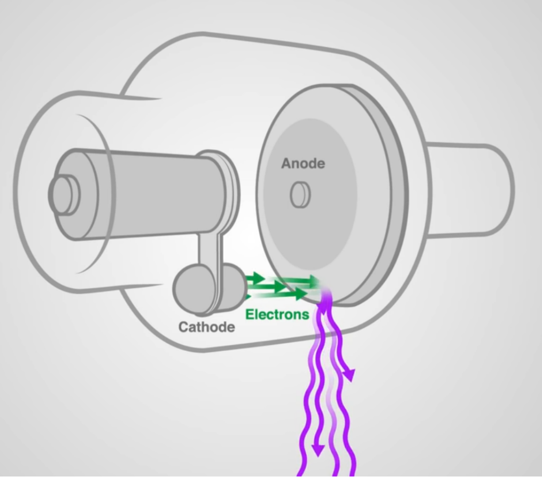
Modern Physics

Contents:

Bragg

Classical wave optics

Bragg’s law 1: X-rays



(XRayTube.mp4)

Bragg’s law 1 Comment

X-rays are produced in cathode ray tubes.

The video shows an example of an X-ray tube.

Electrons are accelerated and stopped in the anode material.

The slowed-down electrons give off some of their kinetic energy as electromagnetic radiation.

Bragg’s law 2

In 1895 Wilhelm Conrad Roentgen took an X-ray of the hand of his wife Anna Berta Röntgen.

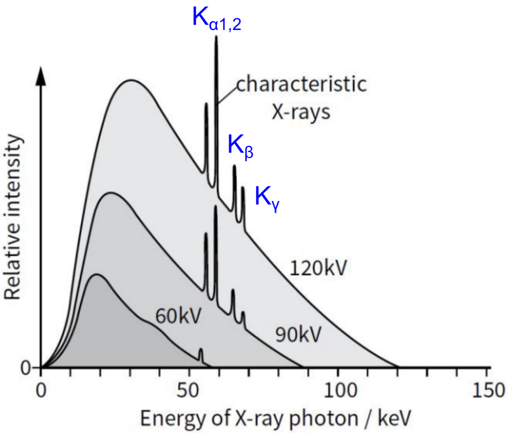
Bragg’s law 2

Comment

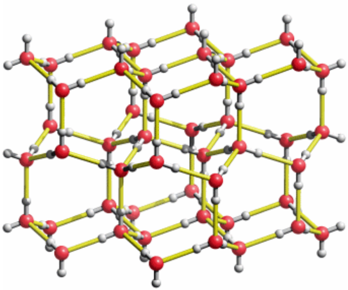
Wilhelm Conrad Roentgen was not the first to experiment with X-rays. But he was the first to recognize the great potential of X-rays.

In 1901 he received the first Nobel Prize in Physics „in recognition of the extraordinary service he has acquired through the discovery of the rays named after him“.

Bragg’s law 3



Ice crystal



(Eiskristall.mp4)

Bragg’s law 3

Comment 1

The figure on the left shows the X-ray spectrum of a tungsten cathode.

The electrons are accelerated with voltages of 60, 90 and 120 kV.

The figure shows the broad spectrum of bremsstrahlung, which results from the deceleration of electrons in the cathode.

The sharp spectral lines of the characteristic X-ray radiation rise above the broad spectrum of bremsstrahlung.

William Henry and William Lawrence Bragg in England and Max von Laue in Germany discovered that the diffraction of the radiation of the sharp characteristic X-ray lines can be used to determine crystal structures.

Bragg’s law 3

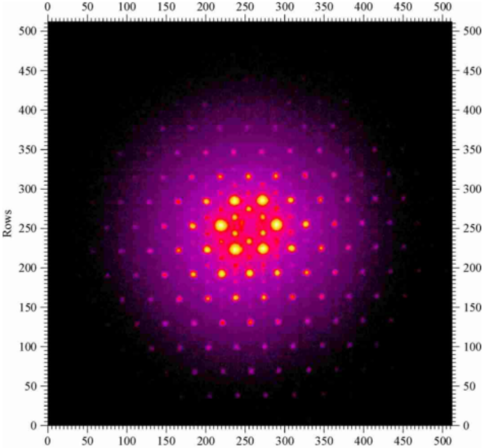
Comment 2

The Nobel Prize was awarded to Max von Laue in 1914: ”For his discovery of the diffraction of X-rays by crystals”, an important step in the development of X-ray spectroscopy”.

The Nobel Prize war awarded to William Henry Bragg and William Lawrence Bragg in 1915: ”For their services in the analysis of crystal structure by means of X-rays, an important step in the development of X-ray crystallography”.

Bragg's law 4

The wavelength of the X-rays is in the range of about 10^{-10} m and is therefore comparable to the distances between atoms in crystal lattices



Bragg’s law 4

Comment

The wavelength of X-rays is comparable to the distances between atoms in molecules and crystal lattices.

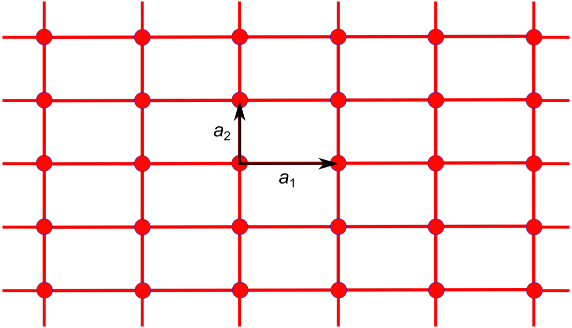
Electromagnetic waves are scattered on the atoms.

The scattered waves interfere, so that a diffraction pattern results.

By analyzing these diffraction patterns, the symmetry of the crystal lattice and the position of the atoms can be determined.

Bragg's law 5

X-rays are scattered at centers that are arranged in a crystal lattice. The distances between these centers are determined by the three vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$. The vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ span the primitive cell of the crystal lattice.



$$\vec{R}_{n_1,n_2,n_3} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

Bragg's law 5 Comment 1

X-rays are scattered at centers usually made up of many atoms.

In the figure, each center is marked with a red dot.

The arrangement of the centers is determined by the three vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$.

These vectors span the primitive cell of a crystal lattice.

The crystal lattice results from the translation of the primitive cells.

The centers for the diffraction of X-rays on a crystal lattice are the primitive cells.

The relative location of the primitive cells is determined by the vectors $\vec{R}$ and the three numbers n_1, n_2 and n_3.

Bragg's law 5

Comment 2

The one-dimensional analog of a crystal lattice is a diffraction grating.

The distance between the slits determines the deflection angles of the main maxima.

In the case of a crystal lattice, the deflection angles are determined by the arrangement of the primitive cells.

The phase function of a single slit determines the intensity of the main maxima of a diffraction grating.

In a crystal lattice, the intensity of the diffraction maxima is determined by the atoms and their arrangement within the primitive cell.

Bragg’s law 5

Comment 3

The positions of the primitive cells in a crystal lattice can therefore be determined with the deflection angles of the maxima.

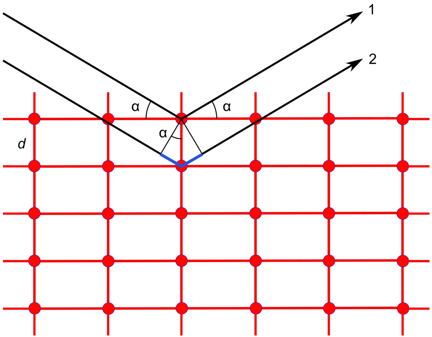
This corresponds to the red dots in the figure.

The intensity of the diffraction maxima determines the location and type of atoms within the primitive cell.

This is the internal structure of the scattering centers, which are only shown in the figure by red dots.

Bragg's law 6

Diffraction on a lattice plane with distance *d*



path difference between ray 1 and 2

$$\boxed{\Delta s = 2d \sin \alpha}$$

Bragg's law 6

Comment

Bragg's law assumes that the light is reflected on lattice planes.

These planes are called Bragg planes.

Bragg planes planes are formed by the primitive cells.

The distance between two neighboring Bragg planes is d and it is not difficult to calculate the path difference between the two rays 1 and 2.

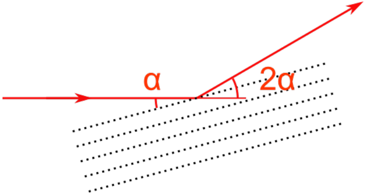
The formula outlined in red indicates the path difference between ray 1 and 2.

Bragg's law 7

The condition for constructive interference is

$$\boxed{m\lambda = 2d\sin\alpha_m}$$

with $m = 1, 2, \ldots$



Bragg's law 7

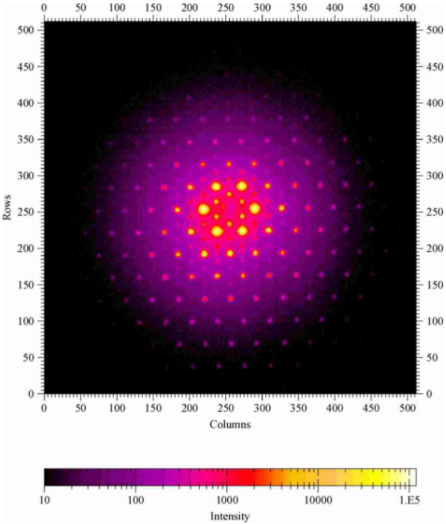
Comment

Constructive interference occurs when the path difference is a multiple of the wavelength.

There are sharp diffraction maxima, since the interference is due to many rays.

The sketch shows that the angle α of Bragg's law is half the deflection angle of the X-ray beam.

Bragg’s law 8


0
50
100
150
200
250
300
350
400
450
500
Rows
Columns
10
100
1000
10000
1.E5
Intensity

Bragg's law 8

Comment

The figure shows again the X-ray diffraction on a crystal lattice.

Each diffraction maximum determines the orientation and the spacing of a set of lattice planes.

Note that the intensity of the diffraction maxima is very different.

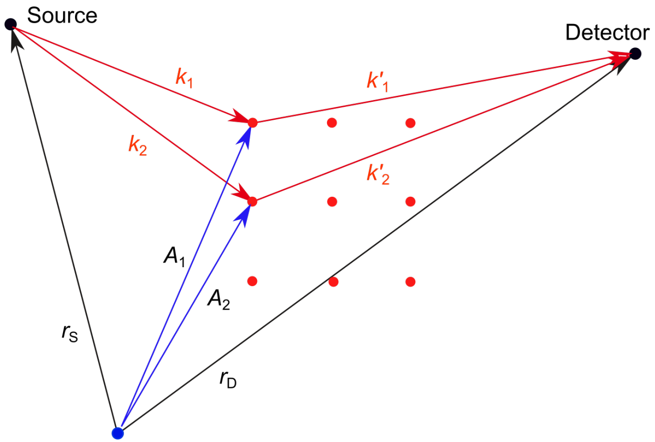
The intensity of the maxima depends on the atoms within the primitive cell.

Laue

Classical wave optics

Laue equations 1

Max von Laue considers the diffraction of X-rays on the primitive cells



Laue equations 1

Comment

It is not obvious how the structure of the crystal lattice and the arrangement of the atoms within the primitive cells can be determined with Bragg's law.

This task can be solved with the Laue equations.

To describe X-ray diffraction, Max von Laue starts out directly from the scattering of X-rays on the primitive cells.

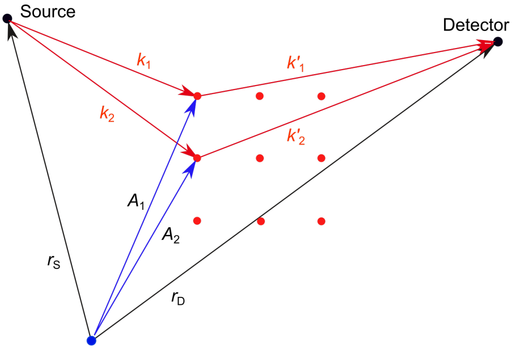
As before, the primitive cells are marked by red dots in the figure.

The position of two primitive cells is given by the vectors $\vec{A}_1$ and $\vec{A}_2$.

The location of the X-ray source and the location of the detector are given by the vectors $\vec{r}_S$ and $\vec{r}_D$, respectively.

The orientation of the wave vectors is given by the rays that connect the source with the primitive cells and the primitive cells with the detector.

Laue equations 2



parallel beams can be used because the crystals are small and the distances in the x-ray diffractometer are large

$$\vec{k}_1 = \vec{k}_2 = \vec{k}$$

$$\vec{k}'_1 = \vec{k}'_2 = \vec{k}'$$

$$\boxed{\begin{aligned}\varphi_1 &= \vec{k}_1(\vec{A}_1 - \vec{r}_S) + \vec{k}'_1(\vec{r}_D - \vec{A}_1)\\ \varphi_2 &= \vec{k}_2(\vec{A}_2 - \vec{r}_S) + \vec{k}'_2(\vec{r}_D - \vec{A}_2)\end{aligned}}$$

$$\underline{\Delta\varphi = \varphi_1 - \varphi_2} = \vec{k}(\vec{A}_1 - \vec{A}_2) + \vec{k}'(\vec{A}_2 - \vec{A}_1) = \underline{(\vec{k} - \vec{k}')(\vec{A}_1 - \vec{A}_2)}$$

Laue equations 2

Comment 1

The phase of the two beams on their way from the source to the detector is indicated by the formulas in the box.

These formulas are simplified considerably if parallel rays are assumed.

The assumption of parallel rays is plausible because the crystals are small compared to the distances in an x-ray diffractometer.

An important additional assumption is that the scattering does not change the wavelength of the X-rays.

If this condition is met, one speaks of elastic scattering.

Laue equations 2

Comment 2

The X-rays do not transmit or receive energy from the crystal.

The wave vectors change their direction due to the diffraction, but not the absolute value.

If the wavelength changes due to the scattering, one speaks of inelastic scattering.

Inelastic scattering is dealt with in the sixth chapter of this lecture.

With these conditions, the phase difference between the two beams can be calculated.

The phase difference depends on the difference in the wave vectors of the incident and the scattered wave, as well as on the difference between the locations of the primitive cells.

Laue equations 3

The difference between the vectors $\vec{A}_1$ and $\vec{A}_2$ is

$$\underline{\vec{R}_{n_1,n_2,n_3} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3}$$

The condition for constructive interference is

$$\boxed{2\pi m = (\vec{k} - \vec{k}\,')\vec{R}_{n_1,n_2,n_3}}$$

with $m = 0, \pm 1, \pm 2, \ldots$

Laue equations 3

Comment

The formula underlined in red gives the difference vector *R* between the positions of two primitive cells.

Constructive interference occurs when the phase difference is a multiple of 2 π.

The formula outlined in red indicates the condition for constructive interference.

That is an important interim result, but not the end of the discussion.

Laue equations 4

In addition to the vectors $\vec{a}_i$, a second set of vectors $\vec{b}_i$ is defined by the scalar product

$$\boxed{\vec{a}_i \vec{b}_j = 2\pi\delta_{ij}}$$

The vectors $\vec{b}_i$ form the reciprocal lattice

$$\boxed{\vec{K}_{hk\ell} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3}$$

The indices $h, k, \ell = 0, \pm 1, \pm 2 ...$ are the Miller indices.

Laue equations 4

Comment

In addition to the three vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$, which span the primitive cell, Laue defines a second set of three vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$.

These vectors are defined by the framed scalar product.

The three vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ also span a special type of primitive cell in analogy to the vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$.

The translation of these primitive cells forms a lattice called the reciprocal lattice.

The second equation outlined in red gives the vectors $\vec{K}$ of the reciprocal lattice.

The indices h, k, ℓ are called the Miller indices.

Laue equations 5

Due to the condition

$$\underline{\vec{a}_i \vec{b}_j = 2\pi\delta_{ij}}$$

the vectors $\vec{b}_i$ are

$$\boxed{\begin{aligned} \vec{b}_1 &= \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_2 \times \vec{a}_3) \\ \vec{b}_2 &= \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_3 \times \vec{a}_1) \\ \vec{b}_3 &= \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_1 \times \vec{a}_2) \end{aligned}}$$

V_{Cell} denotes the volume of the primitive cell

$$\boxed{V_{\text{Cell}} = \vec{a}_1(\vec{a}_2 \times \vec{a}_3)}$$

Laue equations 5

Comment

Due to the definition of the vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$, these three vectors can easily be calculated with the cross product of the vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$.

The cross products must be divided by the volume of the primitive cell.

The volume of the primitive cell is calculated with the scalar triple product of the vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$.

Laue equations 6

Why is it useful to calculate the reciprocal lattice?

$$\underline{\vec{K}_{h,k,\ell}\vec{R}_{n_1,n_2,n_3}} = (h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3)(n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3)$$

$$= \underline{2\pi(n_1 h + n_2 k + n_3 \ell)}$$

Comparison with the condition for constructive interference

$$\underline{(\vec{k} - \vec{k}')\vec{R}_{n_1,n_2,n_3} = 2\pi m}$$

shows

$$\boxed{\vec{k} - \vec{k}' = \vec{K}_{h,k,\ell}}$$

Laue equations 6

Comment

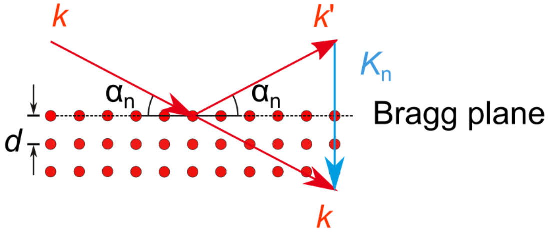
The first formula gives the scalar product of a vector of the reciprocal lattice multiplied by a lattice vector $\vec{R}$, which describes the position of the primitive cells.

Due to the definition of the vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$, this scalar product always results in a multiple of 2 π.

The comparison with the condition for constructive interference shows that the difference between the wave vectors of the incident and the scattered beam is always a vector of the reciprocal lattice.

Laue equations 7

Comparison of the conditions for constructive interference by Bragg and Laue



$$n\lambda = 2d \sin \alpha_n$$

$$\vec{k} - \vec{k}' = \vec{K}_n$$

$$\boxed{k \sin \alpha_n = \frac{K_n}{2}}$$

Laue equations 7

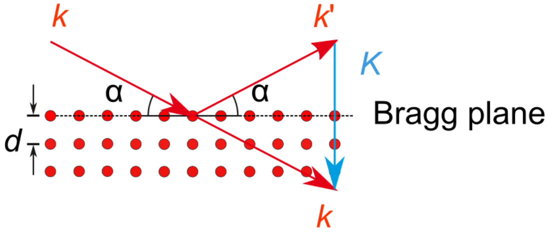
Comment

If the Laue condition is drawn into the picture with which the Bragg condition was derived, one sees that the vectors of the reciprocal lattice are perpendicular to the Bragg planes.

The amount of the wave number vector multiplied by the sine of the diffraction angle α results in half the length of a reciprocal lattice vector.

Laue equations 8

especially for first order diffraction maxima



$$\underline{k \sin \alpha = \frac{K}{2}} = \frac{2\pi}{\lambda} \sin \alpha$$

$$\underline{\lambda = 2d \sin \alpha}$$

Distance between the Bragg planes

$$\boxed{d = \frac{2\pi}{K}}$$

Laue equations 8 Comment 1

If the diffraction maxima of the first order are considered and the indices are omitted, then the formula outlined in red results for the distance between the Bragg planes.

The distance between the Bragg planes is inversely proportional to the length of the reciprocal lattice vectors.

Laue equations 8

Comment 2

With the vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ that determine the position of the primitive cells, the basis vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ of the reciprocal lattice can be calculated.

With that all reciprocal lattice vectors are known, and the distances of all Bragg planes can be calculated.

With the wavelength of the X-ray radiation used and the Bragg formula, all possible scattering angles then result.

Conversely, it is possible to determine the reciprocal lattice from the scattering angles.

If the vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ are known, the lattice vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ can be calculated.

Laue equations 9

Influence of the atoms in the primitive cell

$$\varphi_1 = \vec{k}_1(\vec{A}_1 + \vec{d}_1 - \vec{r}_Q) + \vec{k}'_1(\vec{r}_D - \vec{A}_1 - \vec{d}_1)$$
$$\varphi_2 = \vec{k}_2(\vec{A}_2 + \vec{d}_j - \vec{r}_Q) + \vec{k}'_2(\vec{r}_D - \vec{A}_2 - \vec{d}_j)$$

Phase difference between ray 2 and ray 1 is

$$\underline{\Delta\varphi = \varphi_2 - \varphi_1 = (\vec{k} - \vec{k}')(\vec{A}_2 - \vec{A}_1) + (\vec{k} - \vec{k}')(\vec{d}_j - \vec{d}_1)}$$

The wave function of the diffracted wave

$$\psi = \psi_0 \sum_{\vec{R}} e^{i(\vec{k}-\vec{k}')\vec{R}} \cdot \left(\sum_{j=1}^{N} e^{i(\vec{k}-\vec{k}')(\vec{d}_j-\vec{d}_1)} f_j \right)$$

Laue equations 9 Comment 1

The intensity of the diffraction maxima is determined for a crystal lattice by the atoms in the primitive cell.

The phase of rays 1 and 2 is determined not only by the location of the primitive cells, but also by the location of the atoms within the primitive cell.

In the first two equations, the position vectors of the atoms are written in blue.

The vectors d_j indicate the position of the atoms in relation to the primitive cell.

The phase difference contains a contribution that depends on the difference in the position of the primitive cells, and an additional contribution that depends on the difference in the atomic positions.

This additional contribution is marked in blue in the underlined formula.

Laue equations 9

Comment 2

For the diffracted wave one has to add up the contribution of all primitive cells that are illuminated by the X-ray beam.

As before, the first sum determines the deflection angle of the diffraction maxima.

The brackets written in blue determine the intensity of the diffraction maxima.

The contributions of all atoms within the primitive cell are added up.

Laue equations 9 Comment 3

The additional factor f_j is the atomic structure factor.

The scattering power of an atom increases with the number of electrons in the atom.

Therefore, the scattering power of hydrogen with atomic number 1 is extremely small compared to the scattering power of calcium with atomic number 20.

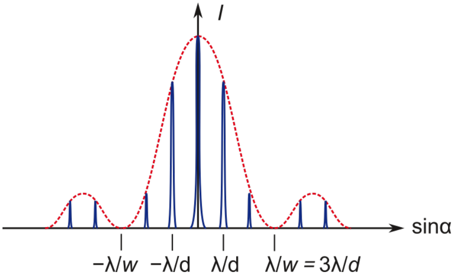
The blue bracket is the structure factor of X-ray diffraction.

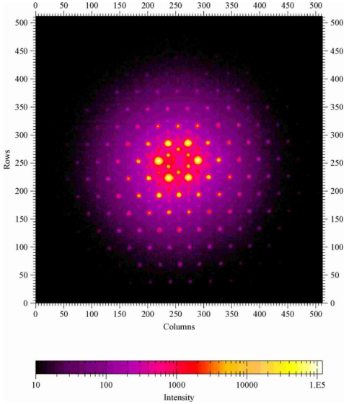
If there is only one atom in the primitive cell, the structure factor is given by the atomic structure factor.

Only in this case do the red dots in the previous figures correspond to the atoms.

Laue equations 10

Comparison of diffraction on the diffraction grating and diffraction on the crystal lattice





Laue equations 10 Comment

Finally, note the analogy of X-ray diffraction and diffraction on a grating.

The first sum written in black corresponds to the sum over the slits.

The second sum written in blue corresponds to the contribution of a single slit.

Just as the intensity of the interference maxima of a grating is modulated due to the single slit, the intensity of the maxima of X-ray diffraction is modulated due to the atoms in the primitive cell.

It turns out that the reciprocal lattice is fundamental for the description of crystalline solids (compare chapter 6: Solids).

Revision

Summary in questions

1. What is the Bragg condition for constructive interference in the diffraction of X-rays?
2. What is the Laue condition for constructive interference in the diffraction of X-rays?
3. Use a sketch to show the relationship between Bragg's condition and Laue's condition.
4. What condition does Laue use to define the reciprocal lattice?
5. Write down the formulas with which the basis vectors of the reciprocal lattice are calculated with the vectors of the primitive unit cell $\vec{a}_{i=1,2,3}$.
6. Write down the formulas used to calculate the basis vectors of the primitive cell from the basis vectors of the reciprocal lattice. (Hint: $\vec{b}_1(\vec{b}_2 \times \vec{b}_3) = (2\pi)^3/V_{\mathrm{Cell}}$)

Modern Physics

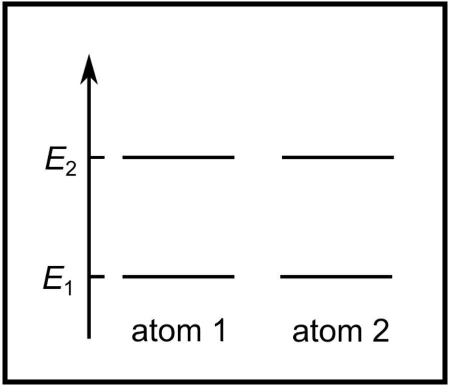
Contents:

Temperature

Essentials of Thermodynamics

Temperature 1

Consider a system with two atoms that have two energy levels



Temperature 1

Comment

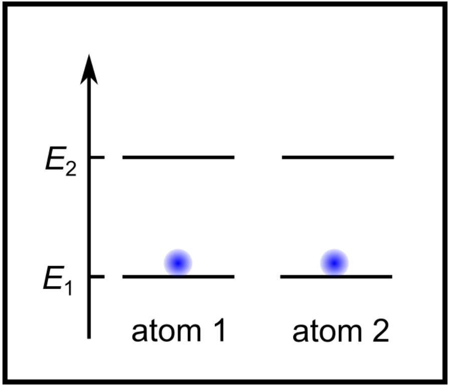
Temperature is a quantity in everyday life.

In physics, temperature is defined in the context of statistical physics.

The figure shows a simple statistical system made up of two atoms with two energy levels.

Temperature 2

There are different configurations, i. e. possibilities of the atoms to occupy the energy levels



Configuration I: $E_{\mathrm{I}} = 2E_1$ and $\Gamma(E_{\mathrm{I}}) = 1$

Temperature 2

Comment

The energy of this model system can have three different values.

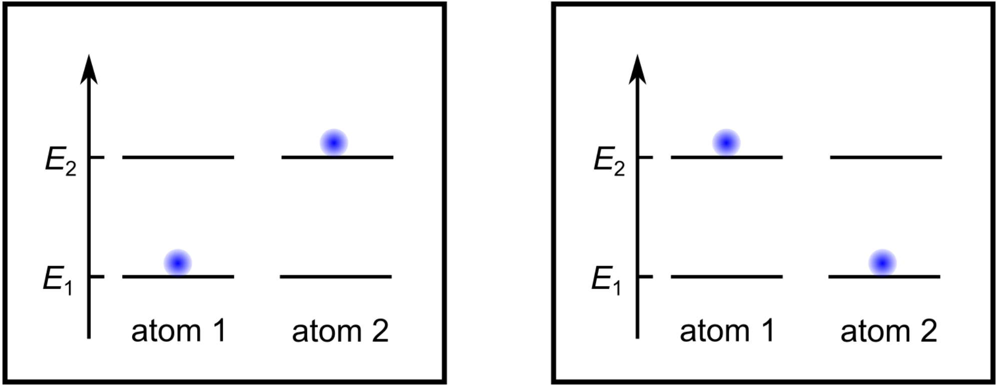
The first figure shows the ground state.

There is only one possibility to realise the ground state.

The number of possibilities for realizing an energy in a system is denoted by the capital letter Γ.

For the ground state, Γ takes the value one.

Temperature 3



Configuration II: $E_{\mathrm{II}} = E_1 + E_2$ and $\Gamma(E_{\mathrm{II}}) = 2$

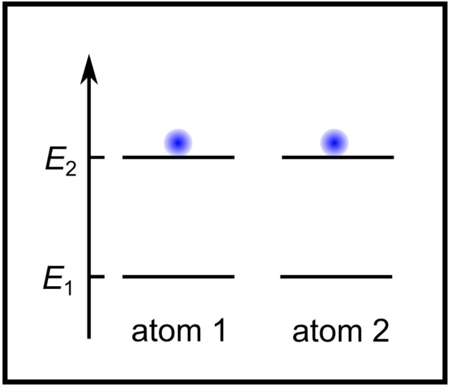
Temperature 3

Comment

When one atom is excited there are two options.

The energy is $E_1 + E_2$ and Γ takes the value 2 for this energy.

Temperature 4



Configuration III: $E_{\text{III}} = 2E_2$ and $\Gamma(E_{\text{III}}) = 1$

Temperature 4

Comment

When both atoms are excited, the energy is $2E_2$.

There is only one way to realize this energy and the value of Γ is 1.

Temperature 5

$\mathit{\Gamma}(E)$ denotes the possibilities for realizing the energy E

The definition of entropy is

$$\boxed{S(E) = k_B \ln \mathit{\Gamma}(E)}$$

Boltzmann constant

$$\underline{k_\mathrm{B} = 1.38 \cdot 10^{-23}\,\mathrm{J/K}}$$

Temperature 5

Comment

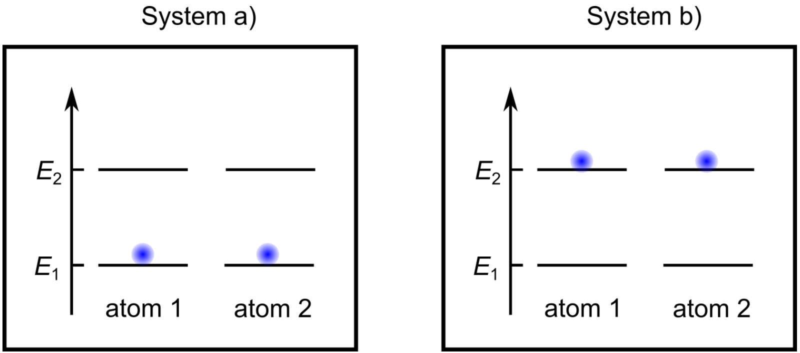
The entropy of a system is determined by the number of possibilities for realizing the energy of a statistical system.

Entropy is denoted by the capital letter *S* and is defined by the equation outlined in red.

The Boltzmann constant is added for practical reasons.

Temperature 6

For two systems a) and b), the total energy and entropy is the sum of the two sub-systems, e.g.



$$E = E_a + E_b \quad \text{and} \quad \Gamma = \Gamma(E_a)\Gamma(E_b) = 1 \quad \text{and} \quad S(E) = k_B \ln \Gamma(E_a) + k_B \ln \Gamma(E_b) = 0$$

Temperature 6 Comment

With two systems, the total energy is the sum of the energy of the two subsystems.

The total number of possibilities for realizing a certain total energy is given by the product of the possibilities for realizing the energy of the individual systems $\Gamma(E_\mathrm{a})$ and $\Gamma(E_\mathrm{b})$.

The total entropy is therefore given by the sum $S_\mathrm{a} + S_\mathrm{b}$.

The figure illustrates this idea.

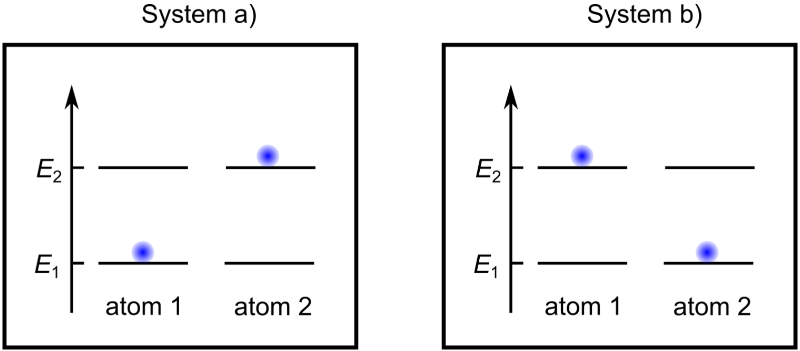
Subsystem a) is in the ground state and subsystem b) is in the state with the largest energy.

The number of possibilities is 1 for each subsystem.

The number is equally one for the combined system. The entropy of each system is zero and the total entropy is also zero.

Temperature 7

another example



$$E = E_a + E_b \quad \text{and} \quad \Gamma = \Gamma_a(E_a)\Gamma_b(E_b) = 4 \quad \text{and} \quad S = S_a + S_b = k_B \ln 2 + k_B \ln 2$$
$$= k_B \ln 4$$

Temperature 7

Comment

The figure shows the situation that only one atom is excited in each of the two subsystems.

There are two ways of realizing the excited energy for each subsystem.

There are four ways of realizing the energy for the entire system.

The total entropy is twice the logarithm of two.

Temperature 8

For two macroscopic systems a) and b) is the total energy

$$\boxed{E = E_a + E_b}$$

the number of configurations

$$\underline{\Gamma(E) = \Gamma_a(E_a) \cdot \Gamma_b(E_b)} \quad \text{and} \quad \ln \Gamma(E) = \ln \Gamma_a(E_a) + \ln \Gamma_b(E_b)$$

the total entropy

$$\boxed{S = S_a + S_b}$$

Temperature 8

Comment

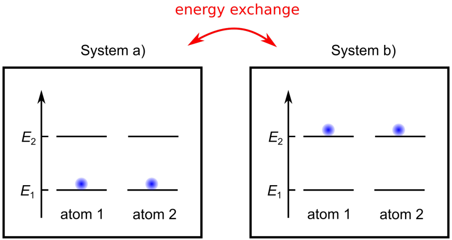
The equations outlined in red summarize these results.

The total energy is the sum of the energies of all subsystems.

The total entropy is the sum of the entropies of all subsystems.

Temperature 9

Two systems in thermal contact can exchange energy



The total energy is conserved

$$E = E_a + E_b = 2E_1 + 2E_2$$

There are different possibilities to distribute the energy within the two subsystems

Temperature 9

Comment

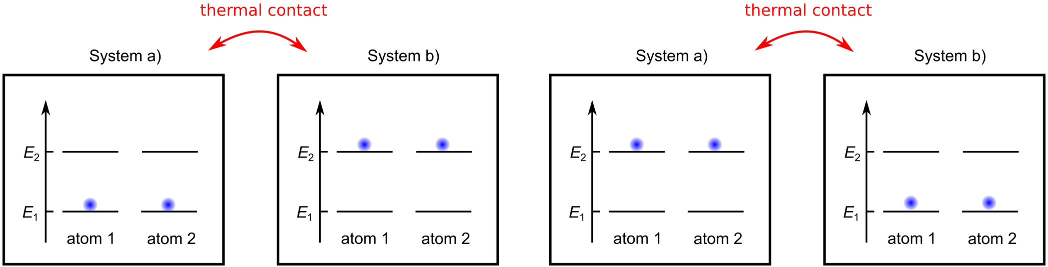
The figure shows the two subsystems again, with one subsystem in the ground state and the other in the most excited state.

The two subsystems can exchange their energy.

There are various ways of distributing the energy within the two subsystems.

Temperature 10

There are 2 configurations if one of the two systems takes all of the excitation energy

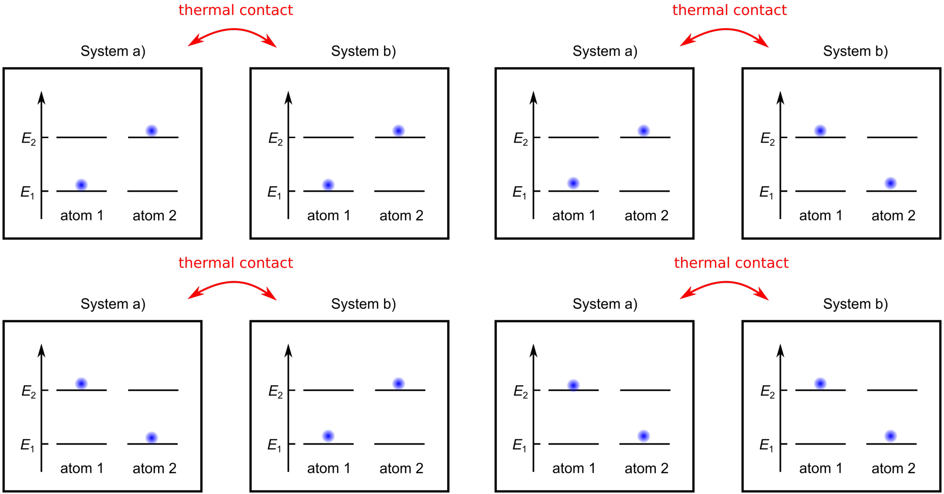


Temperature 10 Comment

This figure shows the two possibilities that either system a) or system b) takes the entire excitation energy.

Temperature 11

There are 4 configurations when each system takes part of the excitation energy



Temperature 11

Comment

This figure shows the four possibilities if each system only takes part of the excitation energy.

Temperature 12

If two macroscopic systems a) and b) are isolated from the rest of the world in thermal contact, both systems have the same temperature in thermal equilibrium

The total energy is constant

$$\boxed{E = E_a + E_b}$$

and the number of possibilities

$$\boxed{\Gamma(E_\mathrm{a} + E_\mathrm{b}) = \Gamma_\mathrm{a}(E_\mathrm{a})\Gamma_\mathrm{b}(E_\mathrm{b})}$$ is maximal

i.e. <u>the entropy $S = k_\mathrm{B} \ln \Gamma$ is maximal</u>

$$\mathrm{S}(E_\mathrm{a}, E_\mathrm{b}) = \mathrm{S}_\mathrm{a}(E_\mathrm{a}) + \mathrm{S}_\mathrm{b}(E_\mathrm{b}) \quad \text{and} \quad \boxed{\frac{\partial S}{\partial E_a} = 0, \qquad \frac{\partial S}{\partial E_b} = 0}$$

Temperature 12

Comment 1

Two macroscopic systems eventually reach the same temperature in thermal contact.

The total energy of the two systems is conserved when the two systems are well isolated from the surrounding world.

The first fundamental assumption of thermodynamics is that a macroscopic system is in thermal equilibrium in a state in which the number of possibilities for realizing the total energy is maximal.

Temperature 12 Comment 2

Since the logarithm is a monotonic function of the number of possibilities, the entropy in thermal equilibrium is also maximal.

The total energy is conserved and therefore constant.

However, the energy of the subsystems can change.

The mathematical criterion for thermal equilibrium is therefore that the partial derivative of the entropy with respect to the energy of each subsystem must be zero.

Temperature 13

With $E =$ constant

$$dE_a = -dE_b$$

therefore

$$\frac{\partial S}{\partial E_a} = 0 = \frac{\partial (S_a + S_b)}{\partial E_a} = \frac{\partial S_a}{\partial E_a} + \frac{\partial S_b}{\partial E_b}\frac{\partial E_b}{\partial E_a} = \frac{\partial S_a}{\partial E_a} - \frac{\partial S_b}{\partial E_b}$$

and

$$\underline{\frac{\partial S_a}{\partial E_a} = \frac{\partial S_b}{\partial E_b}}$$

Since the temperatures of all subsystems are the same in thermal equilibrium, the definition of temperature is

$$\boxed{\frac{1}{T} = \frac{\partial S}{\partial E}}$$

Temperature 13 Comment 1

A small calculation leads to the underlined formula.

The derivation of the entropy of each subsystem with respect to the energy of the subsystem is the same for all subsystems in thermal equilibrium.

Since the temperature of all subsystems must be the same in thermal equilibrium, the reciprocal temperature is defined as the partial derivative of the entropy with respect to the energy.

To understand that it makes sense to use the reciprocal temperature, one can consider two special cases.

At very high temperatures, both the energy and entropy are high.

Temperature 13

Comment 2

The entropy hardly changes when the energy is increased further.

Therefore the derivation of the entropy with respect to the energy tends to zero for very high temperatures and the reciprocal temperature will likewise tend towards zero.

On the other hand, only the ground state is occupied at low temperatures.

The entropy of the ground state is usually zero.

Therefore, the entropy increases enormously when the energy is increased.

The reciprocal temperature will be large and consequently the temperature will be very small.

Boltzmann factor

Essentials of Thermodynamics

1. Temperature
2. **Boltzmann factor**
3. Maxwell's velocity distribution function
4. Ideal gas laws

Boltzmann factor 1

In thermal equilibrium, the Boltzmann factor gives the occupation probability w_n of an energy level E_n of a microscopic system that is in thermal contact with a macroscopic system

Boltzmann factor 2

The energy of the macroscopic system is E_M and that of the microscopic system is E_n.The total energy is

$$\underline{E = E_M + E_n}$$

If there is only one possibility to realize the energy E_n of the microscopic system, the total entropy is equal to the entropy of the macroscopic system

$S(E_M) = k_B \ln \Gamma(E_M)$

The number of possibilities to realize the energy E_M of the macroscopic system is

$$\Gamma(E_M) = \exp\left(\frac{S(E_M)}{k_B}\right) = \exp\left(\frac{S(E - E_n)}{k_B}\right)$$

Boltzmann factor 2 Comment 1

The system is divided into a macroscopic system and a microscopic system.

The macroscopic system could be a crystal and the microscopic system an atom in the crystal.

The total energy is the sum of the energy of the macroscopic and microscopic system.

For the sake of simplicity, it is assumed that there is only one possibility of realizing the energy E_n of the microscopic system, i.e. for each energy in the microscopic system there is only one energy level.

Therefore, the microscopic system does not contribute to the total entropy of the system.

Boltzmann factor 2

Comment 2

The formula written in blue indicates the number of possibilities to realize the energy of the macroscopic system.

The number of possibilities of realizing a state with the energy E_M depends on the energy E_M and changes when the energy of the microscopic system changes.

The energy of the macroscopic system corresponds to the difference between the total energy and the energy of the microscopic system.

Boltzmann factor 3

Taylor expansion ($E_n << E$)

$$S(E - E_n) = S(E) - \frac{\partial S}{\partial E} E_n = \underline{S(E) - \frac{E_n}{T}}$$

and

$$\Gamma(E_M) = \exp\left(\frac{S(E - E_n)}{k_B}\right) = \exp\left(\frac{S(E)}{k_B}\right) \underline{\exp\left(-\frac{E_n}{k_B T}\right)}$$

With the assumption: $\exp\left(\frac{S(E)}{k_B}\right) =$ constant is the occupation probability of energy level E_n

$$\boxed{w_n \propto \Gamma(E_M) \propto \exp\left(-\frac{E_n}{k_B T}\right)}$$

Boltzmann factor 3

Comment 1

The energy of the microscopic system is certainly much smaller than the energy of the macroscopic system.

Even in a small crystal there are about 10^{20} atoms and the energy of a single atom is negligibly small compared to the energy of the whole crystal.

Therefore a Taylor expansion can be used.

Since the derivative of the entropy with respect to the energy is the reciprocal temperature, the underlined formula results for the entropy of the system.

The number of possibilities of the macroscopic system to realize a state with the energy E_M is given by the product of two exponential functions.

Boltzmann factor 3 Comment 2

The exponent of the first exponential function is the entropy divided by the Boltzmann constant.

The exponent of the second exponential function results from the quotient of the energy of the microscopic system and the thermal energy, which is given by the product of the Boltzmann constant with the temperature.

This exponential function underlined in red is the Boltzmann factor.

It is assumed that the first exponential is a constant and that the energy dependence of $\Gamma(E_\mathrm{M})$ is completely determined by the Boltzmann factor.

Boltzmann factor 3

Comment 3

Then the number of possibilities to realize the energy E_M of the macroscopic system is proportional to the Boltzmann factor.

$\Gamma(E_M)$ depends on the excitation energy of the microscopic system.

$\Gamma(E_M)$ decreases as the energy of the microscopic system increases.

It is therefore assumed that the occupation probability w_n of a microscopic energy level E_n is also proportional the $\Gamma(E_M)$.

This assumption has been well confirmed experimentally.

Boltzmann factor 4

$$\underline{w_n \propto \exp(-\frac{E_n}{k_B T})}$$

Constant of proportionality: <u>partition sum Z</u>

$$w_n = \frac{1}{Z}\exp(-\frac{E_n}{k_B T})$$

and

$$\sum_n w_n = 1 = \frac{1}{Z}\sum_n \exp(-\frac{E_n}{k_B T})$$

i.e.

$$\boxed{Z = \sum_n \exp(-\frac{E_n}{k_B T})}$$

Boltzmann factor 4

Comment

The proportionality constant between the occupation probability and the Boltzmann factor is determined by the partition sum.

The equation outlined in red gives the definition of the partition sum.

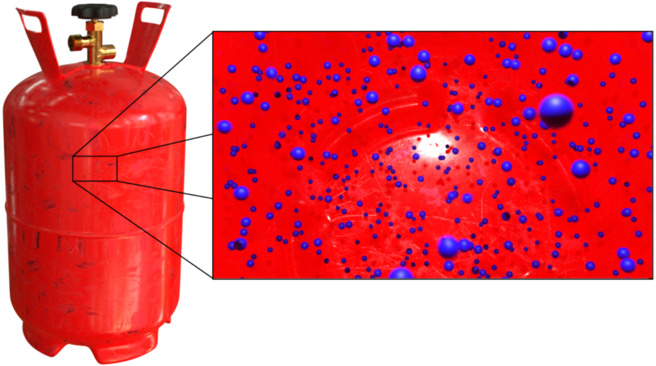
Maxwell distribution function

Essentials of Thermodynamics

1. Temperature
2. Boltzmann factor
3. Maxwell’s velocity distribution function
4. Ideal gas laws

Maxwell’s velocity distribution function 1

The ideal gas



(IdealesGas.mp4)

Maxwell’s velocity distribution function 1

Comment

A simple application of Boltzmann’s theory is the velocity distribution function of an ideal gas.

The distribution function was derived by Boltzmann and Maxwell in 1860.

The video shows an animation of an ideal gas.

The atoms of the gas move randomly at different speeds.

The atoms collide with each other and the wall of the container.

Maxwell’s velocity distribution function 2

The Boltzmann factor for a particle of the gas with the kinetic energy $E_{\mathrm{kin}} = mv^2/2$ is

$$w(E_{kin}) \propto \exp\left(-\frac{E_{kin}}{k_B T}\right) = \exp\left(-\frac{mv^2}{2k_B T}\right)$$

The probability that the velocity of a gas particle lies in an interval $v, v + dv$ is

$$w(v) \propto 4\pi v^2 dv$$

and the number of particles with velocity v in an interval dv is

$$dN(v) = C\, 4\pi v^2 dv \exp\left(-\frac{mv^2}{2k_B T}\right)$$

C is the constant of proportionality

Maxwell's velocity distribution function 2 Comment

The first formula gives the Boltzmann factor for a particle that moves with a certain kinetic energy.

The exponent of the exponential function results from the quotient of the kinetic energy and the thermal energy.

The probability that a particle moves at a particular speed results from the second formula written in blue.

The probability is proportional to the volume of a spherical shell with the radius v and the thickness dv.

The factor $4\pi v^2$ gives the surface of a sphere with the radius v.

The number of particles with the speed in the interval $v, v + dv$ is proportional to the product of the geometric factor $4\pi v^2 \mathrm{d}v$ and the Boltzmann factor.

Maxwell’s velocity distribution function 3

The constant of proportionality C is determined by the integration over all speeds from zero to infinity

$$N = \int_{v=0}^{\infty} dN(v) = \int_{v=0}^{\infty} C\, 4\pi \exp\left(-\frac{mv^2}{2k_BT}\right)v^2 dv \quad \rightarrow \quad \underline{C = \frac{N}{\left(\frac{2\pi k_B T}{m}\right)^{3/2}}}$$

Maxwell’s velocity distribution function

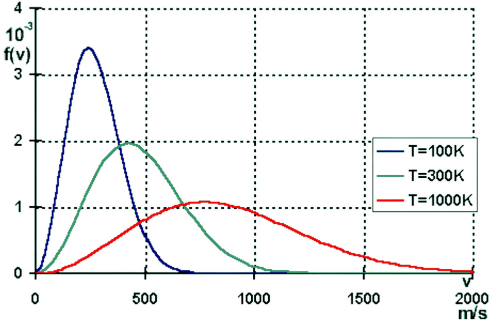
$$\boxed{f(v) = \frac{1}{N}\frac{dN(v)}{dv} = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_BT}\right)}$$

Maxwell’s velocity distribution function 3 Comment

The constant of proportionality is determined by the integration over all speeds from zero to infinity.

The formula outlined in red is Maxwell’s velocity distribution function.

Maxwell’s velocity distribution function 4



The speed for which Maxwell’s velocity distribution function is maximum is

with $\frac{df(v)}{dv} = 0 \quad \rightarrow \quad v_{max}^2 = \frac{2k_BT}{m}$ and $\underline{E_{kin,max}} = \frac{1}{2}mv_{max}^2 = \underline{k_BT}$

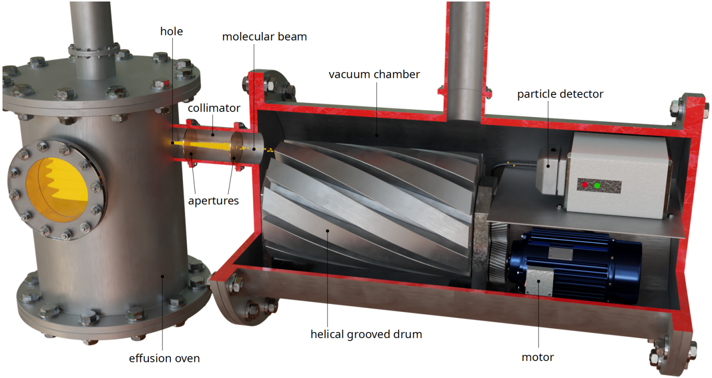
Maxwell’s velocity distribution function 4 Comment

The figure shows Maxwell’s velocity distribution function for three different temperatures.

A calculation shows that the kinetic energy of the particles in the maximum of Maxwell’s velocity distribution function is given by the thermal energy, i.e. the product of Boltzmann’s constant and temperature.

Maxwell’s velocity distribution function 5

Experimental test



(Geschwindigkeitsfilter.mp4)

see also: (https://www.tec-science.com/thermodynamics/kinetic-theory-of-gases/determination-of-the-velocity-distribution-in-a-gas/)

Maxwell's velocity distribution function 5

Comment

The animation shows how the velocity distribution function can be measured.

The particles are vaporized in an oven at a certain temperature.

The vaporized particles are guided through the spiral-shaped grooved roller and counted by the particle detector.

The speed of rotation of the roller determines the speed of the particles reaching the particle detector.

The Maxwell velocity distribution can be determined by counting the number of particles for different rotational speeds of the roller.

Ideal gas laws

Essentials of Thermodynamics

1. Temperature
2. Boltzmann factor
3. Maxwell’s velocity distribution function
4. Ideal gas laws

Ideal gas laws 1

Law of Boyle-Mariotte (1662 and 1676)

$$\boxed{p \propto \frac{1}{V}}$$

Laws of Gay-Lussac (1802)

$$\boxed{\begin{aligned} V &\propto T \\ p &\propto T \end{aligned}}$$

Law of Avogadro (1811)

$$\boxed{V \propto N} \quad \text{and} \quad T = \text{constant},\ p = \text{constant}$$

Ideal gas laws 1

Comment 1

Measuring the temperature of a gas using the velocity distribution function is tedious.

This task can be accomplished much more conveniently when the ideal gas laws are used.

Boyle and Mariotte discovered in the second half of the 17th century that the product of pressure and volume is a constant for a gas.

Gay-Lussac discovered in 1802 that the volume and pressure of a gas are proportional to temperature.

With these laws it became possible to use gases to measure temperature.

Since there is no negative volume, it is immediately clear that there must be absolute zero temperature.

Ideal gas laws 1

Comment 2

A discovery by Avogadro in 1811 opened the door to a scientific understanding of matter.

Avogadro showed that the volume of a gas at constant pressure and temperature is proportional to the number of particles in the gas.

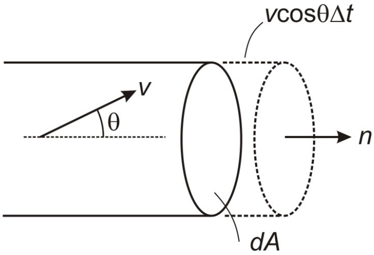
This result does not depend on the type of particles that are in the gas and mixtures of different particles are also possible.

With Avogadro’s law it became possible to determine the relative masses of various chemical compounds in the gas phase.

These measurements finally led to the periodic table of the elements, which was first published in 1869 by Dmitri Ivanovich Mendeleev in St. Petersburg.

Ideal gas laws and Maxwell’s velocity distribution function 2

Kinetic gas theory



$$\boxed{pV = \frac{2}{3} N \langle E_{kin} \rangle}$$

The ideal gas law results when the mean kinetic energy $\langle E_{kin} \rangle$ is calculated with the Maxwell velocity distribution function

$$\langle E_{kin} \rangle = \frac{1}{2} m \int_{v=0}^{\infty} v^2 f(v) dv = \frac{3}{2} k_B T \quad \text{and} \quad \boxed{pV = N k_B T}$$

Ideal gas laws 2

Comment 1

The kinetic gas theory shows that the product of pressure and volume is proportional to the mean kinetic energy of the particles.

The kinetic gas theory is based on the assumption that the particles collide elastically with one other and with the walls.

In order to calculate the pressure, the force that the gas particles exert on the wall of the container must be determined.

The figure shows how the number of particles that hit the container wall in the time interval Δt can be determined.

The number of particles results from the density of the gas particles and the volume shown in dashed lines.

Ideal gas laws 2

Comment 2

The momentum transfer per time interval is the force and the force per area is the pressure.

The mean kinetic energy of the gas can be calculated with Maxwell's velocity distribution function by integrating over the velocities.

The calculation results in the well-known ideal gas law.

The temperature measurable with the ideal gas law is the temperature defined by the statistical arguments of Boltzmann, i.e. $\frac{1}{T} = \frac{\partial S}{\partial E}$.

Ideal gas laws 2

Details of calculation

The number of particles with velocity v is

$$dN(v) = Nf(v)dv$$

The number of particles with velocity v in direction θ is

$$dN(v,\theta) = Nf(v)dv \cdot \frac{2\pi \sin\theta d\theta}{4\pi} = \frac{1}{2} Nf(v)dv \sin\theta d\theta,$$

i.e. the fraction between the solid angle $2\pi \sin\theta d\theta$ and the total solid angle 4π.

The momentum transfer of one particle to the wall is

$$\Delta p = 2mv\cos\theta$$

Ideal gas laws 2

The density of particles with velocity v in direction θ is

$$\frac{dN(v,\theta)}{V} = \frac{1}{2}\frac{N}{V} f(v) dv \sin\theta d\theta,$$

The number of particles which transfer momentum during the time interval Δt on the area dA of the wall is

$$\frac{dN(v,\theta)}{V} dA v \cos\theta \Delta t$$

The force due to the momentum transfer on area dA is ($F = \Delta p/\Delta t$)

$$dF = 2mv\cos\theta \cdot \frac{dN(v,\theta)}{V} dA v \cos\theta$$

Ideal gas laws 2

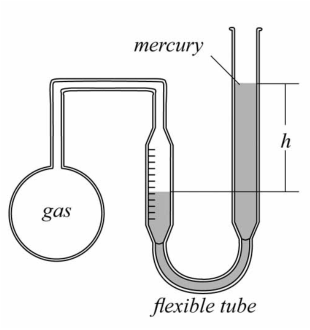
Comment 5

The pressure dF/dA times volume is

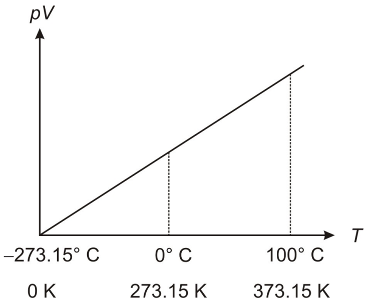
$$
\begin{aligned}
pV = & \int 2mv^2 \cos^2\theta dN(v,\theta) \\
=& mN \int_{v=0}^{\infty} dv v^2 f(v) \int_{\theta=0}^{\pi/2} d\theta \cos^2\theta \sin\theta \\
=& mN \int_{v=0}^{\infty} dv v^2 f(v) \cdot \frac{1}{3} \\
=& \frac{2}{3} N \int_{v=0}^{\infty} dv \frac{1}{2} m v^2 f(v) \\
=& \frac{2}{3} N \langle E_{kin} \rangle
\end{aligned}
$$

Ideal gas laws 3

Gas thermometer



Kelvin and the degree Celsius temperature scale



Ideal gas laws 3

Comment

The left figure shows a gas thermometer.

To measure the temperature, you have to keep the volume constant with the mercury column and determine the pressure of the gas.

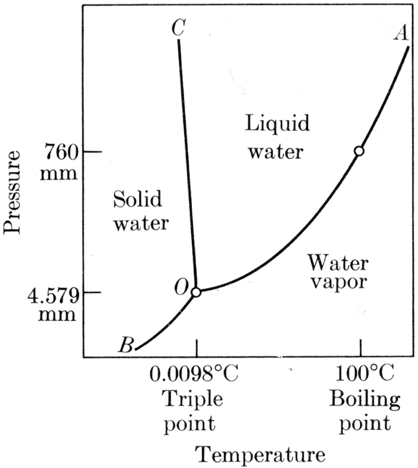
The height of the mercury column is then proportional to the temperature.

The right figure shows the definition of the degree Celsius temperature scale.

Ice water and boiling water define the two fixed points on the temperature scale.

Ideal gas laws 4

Definition of the degree Celsius temperature scale



Ideal gas laws 4

Comment

The figure shows the phase diagram of water, with which the fixed points of the degree Celsius temperature scale are defined.

The absolute temperature scale can be defined with the degree Celsius temperature scale and the ideal gas law.

The absolute temperature is measured in Kelvin.

The absolute zero of the temperature corresponds to -273.15 ° C when the degree Celsius temperature scale is used.

The experimental definition of the temperature scale explains why the Boltzmann constant has to be introduced into the definition of entropy.

If the Boltzmann constant is replaced by 1, the temperature is measured in units of energy.

Revision

Summary in questions

1. What is entropy in physics?
2. How is temperature defined in physics?
3. Write down the Boltzmann factor.
4. Write down the partition sum.
5. How is Maxwell's velocity distribution function defined?
6. Write down Maxwell's velocity distribution function without pre-factors.
7. Sketch Maxwell's velocity distribution function for two different temperatures.
8. What is the kinetic energy of the gas particles in the maximum of the velocity distribution function?
9. Write down the ideal gas law.
10. Explain the definition of the Kelvin and the degree Celsius temperature scale.