac{M}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{\frac{1}{2}Mv^2}{kT}}$$



$$P_{He} (v > v_{escape}) \sim 10^{-43}$$

$$P_{O_2} (v > v_{escape}) \sim 10^{-175}$$

Average translational kinetic energy in a gas

$$K_{trans} = \frac{1}{2} M v^2 = \frac{1}{2} M v_x^2 + \frac{1}{2} M v_y^2 + \frac{1}{2} M v_z^2$$

$$\overline{\left(\frac{1}{2} M v_x^2 \right)} = \frac{1}{2} kT \quad (\text{see book for details})$$

Each “degree of freedom” contributes $\frac{1}{2}kT$

Average translational kinetic energy
for an ideal gas:

$$\bar{K}_{trans} = \frac{3}{2} kT$$

(high temperature, if $kT \gg \hbar\omega_0$)

Root mean square
(rms) speed:

$$v_{rms} \equiv \sqrt{\overline{v^2}} \quad \frac{1}{2} M v_{rms}^2 = \frac{3}{2} kT$$

$$v_{rms} = \sqrt{3kT/M}$$

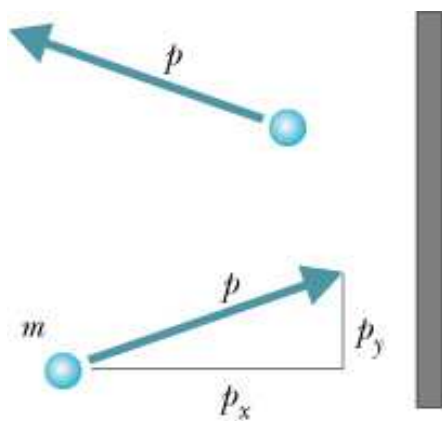
Note: $\bar{v} \neq v_{rms}$

$$\bar{v} = 0.92 v_{rms}$$

Pressure of a gas

PRESSURE: $P = F/A$

$$F = \frac{\Delta p}{\Delta t} = \left(\frac{\Delta p}{atom} \right) \left(\frac{atoms}{\Delta t} \right)$$



It so turns out that (see Sec 13.4 in book for details)

$$P = nm\bar{v}_x^2$$

$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2 = 3\bar{v}_x^2$$

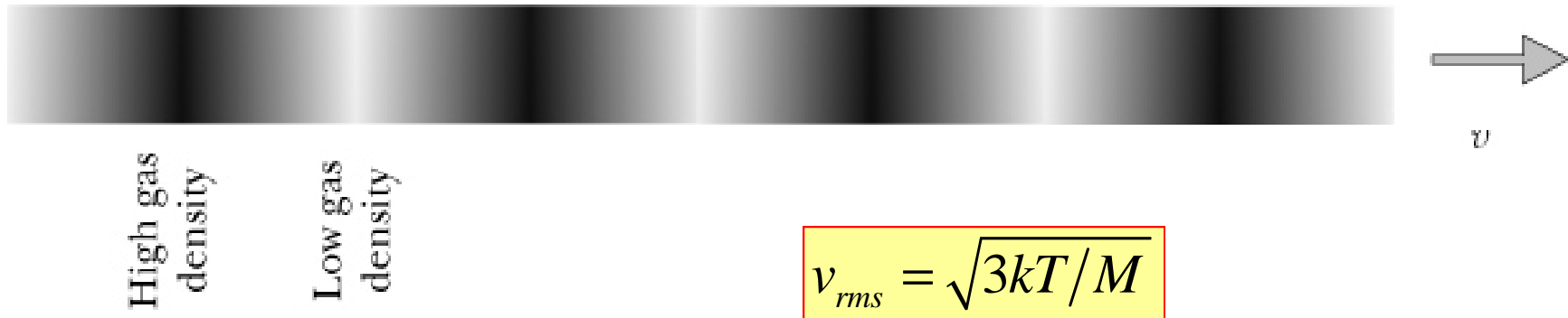
Same

$$P = nm\bar{v}_x^2 = \frac{1}{3}nm\bar{v}^2 = \frac{2}{3}n \left(\underbrace{\frac{1}{2}m\bar{v}^2}_{\overline{K_{trans}}} \right) = nkT = P$$

$$\overline{K_{trans}} = \frac{3}{2}kT$$

**IDEAL
GAS
LAW!**

Speed of sound in a gas



$$v_{rms} = \sqrt{3kT/M}$$

Example: N_2 at 293 K $v_{rms} = 496$ m/s

Speed of sound = 344 m/s

CLICKER: In which of the gases speed of sound is highest?
(at the same temperature)

- A) H_2 (2 g/mol)
- B) N_2 (28 g/mol)
- C) O_2 (32 g/mol)
- D) Ar (40 g/mol)
- E) Xe (131 g/mol)

Vibrational energy in a diatomic molecule

$$P(E) \propto \left(e^{-\frac{K_{trans}}{kT}} dv_x dv_y dv_z \right) \left(e^{-\frac{Mgy}{kT}} dx dy dz \right) \left(e^{-\frac{E_{vib}}{kT}} \right) \left(e^{-\frac{E_{rot}}{kT}} \right)$$

$$P(E_{vib}) \propto e^{-\frac{E_{vib}}{kT}}$$

Monoatomic gas: no vibration!

$$\bar{E}_{vib} = 0$$

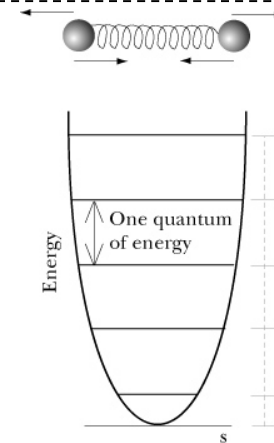
Diatomic gas, high T:

Contributions:

Energy of motion along one axis: $\frac{1}{2}kT$

Potential energy of spring: $\frac{1}{2}kT$

$$\bar{E}_{vib} = kT$$



Rotational energy in a diatomic molecule

$$P(E) \propto \left(e^{-\frac{K_{trans}}{kT}} dv_x dv_y dv_z \right) \left(e^{-\frac{Mgy}{kT}} dx dy dz \right) \left(e^{-\frac{E_{vib}}{kT}} \right) \left(e^{-\frac{E_{rot}}{kT}} \right)$$
$$P(E_{rot}) \propto e^{-\frac{E_{rot}}{kT}}$$

Monoatomic gas: no rotation!

$$\bar{E}_{rot} = 0$$

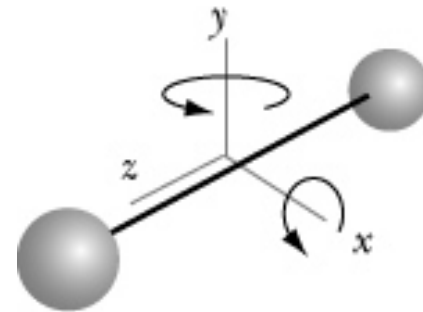
Diatomic gas, high T:

Contributions:

Energy of rotation around x: $\frac{1}{2}kT$

Energy of rotation around y: $\frac{1}{2}kT$

$$\bar{E}_{rot} = kT$$



Heat capacity of a gas

$$C = \frac{\Delta E}{\Delta T}$$

$$\bar{E}_{tot} = \bar{K}_{trans} + \bar{E}_{vib} + \bar{E}_{rot} + Mg\bar{y}_{cm}$$

↑
per molecule

$$\frac{3}{2}kT$$

$$kT$$

$$kT$$

↑ Hardly changes for
small volume

Total average energy of a **diatomic** molecule: $\bar{E}_{tot} = \frac{7}{2}kT$

Heat capacity per **diatomic** molecule: $c_v = \frac{\Delta E}{\Delta T} = \frac{7}{2}k$

Notes: fixed volume (no work done!)
per atom!

high temperatures: $\hbar\omega_0 \ll kT$

not too high temp: $kT \ll E_{\text{electronic}}$

Heat capacity of a gas versus temperature

$$\bar{E}_{tot} = \bar{K}_{trans} + \bar{E}_{vib} + \bar{E}_{rot} + Mg\bar{y}_{cm}$$

$$\frac{3}{2}kT \quad kT \quad kT$$

