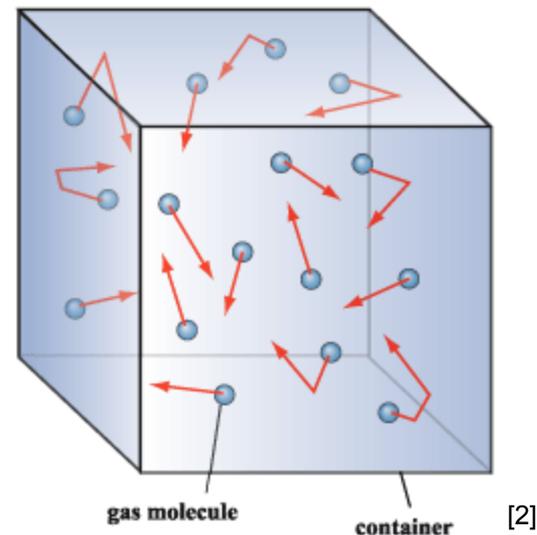# The Maxwell-Boltzmann Distribution

Brennan 5.4

Lecture prepared by Melanie Hill

Maxwell-Boltzmann Distribution

Scottish physicist James Clerk Maxwell developed his kinetic theory of gases in 1859. Maxwell determined the distribution of velocities among the molecules of a gas. Maxwell's finding was later generalized in 1871 by a German physicist, Ludwig Boltzmann, to express the distribution of energies among the molecules.

Maxwell pictured the gas to consist of billions of molecules moving rapidly at random, colliding with each other and the walls of the container.

This was qualitatively consistent with the physical properties of gases, if we accept the notion that raising the temperature causes the molecules to move faster and collide with the walls of the container more frequently.[1]
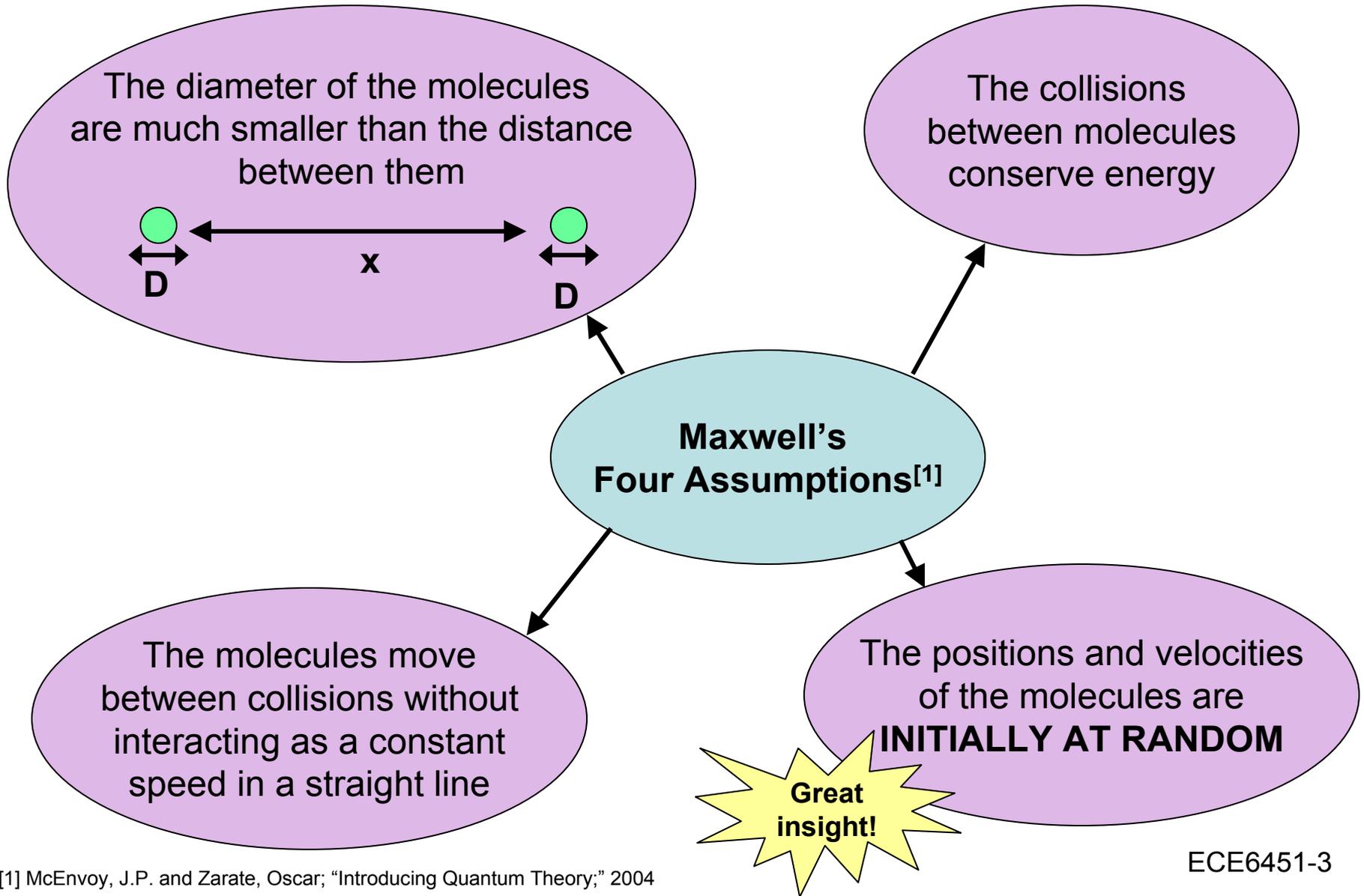

gas molecule   container   [2]

Maxwell made four assumptions…

[1] McEnvoy, J.P. and Zarate, Oscar; "Introducing Quantum Theory;" 2004
[2] http://www.hk-phy.org/contextual/heat/tep/trans01_e.html

Maxwell-Boltzmann Distribution

The diameter of the molecules are much smaller than the distance between them

D   **x**   **D**

The collisions between molecules conserve energy

Maxwell's Four Assumptions[1]

The molecules move between collisions without interacting as a constant speed in a straight line

The positions and velocities of the molecules are **INITIALLY AT RANDOM**

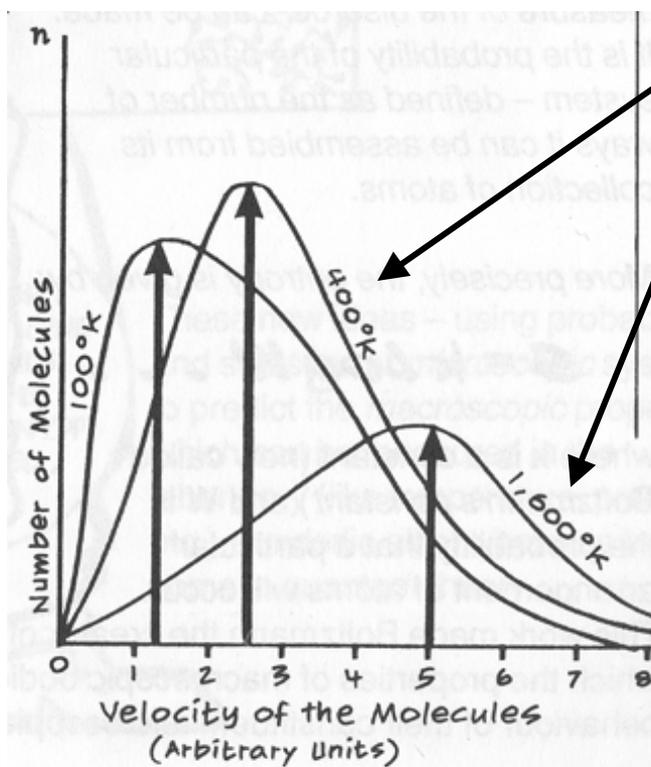**Great insight!**

[1] McEnvoy, J.P. and Zarate, Oscar; "Introducing Quantum Theory;" 2004

Maxwell-Boltzmann Distribution

By making these assumptions, Maxwell could compute the probability that a molecule chosen at random would have a particular velocity.

Raising the temperature causes the curve to skew to the right, increasing the most probable velocity.

This set of curves is called the Maxwell Distribution. It provides useful information about the billions and billions of molecules within a system; when the motion of an individual molecule can't be calculated in practice. [1]

We will derive the Maxwell-Boltzmann Distribution, which will provide useful information about the energy.

[1] McEnvoy, J.P. and Zarate, Oscar; "Introducing Quantum Theory;" 2004

Maxwell-Boltzmann Distribution

Why use statistical mechanics to predict molecule behavior? Why not just calculate the motion of the molecules exactly?

Even though we are discussing classical physics, there exists a degree of "uncertainty" with respect to the fact that the motion of every single particle at all times cannot be determined in practice in any large system.

Even if we were only dealing with one mole of gas, we would still have to determine characteristics of $\underline{6x10^{23}}$ molecules!!

Maxwell's theory was based on statistical averages to see if the macrostates, (i.e. measurable, observable) could be predicted from the microstates.

Maxwell-Boltzmann Distribution

In Section 5.3, it was determined that the thermal equilibrium is established when the temperatures of the subsystems are equal. So…

What is the nature of the equilibrium distribution for a system of N non-interacting gas particles?

The equilibrium configuration corresponds to the most probable (most likely) configuration of the system.

Consider the simplest case, a system of N non-interacting **classical** gas particles.
- Classical system:
  - there are no restrictions on how many particles can be put into any one state simultaneously
  - the particles are distinguishable, i.e. each particle is labeled for all time

First, we'll need to determine the number of microstates within any given configuration, i.e. the number of ways in which N objects can be arranged into n distinct groups, also called the Multiplicity Function.

Maxwell-Boltzmann Distribution

The Multiplicity Function - determine the number of ways in which N objects can be arranged into n containers.

Consider the first twelve letters of the alphabet:

a b c d e f g h i j k l

Arrange the letters into 3 containers without replacement. Container 1 holds 3 letters, Container 2 holds 4 letters, and Container 3 holds 5 letters.

| _ _ _ | | _ _ _ _ | | _ _ _ _ _ |

For the 1st slot, there are 12 possibilities. | c _ _ | | _ _ _ _ | | _ _ _ _ _ |

For the 2nd slot, there are 11 possibilities. | c h _ | | _ _ _ _ | | _ _ _ _ _ |

For the 3rd slot, there are 10 possibilities. | c h k | | _ _ _ _ | | _ _ _ _ _ |

etc…

There are **12!** possible arrangements if the containers are ignored.

Maxwell-Boltzmann Distribution

(cont.) The Multiplicity Function - determine the number of ways in which N objects can be arranged into n containers

Since we care about the containers but we don't care about the order of the letters within each container, we divide out the number of arrangements within each given container, resulting in:

$$\frac{12!}{3! \cdot 4! \cdot 5!} = 27,720$$

There are **27,720** ways of partitioning 12 letters into the 3 containers

In general, the number of distinct arrangements of N particles into n groups containing $N_1, N_2, \ldots, N_i, \ldots, N_n$ objects becomes:

$$\frac{N!}{N_1! \cdot N_2! \cdot \ldots \cdot N_i! \cdot \ldots \cdot N_n!}$$

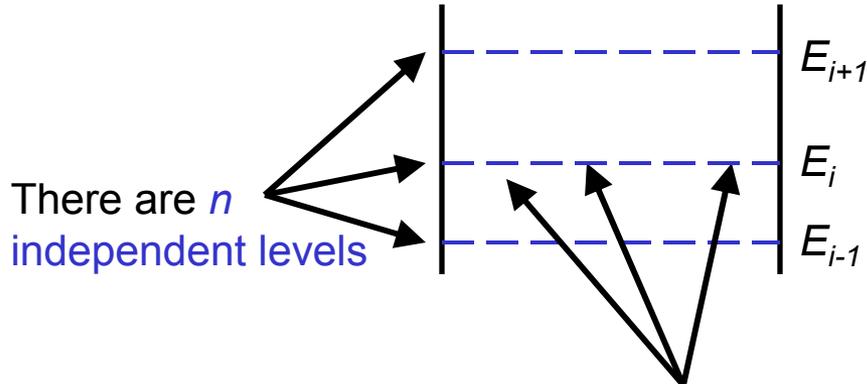Where N_i is the number of objects in container i

The Multiplicity Function:

$$Q(N_1, N_2, \ldots, N_i, \ldots, N_n) = \frac{N!}{N_1! \cdot N_2! \cdot \ldots \cdot N_i! \cdot \ldots \cdot N_n!} = \frac{N!}{\prod\limits_{i=1}^{n} N_i!}$$

Maxwell-Boltzmann Distribution

Physically, each container corresponds to a state in which each particle can be put.

- In the **classical case,** there are no restrictions on how many particles that can be put into any one container or state
- See Section 5.7 for the **quantum case** where there are restrictions for some particles


There are n independent levels

E_{i+1}

E_i

E_{i-1}

The states are classified in terms of their energy, E_i, and degeneracy, g_i

Degenerate states are different states that have the same energy level. The number of states available is known as the *degeneracy* of that level.

Each level has g_i degenerate states into which N_i particles can be arranged

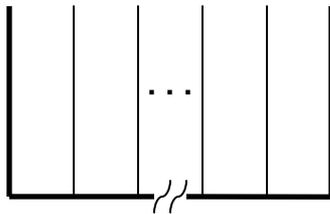Think of the system as n containers with g_i subcontainers.

So, how can we arrange N_i particles in these g_i subcontainers?
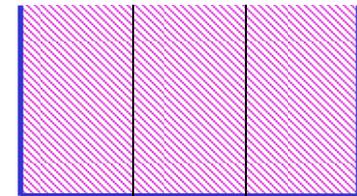
Maxwell-Boltzmann Distribution

Since we are dealing with the *classical case:*
- there are no restrictions on how many particles can be put into any one subcontainer or state simultaneously
- the particles are distinguishable, i.e. each particle is labeled for all time
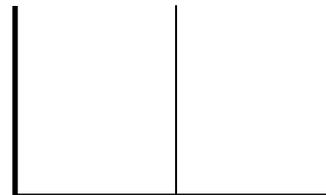
n containers with g_i subcontainers.

So, how many arrangements of N_i particles in these g_i subcontainers are possible?

Consider an example where we have 3 particles and 2 subcontainers:

3 particles   2 subcontainers

Maxwell-Boltzmann Distribution

(cont.) How many arrangements of N_i particles in these g_i subcontainers are possible?
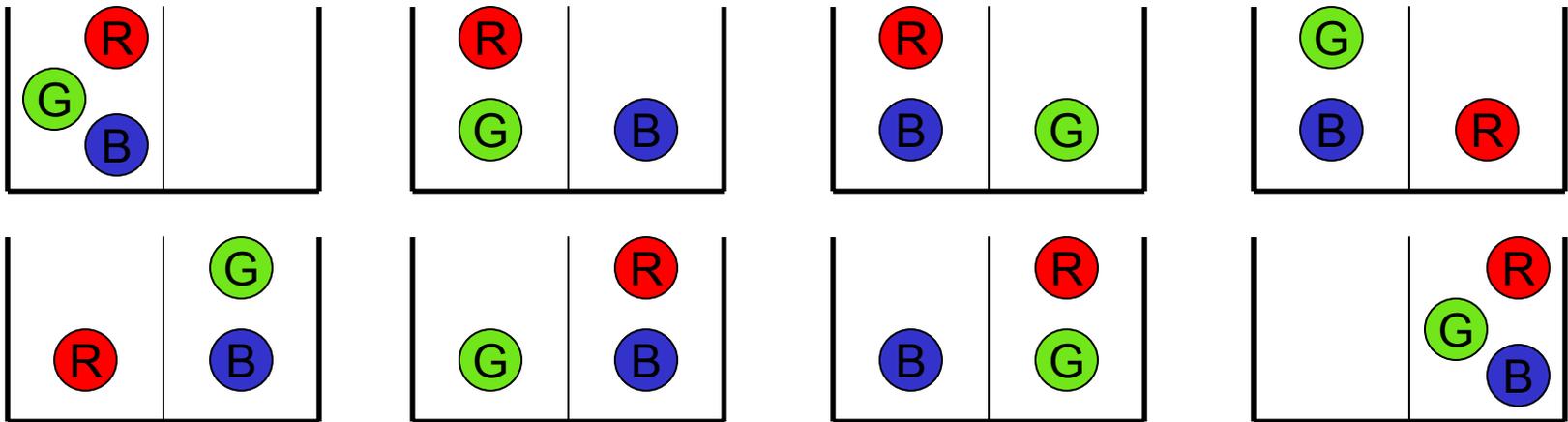
There are **8** possible arrangements, or **2³**

In general, the possible arrangements of N_i particles into g_i subcontainers is:

$$g_i^{N_i}$$

Therefore, if our system has a particular state that has a particular degeneracy, there is an additional multiplicity of $g_i^{N_i}$ for that particular state.

Maxwell-Boltzmann Distribution

(cont.) Therefore, the **total** Multiplicity Function for a collection of classical particles is:

$$Q(N_1, N_2, ..., N_i, ..., N_n) = \left[\frac{N!}{\prod\limits_{i=1}^{n} N_i!} \right] \prod\limits_{i=1}^{n} g_i^{N_i}$$

⭐ The equilibrium configuration corresponds to the most probable (most likely) configuration of the system, i.e. the configuration with the greatest multiplicity! To find the greatest multiplicity, we need to maximize Q subject to constraints.

There are two physical constraints on our **classical** system:
1.   the total number of particles must be conserved
2.   the total energy of the system must be conserved

Constraint 1 implies:

$$\phi = \sum_{i=1}^{n} N_i = N \qquad \longleftarrow \text{Constant}$$

Constraint 2 implies:

$$\psi = \sum_{i=1}^{n} E_i N_i = U \qquad \longleftarrow \text{Constant}$$

where U is the total energy for the system

Maxwell-Boltzmann Distribution

From previous slide:

$$Q(N_1, N_2, ..., N_i, ..., N_n) = \left[\frac{N!}{\prod\limits_{i=1}^{n} N_i!} \right] \prod\limits_{i=1}^{n} g_i^{N_i}$$

This equation will be easier to deal with if we take the logarithm of both sides:

$$\ln Q = \ln N! + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} \ln N_i!$$

Applying Stirling's approximation, for large x:

$$\ln x! \approx x \ln x - x$$

Almost exact because we're dealing with **very** large x, 10^{23} particles!

$$\ln Q = N \ln N - N + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} N_i \ln N_i + \sum_{i=1}^{n} N_i$$

In order to maximize, we need to make use of Lagrange multipliers and Constraints 1 and 2:

The derivatives of the 1st and 2nd constraints are zero because the constraints are equal to constants

$$\frac{\partial}{\partial N_j} \ln Q + \alpha \frac{\partial \phi}{\partial N_j} - \beta \frac{\partial \psi}{\partial N_j} = 0$$

All we are doing is adding and subtracting constants multiplied by zero!

Maxwell-Boltzmann Distribution

From previous slide:

$$\ln Q = N \ln N - N + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} N_i \ln N_i + \sum_{i=1}^{n} N_i$$

$$\frac{\partial}{\partial N_j} \ln Q + \alpha \frac{\partial \phi}{\partial N_j} - \beta \frac{\partial \psi}{\partial N_j} = 0$$

Substituting in *In Q* and Constraints 1 and 2:

$$\frac{\partial}{\partial N_j}\left(N \ln N - N + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} N_i \ln N_i + \sum_{i=1}^{n} N_i \right) + \alpha \frac{\partial}{\partial N_j}\left(\sum_{i=1}^{n} N_i \right) - \beta \frac{\partial}{\partial N_j}\left(\sum_{i=1}^{n} E_i N_i \right) = 0$$

Taking the derivative, noting that *N* is constant and the only terms that are nonzero are when *i = j*:

$$\ln g_j - \left(1 \cdot \ln N_j + N_j \cdot \frac{1}{N_j} \right) + 1 + \alpha - \beta E_j = 0$$

$$\ln g_j - \ln N_j + \alpha - \beta E_j = 0$$

Maxwell-Boltzmann Distribution

From previous slide:

$$\ln g_j - \ln N_j + \alpha - \beta E_j = 0$$

$$\ln \frac{N_j}{g_j} = \alpha - \beta E_j$$

What are α and β?

$$f(E_j) = \frac{N_j}{g_j} = e^{\alpha - \beta E_j}$$

To find β, we need to determine the total number of particles, N, in the system and the total energy, E, of the system.

If the states are closely spaced in energy, they form a quasi-continuum and the total number of particles, N, is given by:

$$N = \int_0^\infty f(E)D(E)dE$$

Where $D(E)$ is the Density of States Function found in Section 5.1

Maxwell-Boltzmann Distribution

From previous slide:

$$N = \int_0^\infty f(E)D(E)\,dE$$

$$f(E) = \frac{N_j}{g_j} = e^{\alpha - \beta E} \qquad\qquad D(E) = \frac{m^{3/2}\sqrt{2E}}{\hbar^3 \pi^2}$$

$$N = \frac{m^{3/2}\sqrt{2}}{\hbar^3 \pi^2} e^{\alpha} \int_0^\infty \sqrt{E}\, e^{-\beta E}\, dE$$

Using the standard integral:

$$\int_0^\infty x^n e^{-ax}\, dx = \frac{\Gamma(n+1)}{a^{n+1}}$$

$$N = \frac{m^{3/2}\sqrt{2}}{\hbar^3 \pi^2} e^{\alpha} \frac{\Gamma\left(\frac{3}{2}\right)}{\beta^{3/2}}$$

Maxwell-Boltzmann Distribution

The total energy, *E*, of the system can be found by:

$$E = \int\limits_0^\infty Ef(E)D(E)dE$$

$$f(E) = \frac{N_j}{g_j} = e^{\alpha - \beta E} \qquad\qquad D(E) = \frac{m^{3/2}\sqrt{2E}}{\hbar^3 \pi^2}$$

$$E = \frac{m^{3/2}\sqrt{2}}{\hbar^3 \pi^2} e^{\alpha} \int\limits_0^\infty E^{3/2} e^{-\beta E} dE$$

Using the standard integral again:

$$\int\limits_0^\infty x^n e^{-ax} dx = \frac{\Gamma(n+1)}{a^{n+1}}$$

$$E = \frac{m^{3/2}\sqrt{2}}{\hbar^3 \pi^2} e^{\alpha} \frac{\Gamma\left(\dfrac{5}{2}\right)}{\beta^{5/2}}$$

Maxwell-Boltzmann Distribution

The average energy per particle is given as:

$$\frac{\overline{E}}{N} = \frac{3}{2}k_B T \qquad\qquad k_B = 8.6175 \times 10^{-5} \, eV\!\!\Big/\!K$$

Where k_B is the Boltzmann constant.

Equating the average energy per particle with the ratio of our equations for *E* and *N*:

$$\frac{E}{N} = \frac{\dfrac{m^{3\!/\!2}\sqrt{2}}{\hbar^3 \pi^2} e^{\alpha} \dfrac{\Gamma\!\left(\dfrac{5}{2}\right)}{\beta^{5\!/\!2}}}{\dfrac{m^{3\!/\!2}\sqrt{2}}{\hbar^3 \pi^2} e^{\alpha} \dfrac{\Gamma\!\left(\dfrac{3}{2}\right)}{\beta^{3\!/\!2}}} = \frac{3}{2}k_B T = \frac{\overline{E}}{N}$$

$$\frac{\Gamma\!\left(\dfrac{5}{2}\right)}{\beta^{5\!/\!2}} \cdot \frac{\beta^{3\!/\!2}}{\Gamma\!\left(\dfrac{3}{2}\right)} = \frac{3}{2}k_B T$$

Maxwell-Boltzmann Distribution

From previous slide:

Use the relationship[1]:

$$\Gamma(1+z) = z\Gamma(z)$$

$$\frac{\Gamma\left(\frac{5}{2}\right)}{\beta^{5/2}} \cdot \frac{\beta^{3/2}}{\Gamma\left(\frac{3}{2}\right)} = \frac{3}{2}k_B T$$

$$\frac{\frac{3}{2} \cdot \Gamma\left(\frac{3}{2}\right)}{\beta \cdot \Gamma\left(\frac{3}{2}\right)} = \frac{3}{2}k_B T$$

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

$$\beta = \frac{1}{k_B T}$$

[1] http://mathworld.wolfram.com/GammaFunction.html eq. 37

Maxwell-Boltzmann Distribution

Now we have β but we still need α. α will be derived in Section 5.7.

$$\alpha = \frac{\mu}{k_B T} \qquad\qquad \text{(Eq. 5.7.26)}$$

Where μ is the chemical potential. In Section 5.8, we will find out that the chemical potential, μ, is exactly equal to the Fermi Energy, E_F — Leaving us with an α of:

$$\alpha = \frac{E_F}{k_B T}$$

From previous slides:

$$f(E_j) = \frac{N_j}{g_j} = e^{\alpha - \beta E_j} \qquad\qquad \beta = \frac{1}{k_B T}$$

Substituting α and β into $f(E_j)$:

$$f(E_j) = \frac{N_j}{g_j} = e^{\frac{E_F - E_j}{k_B T}}$$

Maxwell-Boltzmann Distribution

From previous slide:

$$f(E_j) = \frac{N_j}{g_j} = e^{\frac{E_F - E_j}{k_B T}}$$

Reversing terms in the numerator of the exponent:

Maxwell-Boltzmann Distribution

It's intuitive! For a given temperature, the chance of higher energy states being occupied decreases exponentially.

$$f(E_j) = \frac{N_j}{g_j} = e^{\frac{-(E_j - E_F)}{k_B T}}$$

This distribution gives the number of particles in the jth state, where the jth state has a degeneracy, g_j.

If we want to find the probability of finding the particle in the jth state, we need to normalize. We'll start by dividing the number of particles in the jth state, N_j, by the total number of particles, N.

Using Constraint 1 and *f(E)*:

$$N = \sum_{j=1}^{n} N_j = e^{\alpha} \sum_{j=1}^{n} g_j e^{-E_j / k_B T}$$

Maxwell-Boltzmann Distribution

From previous slide:

$$N = \sum_{j=1}^{n} N_j = e^{\alpha} \sum_{j=1}^{n} g_j e^{-E_j/k_B T}$$

Solving for e^{α}:

$$e^{\alpha} = \frac{N}{\sum\limits_{j=1}^{n} g_j e^{-E_j/k_B T}}$$

Substituting e^{α} into $f(E_j)$:

$$f(E_j) = N_j = g_j e^{\alpha} e^{-E_j/k_B T}$$

$$N_j = \frac{N g_j e^{-E_j/k_B T}}{\sum\limits_{j=1}^{n} g_j e^{-E_j/k_B T}}$$

Normalizing:

$$\frac{N_j}{N} = \frac{g_j e^{-E_j/k_B T}}{\sum\limits_{j=1}^{n} g_j e^{-E_j/k_B T}}$$

Maxwell-Boltzmann Distribution

From previous slide:

$$\frac{N_j}{N} = \frac{g_j e^{-E_j/k_B T}}{\sum\limits_{j=1}^{n} g_j e^{-E_j/k_B T}}$$

This normalized distribution is the probability, P_j, of finding the particle in the jth state with energy E_j:

$$P_j = \frac{N_j}{N} = \frac{g_j e^{-E_j/k_B T}}{\sum\limits_{j=1}^{n} g_j e^{-E_j/k_B T}}$$

Since j is just a dummy index, the probability of finding of a particle having an energy E_r is:

$$P_r = \frac{g_r e^{-E_r/k_B T}}{\sum\limits_{j=1}^{n} g_j e^{-E_j/k_B T}}$$

Maxwell-Boltzmann Distribution

If the degeneracy factor is 1, i.e. no repeatable arrangements, the probability becomes:

$$P_r = \frac{e^{-E_r/k_B T}}{\sum_{j=1}^{n} e^{-E_j/k_B T}}$$

If we want to find out the mean value of a physical observable, y, we can make use of the following equation derived in Chapter 1:

$$\bar{y} = \frac{\sum_r P_r y_r}{\sum_r P_r}$$

For example, the mean energy of a system can be determined by:

$$\bar{E} = \frac{\sum_r E_r e^{-E_r/k_B T}}{\sum_r e^{-E_r/k_B T}}$$

Maxwell-Boltzmann Distribution

From previous slide:

$$\overline{E} = \frac{\sum_r E_r e^{-E_r/k_B T}}{\sum_r e^{-E_r/k_B T}}$$

This denominator occurs very often—every time a mean value is calculated in the Maxwell-Boltzmann Distribution. Since it occurs so often, it is given a special name, the classical Partition Function, Z.

The classical partition function:

$$Z = \sum_r e^{-E_r/k_B T} \quad ; \quad \beta = \frac{1}{k_B T} \quad \Rightarrow \quad Z = \sum_r e^{-\beta E_r}$$

We can use the classical partition function to easily calculate the mean value of the energy.

First, we need to note the following relationships:

$$\sum_r E_r e^{-\beta E_r} = -\sum_r \frac{\partial}{\partial \beta} e^{-\beta E_r}$$

$$-\sum_r \frac{\partial}{\partial \beta} e^{-\beta E_r} = -\frac{\partial}{\partial \beta}\left(\sum_r e^{-\beta E_r}\right) = -\frac{\partial}{\partial \beta} Z$$

Maxwell-Boltzmann Distribution

From previous slide:

$$\overline{E} = \frac{\sum_r E_r e^{-E_r/k_B T}}{\sum_r e^{-E_r/k_B T}}$$

$$\sum_r E_r e^{-\beta E_r} = -\frac{\partial}{\partial \beta} Z$$

$$Z = \sum_r e^{-\beta E_r}$$

Substituting into the mean energy equation:

$$\overline{E} = \frac{-\frac{\partial}{\partial \beta} Z}{Z}$$

$$\overline{E} = -\left(\frac{1}{Z}\right)\frac{\partial}{\partial \beta} Z$$

The mean energy equation

$$\overline{E} = -\frac{\partial}{\partial \beta}\left(\ln Z\right)$$

Maxwell-Boltzmann Distribution

Summarizing:

$$f(E_j) = \frac{N_j}{g_j} = e^{\frac{-(E_j - E_F)}{k_B T}}$$

$$\alpha = \frac{E_F}{k_B T}$$

$$f(E) = e^{\frac{-(E - E_F)}{k_B T}}$$

$$\beta = \frac{1}{k_B T}$$

$$P_r = \frac{g_r e^{-E_r/k_B T}}{\sum_{j=1}^{n} g_j e^{-E_j/k_B T}}$$

$$\overline{E} = \frac{\sum_r E_r e^{-E_r/k_B T}}{\sum_r e^{-E_r/k_B T}}$$

$$Z = \sum_r e^{-\beta E_r}$$

$$\overline{E} = -\frac{\partial}{\partial \beta}(\ln Z)$$

Maxwell-Boltzmann Distribution

Summarizing:

$$f(E) = e^{\frac{-(E-E_F)}{k_B T}} \qquad \overline{E} = -\frac{\partial}{\partial \beta}(\ln Z)$$

$$P_r = \frac{g_r e^{-E_r/k_B T}}{\sum\limits_{j=1}^{n} g_j e^{-E_j/k_B T}}$$

- For a given temperature, the chance of higher energy states being occupied decreases exponentially
- The area under the curve, i.e. the total number of molecules in the system, does **NOT** change
- The most probable energy value is at the peak of the curve, when dP/dE = 0
- The average energy value is greater than the most probable energy value
- If the temperature of the system is increased, the most probable energy and the average energy also increase because the distribution skews to the right **BUT** the area under the curve remains the same

http://www.bustertests.co.uk/studies/kinetics-collision-theory-maxwell-boltzmann-distribution.php