# Lecture 13

## 03.10.2018

## Boltzmann statistics

# So far…

- We have worked mainly with the second law of thermodynamics.
- and we often needed to do measurements (enthalpy, entropy) to get some results…
- But we want to calculate all thermodynamics quantities from first principles and microscopic models.
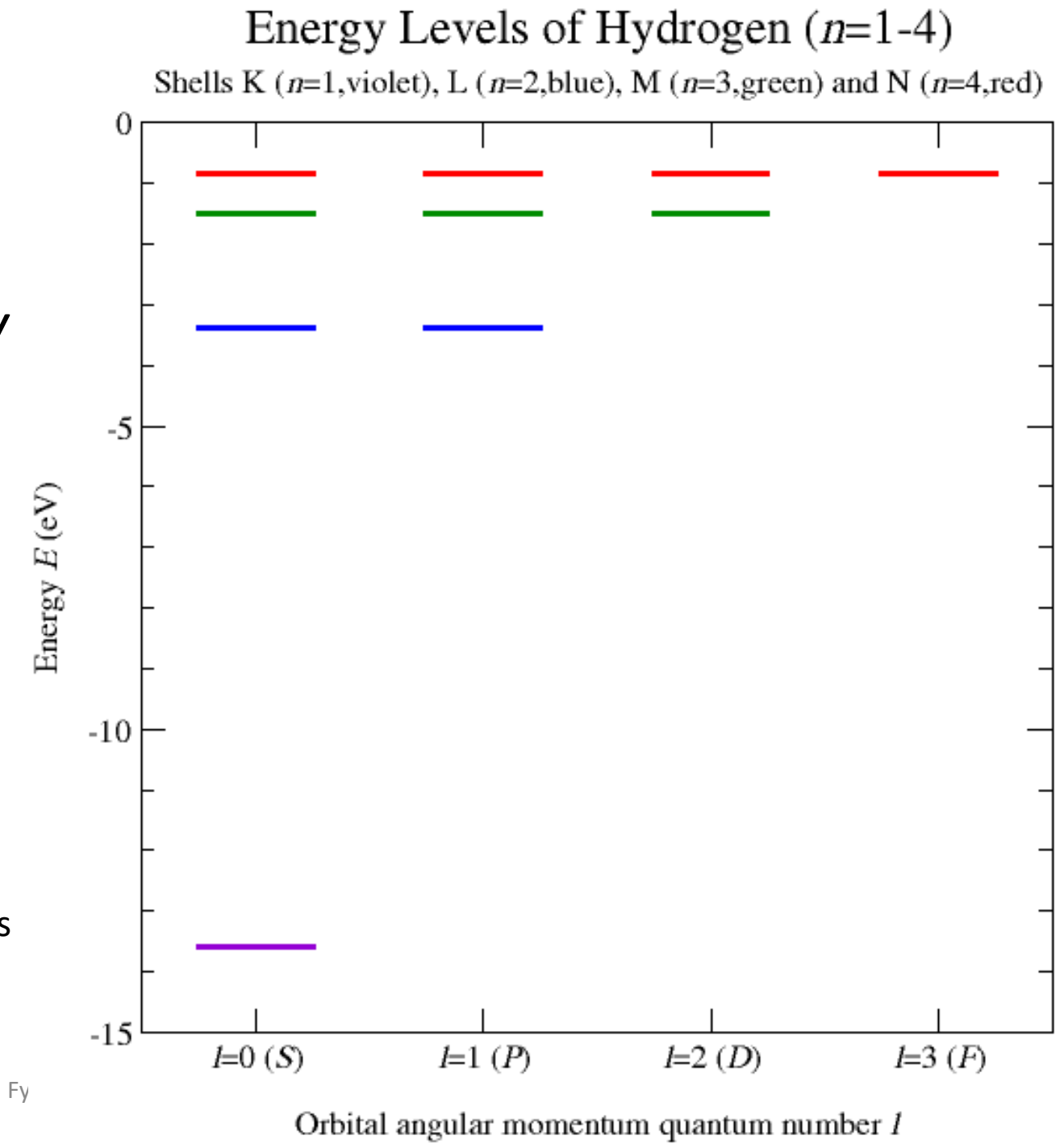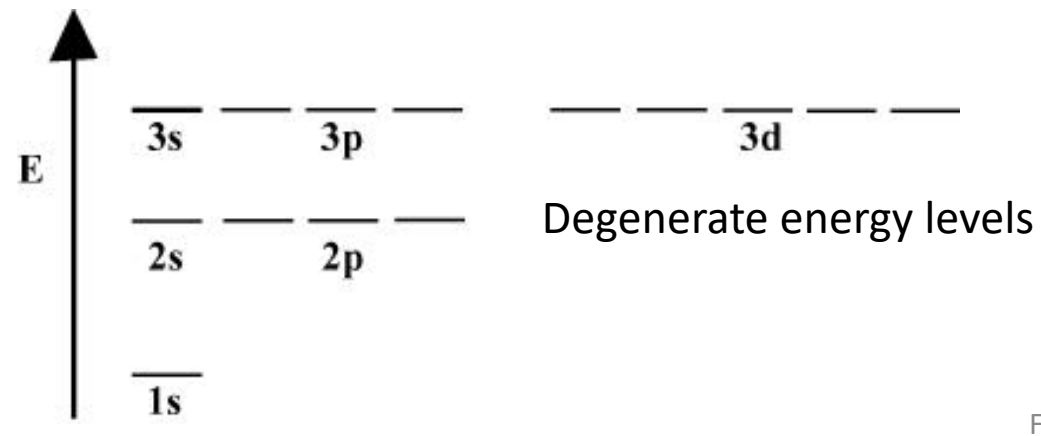- We tried to use direct combinatoric models with multiplicity $\Omega$.

# Boltzmann statistics

- We will introduce the MOST powerful tool in all statistical mechanics
- We want to find the PROBABILITY of **a** system in any given microstate.
- For an atom microstates would be various energy levels...
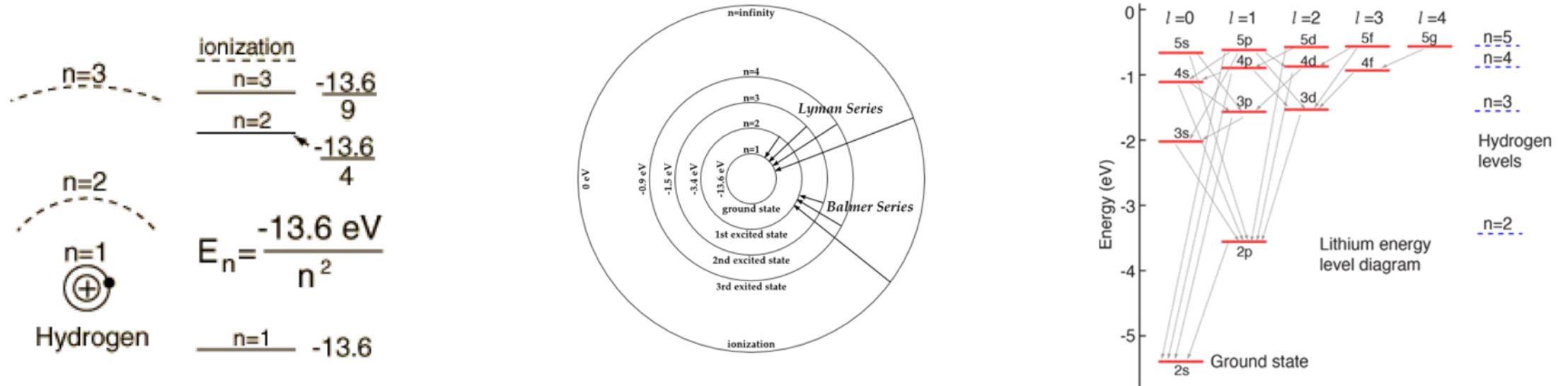
# Boltzmann statistics

- We want to find the PROBABILITY of **a** system in any given microstate.

- For an atom microstates would be various energy levels...



Degenerate energy levels

Fy



## Energy Levels of Hydrogen (*n*=1-4)

Shells K (*n*=1,violet), L (*n*=2,blue), M (*n*=3,green) and N (*n*=4,red)

# Atom in contact with reservoir…

- Temperature of reservoir is fixed.
- Any microstate possible, but some are more probable (energy is the key factor)
- Probability depends on how many possible microstates there are!
- We take two states: $E(s_1)$ and $E(s_2)$. Probabilities: $P(s_1)$ and $P(s_2)$.
- Recall: all accessible microstates in isolated system equally possible.
- But what about reservoir???
- Atom + reservoir = isolated system. Together they are in all microstates.

# Atom in contact with reservoir...

- $\Omega_R(s_1)$ – Multiplicity of reservoir when atom is in state $s_1$.
- $\Omega_R(s_2)$ – Multiplicity of reservoir when atom is in state $s_2$.
- They are different. If $E(s_1) < E(s_2)$, then more energy is left for R.
- But all microstates are equally probable.
- Probability of atom in a given state is proportional to number of microstates accessible to the reservoir.

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}$$

# Atom in contact with reservoir...

- We remember that $S = k \ln \Omega$, then we can write:

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{[S_R(s_2) - S_R(s_1)]/k}$$

- So we have probability related to change in the entropy of the reservoir. Change related to one atom – tiny...

- Thermodynamic identity gives:

$$dS_R = \frac{1}{T}(dU_R + PdV_R - \mu dN_R)$$

- But we can forget about the two last terms: $\quad dS_R = \frac{1}{T}dU_R$

# Atom in contact with reservoir...

- And we get:

$$S_R(s_2) - S_R(s1) = \frac{1}{T}[U_R(s_2) - U_R(s_1)] = -\frac{1}{T}[E(s_2) - E(s_1)]$$

- By putting it back to the equation for probability, we get:

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = e^{-[E(s_2)-E(s_1)]/kT} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}$$

- The ratio of probabilities is related to the ratio of exponential factors related to energy of a microstate and temperature of reservoir!
- The exponent is called Boltzmann factor

# Boltzmann factor $e^{-E(s)/kT}$

- So it follows that the probability is proportional to the Boltzmann factor:

$$P(s) = \frac{1}{Z} e^{-E(s)/kT}$$

- The higher the energy the smaller probability

- The ground state has highest probability



$T_3 > T_2 > T_1$
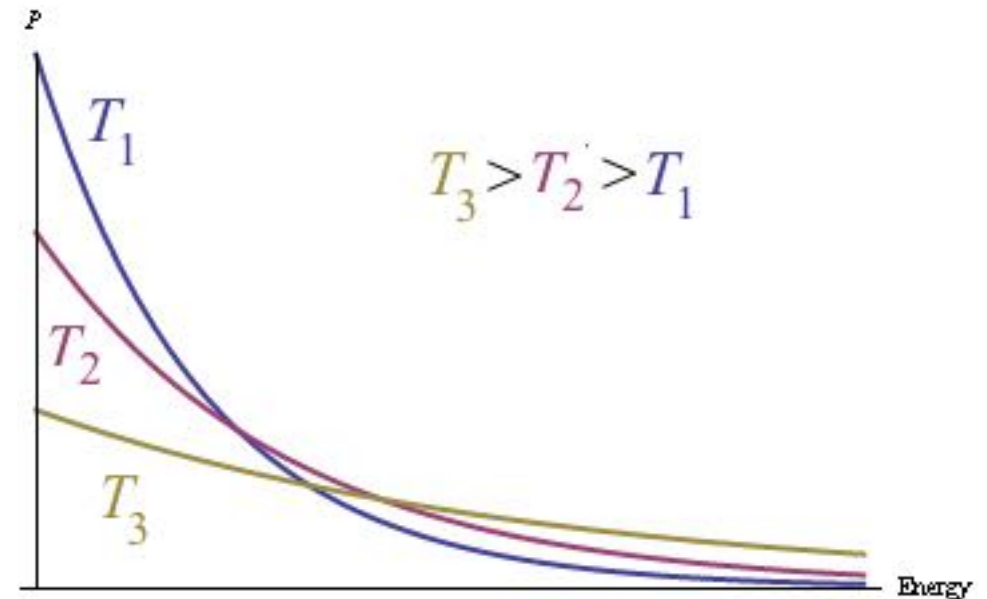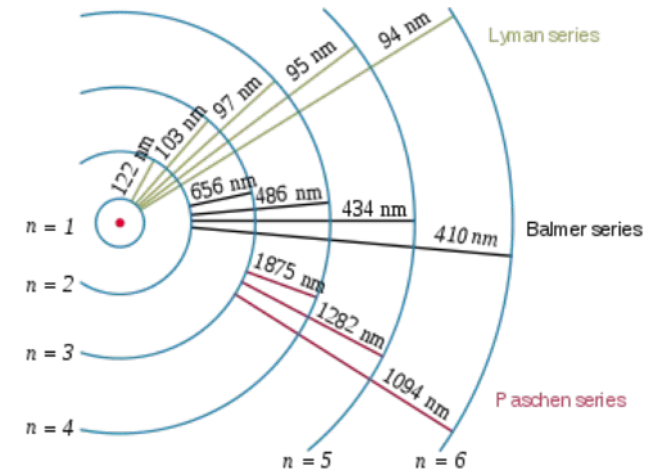
# $Z$ – the partition function

- Sum of probabilities is unity

$$1 = \sum_s P(s) = \sum_s \frac{1}{Z} e^{-E(s)/kT} = \frac{1}{Z} \sum_s e^{-E(s)/kT}$$
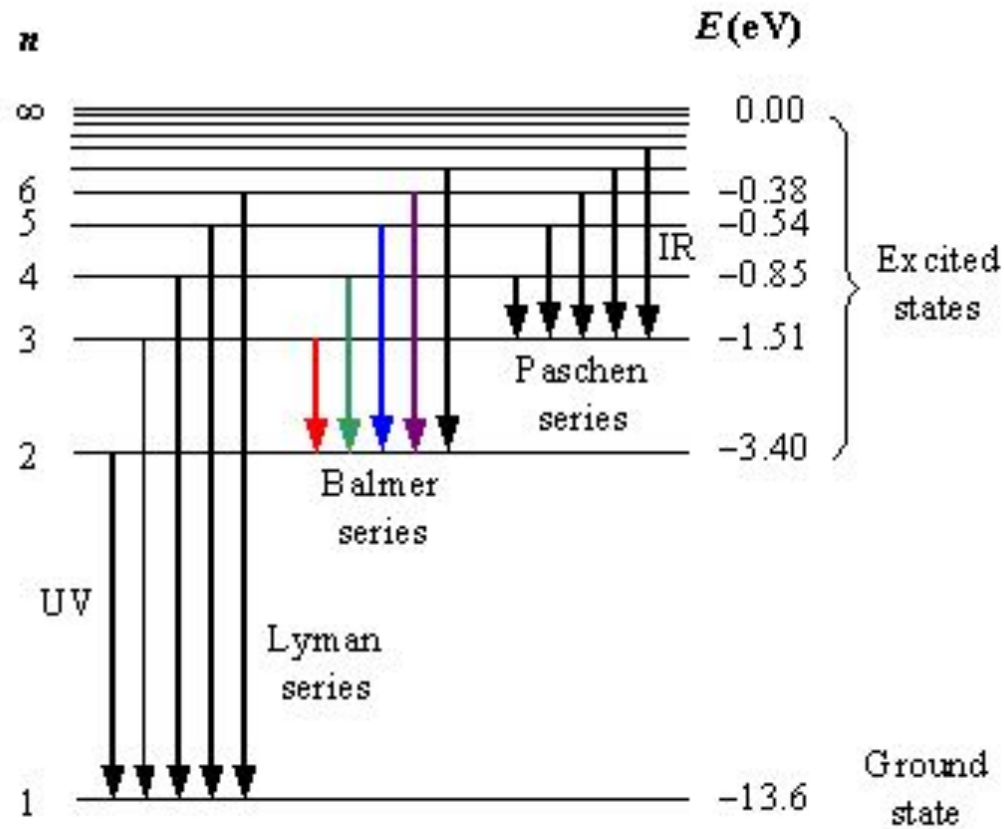
- So Z is a sum of ALL Boltzmann factors!

$$Z = \sum_s e^{-E(s)/kT}$$

- Z depends on temperature. It «counts» how many states are accessible by the atom by weighting them with their probability.

- Z larger at larger T. If we shift everything, Z will reflect that by a constant.

# Example: Hydrogen in the solar atmosphere



Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated.
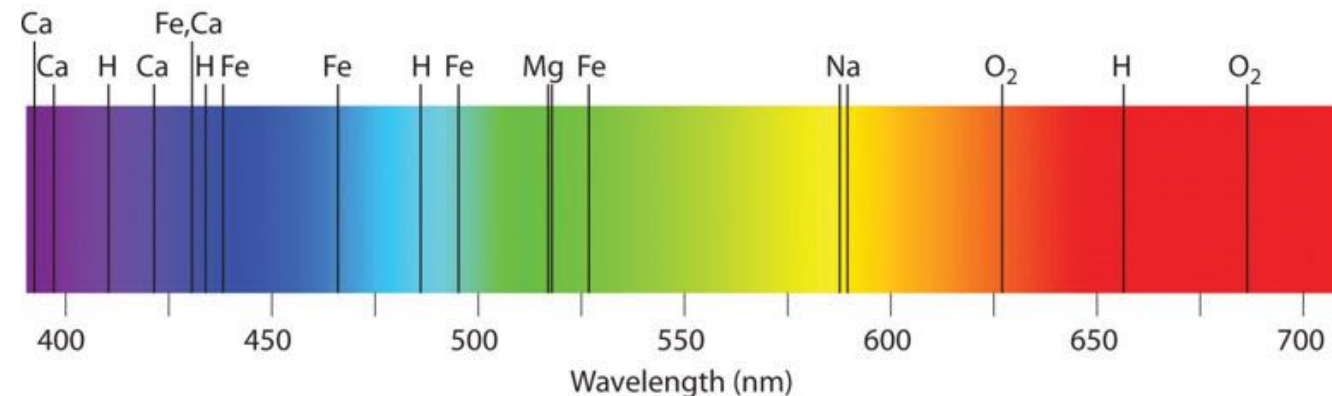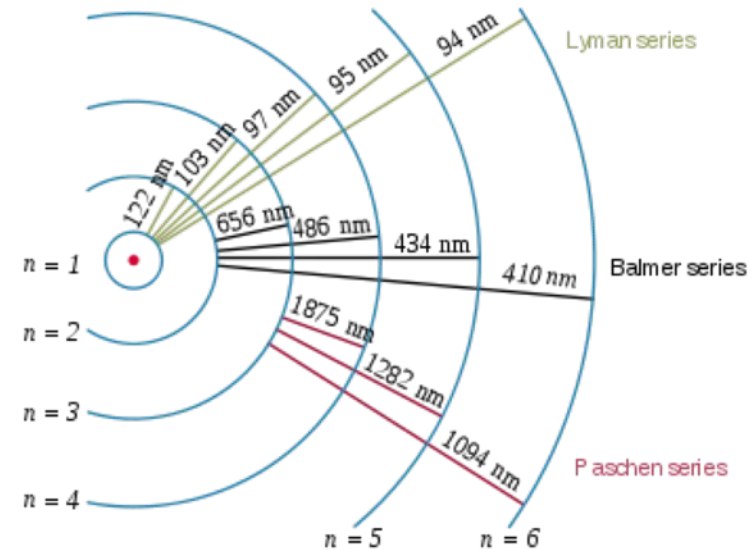
# Average values

- One way of calculating average Energy $\bar{E} = \dfrac{aE_1 + bE_2 + cE_3}{a + b + c}$

- And another way $\bar{E} = \dfrac{a}{a + b + c}E_1 + \dfrac{b}{a + b + c}E_2 + \dfrac{c}{a + b + c}E_3$

- This gives us the general formula

$$\bar{E} = \frac{\sum_s E(s)N(s)}{N} = \sum_s E(s)\frac{N(s)}{N} = \sum_s E(s)\mathcal{P}(s)$$

- Which translated into our probability with the Boltzmann factor and Partition function:

$$\bar{E} = \frac{1}{Z}\sum_s E(s)e^{-E(s)/kT}$$

# Average value (for any variable X)

$$\bar{X} = \sum_s X(s)\mathcal{P}(s) = \frac{1}{Z}\sum_s X(s)e^{-\beta E(s)}$$

Here *β=1/kT*
and *X* any variable

*Note: average values are additive:* $U = N\bar{E}$

# Equipartition theorem

- Applies to systems with energy with quadratic degrees of freedom: *E(q)=cq²* examples are coordinate or momentum variables.
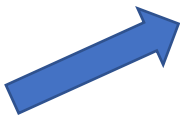
$$Z = \sum_q e^{\beta E(q)} = \sum_q e^{-\beta c q^2}$$

- My system has now a partition function (just one variable q):

$$Z = \frac{1}{\Delta q} \sum_q e^{-\beta c q^2} \Delta q \qquad \Longrightarrow \qquad Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta c q^2} dq$$

# Equipartition theorem

- This is a Gaussian function, which we can integrate

$$\int_{-\infty}^{\infty} e^{-x^2}\, dx = \sqrt{\pi}$$

$$Z = \frac{1}{\Delta q}\frac{1}{\sqrt{\beta c}}\int_{-\infty}^{\infty} e^{-x^2}\, dx$$
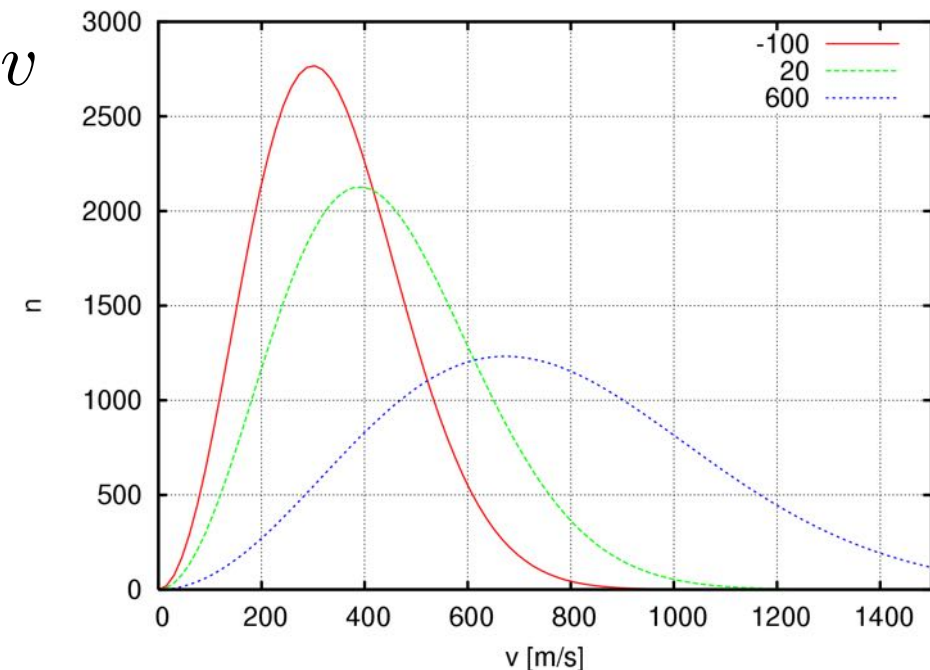
- And this gives us

$$Z = \frac{1}{\Delta q}\sqrt{\frac{\pi}{\beta c}} = C\beta^{-1/2} = C\sqrt{kT}$$

- If we have explicit formula for Z, we can calculate the average energy...

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{1}{2}kT$$

# Maxwell distribution for speed

- From equipartition theorem: $v_{rms} = \sqrt{\dfrac{3kT}{m}}$

- The «average» . But what if we need to know exactly how many particles have speeds in some interval?

- Probability: $\mathcal{P}(v \cdots v + dv) = D(v)dv$

- *D(v)* is the distribution function.

- What does *D(v)* correspond to?

# Distribution function

- D(v) proportional to:

    Probability of molecule having velocity **v**

    **X**

    Number of vectors **v** that correspond to speed *v*

# Distribution function

- D(v) proportional to:

    Probability of molecule having velocity **v** =>  $e^{-mv^2/2kT}$

    **X**

    Number of vectors **v** that correspond to speed *v* =>

# Distribution function

- D(v) proportional to:

Probability of molecule having velocity **v** is proportional to

$$e^{-mv^2/2kT}$$
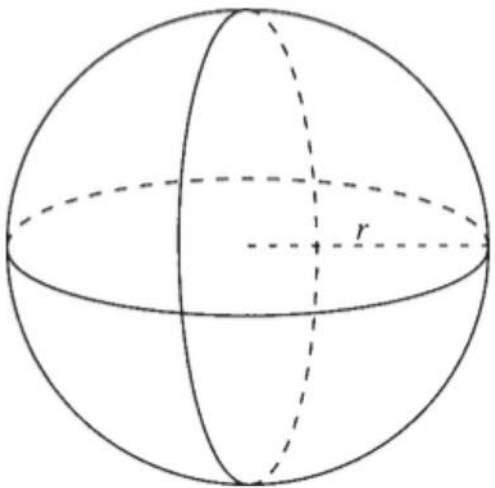
The most probable velocity **vector** is 0 in ideal gas!

Translational kinetic energy

# Distribution function

- D(v) proportional to:

Number of vectors **v** that correspond to speed *v*

*is proportional to the area of the sphere:*  $4\pi v^2$



*Note: we can also figure it out from the change of coordinate system to the spherical coordinates:*

$$d^3v = dv_x dv_y dv_z \implies d^3v = v^2 dv d\Omega$$

# Distribution function

- D(v) can now be written down:

$$\mathcal{D}(v) = C \cdot 4\pi v^2 e^{-mv^2/2kT}$$

- We only need to normalize it now; recall that total probability is 1:

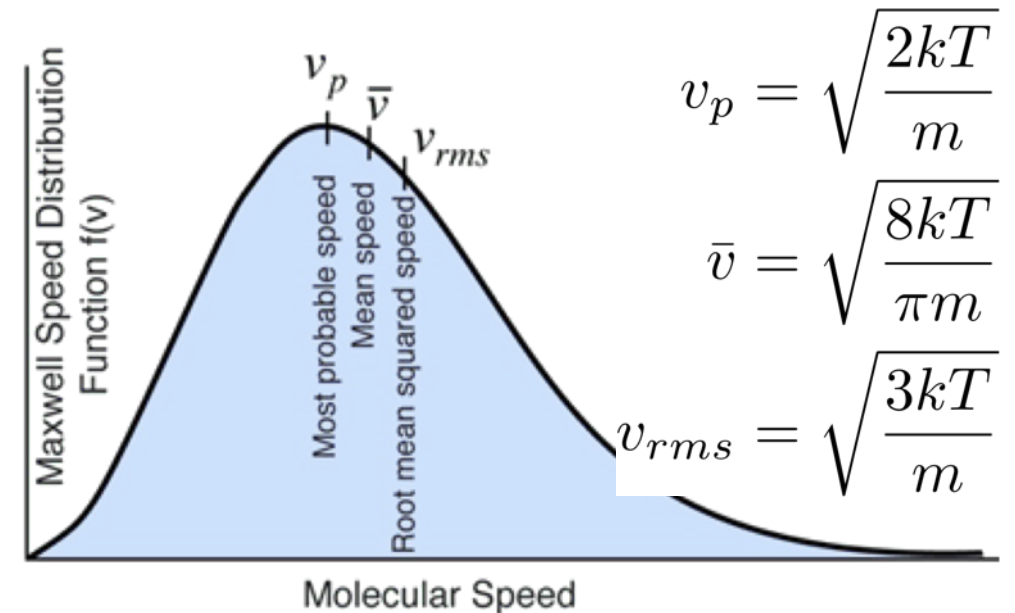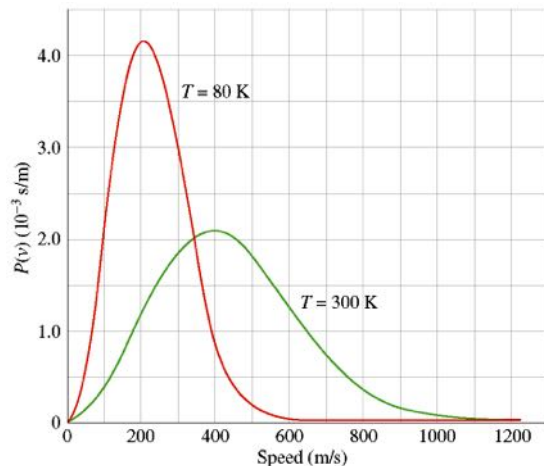$$1 = \int_0^\infty \mathcal{D}(v)dv = 4\pi C \int_0^\infty v^2 e^{-mv^2/2kT}dv$$

- And we can get:

$$1 = \int_0^\infty \mathcal{D}(v)dv = 4\pi C \left(\frac{2kT}{m}\right)^{3/2} \int_0^\infty x^2 e^{-x^2}dx$$

# Maxwell distribution function

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

- Distribution of speeds in an ideal gas...

$$v_p = \sqrt{\frac{2kT}{m}}$$

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

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

# Partition function for composite systems

- Partition function of two noninteracting particles:

$$Z = \sum_s e^{-\beta[E_1(s) + E_2(s)]} = \sum_s e^{-\beta E_1(s)} e^{-\beta E_2(s)}$$

We can distinguish them, so take into account all pairs...

$$Z_T = \sum_{s_1} \sum_{s_2} e^{-\beta E_1(s_1)} e^{-\beta E_2(s_2)}$$

- If we can distinguish them:
- If we can not distinguish them:

$$Z_t = Z_1 Z_2$$

$$Z_t = \frac{1}{2} Z_1 Z_2$$

**Many particles:**
- If we can distinguish them:
- If we can not distinguish them:

$$Z_t = Z_1 Z_2 ... Z_N$$

$$Z_t = \frac{1}{N!} Z_1^N$$