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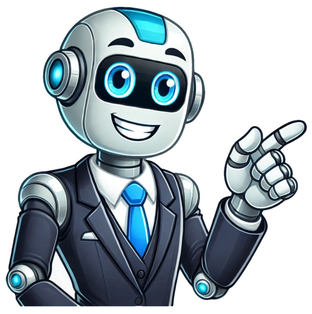

From the kinetic theory of gases, we have learnt that all the particles in air travel at different speeds and the speed of each particle are due to the collisions between the particles present in the air. Thus, we cannot tell the speed of each particle in the gas or air. Instead, we can tell the number of particles or in other words, we can say that the distribution of particles with a particular speed in gas at a certain temperature can be known. James Maxwell and Ludwig Boltzmann showed the distribution of the particles having different speeds in an ideal gas. Let us look further into Maxwell Boltzmann's distribution. Maxwell Boltzmann DistributionThe Maxwell Boltzmann distribution can be studied with the help of a graph given below in this article. The graph shows the number of molecules possessing a certain speed on the Y-axis and their respective speeds on the X-axis. We can see that the maximum speed is only possessed by a very small number of molecules whereas most of the molecules possess a speed called most probable speed. Let us see the Maxwell-Boltzmann distribution curve for an ideal gas at two different temperatures T1 and T2 where T1>T2. It can be seen from the above graph that as the temperature rises, the curve begins to flatten and broaden. Also, the particles that possess the most probable speed reduce but the area under the graph increases which shows that more particles gain energy and are set in motion. Derivation of the Maxwell Boltzmann FormulaConsider an isolated system containing a gas which contains a number of particles. Let us assume that there are n number of particles and the volume and energy of the gas are fixed which is denoted by V and U respectively. Suppose the system has n energy levels which are e0, e1, e2........, er. Now we need to calculate the number of particles having a certain energy level. We know that different particles have different energy. Suppose the number of particles with energy e0 is n0, with energy e1 is n1 and so on. Thus the number of particles at different energy levels are n1, n2, ..., nr. Let W be the number of ways to attain a certain energy level. This can be calculated using, W = \frac{n!}{n_0!n_1!\dots n_r!} Rewriting the above equation using, we get ln(n!) \cong n \space ln(n)-n+\frac{1}{2}ln(2\pi n) When n becomes very large, this equation can be written as, ln(n!) \cong n \space ln(n)-n This equation can be written as follows in terms of W ln W \cong n\space ln(n)-\Sigma n_i\space ln(n_i) - (n-\Sigma n_i) We know that \Sigma n_i = n Thus, ln W \cong n\space ln(n)-\Sigma n_i\space ln(n_i) Differentiating the above equation with respect to dn_i d(lnW) = -\Sigma (1+ln(n_i))dn_i = -\Sigma ln(n_i)dn_i Using Lagrange's multipliers, d(lnW)= -\Sigma ln(n_i)dn_i-\alpha\Sigma dn_i -\beta\Sigma dn_i The above equation will attain maximum value when d(lnW)=0 0=-\Sigma ln(n_i)dn_i-\alpha\Sigma dn_i -\beta\Sigma dn_i 0=-\Sigma (ln(n_i)+\alpha +\beta e_i)\ dn_i ln(n_i)=-\alpha-\beta e_i Taking antilogarithm on both sides, n_i = e^{-\alpha}e^{-\beta e_i} Using the 0th law of thermodynamics we can calculate the value of \beta as \beta = -1/k_bT where kb is the Boltzmann constant. This equation is used to plot the graph shown above and is not used for solving numerical problems. Different Types of Speed from Maxwell Boltzmann DistributionThe Maxwell-Boltzmann distribution gives information about various types of speeds possessed by the molecules of gas. In general, a molecule's speed can be studied under three heading Most-Probable SpeedAverage SpeedRoot Mean Square SpeedLet us see the different types of speeds that can be calculated from the Maxwell-Boltzmann distribution. Most-Probable SpeedThis is the speed that is possessed by the majority of the molecules or the maximum number of molecules in a gas. It is represented as v_{mp} and can be calculated as, v_{mp}=\sqrt{\frac{2RT}{M}} where,R is the universal gas constant,T is the absolute temperature of the gas in KelvinM is the molar mass of the gas Average SpeedIt is defined as the average speed of all the molecules in a gas. It can be found by dividing the sum of the speeds of all the molecules by the total number of molecules in the gas. It is represented as v_{avg} . It is calculated using, v_{avg}=\sqrt{\frac{8RT}{\pi M}} where,R is the universal gas constant,T is the absolute temperature of the gas in KelvinM is the molar mass of the gas Root Mean Square SpeedIt is the square root of the average of the squares of the speed of all the molecules in the gas. It is represented as v_{rms} . It can be calculated using, v_{rms}=\sqrt{\frac{3RT}{M}} where,R is the universal gas constant,T is the absolute temperature of the gas in KelvinM is the molar mass of the gas Read More Solved ExamplesExample 1: Calculate the average speed of CO2 gas at 300K. Solution: T = 300 K M = 44 g v_{avg}=\sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8×8.314×300}{3.14×44}} = 12.01 m/s Thus, the average speed of the gas is 12.01 m/s. Example 2: Calculate the Vrms speed of the NO gas at 600K. Solution: T = 600 K M = 30 g v_{rms}=\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3×8.314×600}{30}} = 22.33 m/s Thus, the Vrms speed of the gas is 22.33 m/s. Example 3: Calculate the most probable speed of the gas with a molar mass of 20g at 100K. Solution: T = 100 K M = 20 g v_{mp}=\sqrt{\frac{2RT}{M}} = \sqrt{\frac{2×8.314×100}{20}} = 9.12 m/s Thus, the most probable speed of the gas is 9.12 m/s. Example 4: Which of the following gases have a higher Vrms speed, O2 at 200K or N2 at 400K? Solution: For O2 T = 200 K M = 32 g v_{rms}=\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3×8.314×200}{32}} = 12.48 m/s Thus, the most probable speed of the O2 is 12.48 m/s. For N2 T = 400 K M = 28 g v_{rms}=\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3×8.314×400}{28}} = 18.87 m/s Thus, the most probable speed of the N2 is 18.87 m/s. Vrms speed of N2 is higher than O2 at the given conditions. Example 5: Calculate the temperature of the SO2 gas if its average speed is 5m/s. Solution: M = 64g v_{avg}=50ms^{-1} v_{avg}=\sqrt{\frac{8RT}{\pi M}} 5 =\sqrt{\frac{8×8.314×T}{3.14×64}} 25 =\frac{8×8.314×T}{3.14×64} T = 75.53K Thus, the temperature of the SO2 gas is 75.53K. Not to be confused with Maxwell–Boltzmann distribution. Statistical distribution used in many-particle mechanicsStatistical mechanics Thermodynamics Kinetic theory Particle statistics Spin–statistics theorem Indistinguishable particles Maxwell–Boltzmann Bose–Einstein Fermi–Dirac Parastatistics Anyonic statistics Braid statistics Thermodynamic ensembles NVE Microcanonical NVT Canonical µVT Grand canonical NPH Isoenthalpic–isobaric NPT Isothermal–isobaric Models Debye Einstein Ising Potts Potentials Internal energy Enthalpy Helmholtz free energy Gibbs free energy Grand potential / Landau free energy Scientists Maxwell Boltzmann Helmholtz Bose Gibbs Einstein Dirac Ehrenfest von Neumann Tolman Debye Fermi Synge Ising Landau vte Maxwell–Boltzmann statistics can be used to derive the Maxwell–Boltzmann distribution of particle speeds in an ideal gas. Shown: distribution of speeds for 106 oxygen molecules at -100, 20, and 600 °C. In statistical mechanics, Maxwell–Boltzmann statistics describes the distribution of classical material particles over various energy states in thermal equilibrium. It is applicable when the temperature is high enough or the particle density is low enough to render quantum effects negligible. The expected number of particles with energy ε i {\displaystyle \varepsilon _{i}} for Maxwell–Boltzmann statistics is ⟨ N i ⟩ = g i e (ε i − μ) / k T = N Z g i e − ε i / k T , {\displaystyle \langle N_{i}\rangle ={\frac {g_{i}}{e^{(\varepsilon _{i}-\mu)/kT}}}={\frac {N}{Z}}\,g_{i}e^{-\varepsilon _{i}/kT},} where: ε i {\displaystyle \varepsilon _{i}} is the energy of the i-th energy level, ⟨ N i ⟩ {\displaystyle \langle N_{i}\rangle } is the average number of particles in the set of states with energy ε i {\displaystyle \varepsilon _{i}} , g i {\displaystyle g_{i}} is the degeneracy of energy level i, that is, the number of states with energy ε i {\displaystyle \varepsilon _{i}} which may nevertheless be distinguished from each other by some other means,[nb 1] μ is the chemical potential, k is the Boltzmann constant, T is absolute temperature, N is the total number of particles: N = ∑ i N i , {\displaystyle N=\sum _{i}N_{i},} Z is the partition function: Z = ∑ i g i e − ε i / k T , {\displaystyle Z=\sum _{i}g_{i}e^{-\varepsilon _{i}/kT},} e is Euler's number Equivalently, the number of particles is sometimes expressed as ⟨ N i ⟩ = 1 e (ε i − μ) / k T = N Z e − ε i / k T , {\displaystyle \langle N_{i}\rangle ={\frac {1}{e^{(\varepsilon _{i}-\mu)/kT}}}={\frac {N}{Z}}\,e^{-\varepsilon _{i}/kT},} where the index i now specifies a particular state rather than the set of all states with energy ε i {\displaystyle \varepsilon _{i}} , and Z = ∑ i e − ε i / k T {\textstyle Z=\sum _{i}e^{-\varepsilon _{i}/kT}} . Further information: Maxwell–Boltzmann distribution Maxwell–Boltzmann statistics grew out of the Maxwell–Boltzmann distribution, most likely as a distillation of the underlying technique.[dubious – discuss] The distribution was first derived by Maxwell in 1860 on heuristic grounds. Boltzmann later, in the 1870s, carried out significant investigations into the physical origins of this distribution. The distribution can be derived on the ground that it maximizes the entropy of the system. Maxwell–Boltzmann distribution and Maxwell–Boltzmann statistics are closely related. Maxwell–Boltzmann statistics is a more general principle in statistical mechanics that describes the probability of a classical particle being in a particular energy state: P i = e − E i / k B T Z {\displaystyle P_{i}={\frac {e^{-E_{i}/k_{B}T}}{Z}}} where: Z {\displaystyle Z} is the partition function: Z = ∑ i e − E i / k B T {\displaystyle Z=\sum _{i}e^{-E_{i}/k_{B}T}} , E i {\displaystyle E_{i}} is the energy of state i {\displaystyle i} , k B {\displaystyle k_{B}} is Boltzmann's constant, T {\displaystyle T} is the absolute temperature. Maxwell–Boltzmann distribution is a specific application of Maxwell–Boltzmann statistics to the kinetic energies of gas particles. The distribution of velocities (or speeds) of particles in an ideal gas follows from the statistical assumption that the energy levels of a gas molecule are given by its kinetic energy: f (v) = (m 2 π k B T) 3 / 2 4 π v 2 e − m v 2 2 k B T {\displaystyle f(v)=\left({\frac {m}{2\pi k_{B}T}}\right)^{3/2}4\pi v^{2}e^{-{\frac {mv^{2}}{2k_{B}T}}}} where: f (v) {\displaystyle f(v)} is the probability density function of particle speeds, m {\displaystyle m} is the mass of a particle, k B {\displaystyle k_{B}} is Boltzmann's constant, T {\displaystyle T} is the absolute temperature, v {\displaystyle v} is the speed of the particle. We can deduce the Maxwell–Boltzmann distribution from Maxwell–Boltzmann statistics, starting with the Maxwell-Boltzmann probability for energy states and substituting the kinetic energy E = 1 2 m v 2 {\displaystyle E={\frac {1}{2}}mv^{2}} to express the probability in terms of velocity: P (E) = 1 Z exp (− E k B T) → P (v) = 1 Z exp (− m v 2 2 k B T) {\displaystyle {\begin{aligned}P(E)&={\frac {1}{Z}}~\exp \left({\frac {-E}{k_{B}T}}\right)\\\rightarrow P(v)&={\frac {1}{Z}}~\exp \left({\frac {-mv^{2}}{2k_{B}T}}\right)\end{aligned}}} In 3D, this is proportional to the surface area of a sphere, 4 π v 2 {\displaystyle 4\pi v^{2}} . Thus, the probability density function (PDF) for speed v {\displaystyle v} becomes: f (v) = C ⋅ 4 π v 2 exp (− m v 2 2 k B T) {\displaystyle f(v)=C\cdot 4\pi v^{2}\exp \left(-{\frac {mv^{2}}{2k_{B}T}}\right)} To find the normalization constant C {\displaystyle C} , we require the integral of the probability density function over all possible speeds to be unity: ∫ 0 ∞ f (v) d v = 1 → C ∫ 0 ∞ 4 π v 2 exp (− m v 2 2 k B T) d v = 1 {\displaystyle {\begin{aligned}\int _{0}^{\infty }f(v)dv&=1\\\rightarrow C\int _{0}^{\infty }4\pi v^{2}\exp \left(-{\frac {mv^{2}}{2k_{B}T}}\right)dv&=1\end{aligned}}} Evaluating the integral using the known result ∫ 0 ∞ v 2 e − a v 2 d v = π 4 a 3 / 2 {\displaystyle \int _{0}^{\infty }v^{2}e^{-av^{2}}dv={\frac {\sqrt {\pi }}{4a^{3/2}}}} , with a = m 2 k B T {\displaystyle a={\frac {m}{2k_{B}T}}} , we obtain: C ⋅ 4 π ⋅ π 4 (m 2 k B T) 3 / 2 = 1 → C = (m 2 π k B T) 3 / 2 {\displaystyle {\begin{aligned}C\cdot 4\pi \cdot {\frac {\sqrt {\pi }}{4\left({\frac {m}{2k_{B}T}}\right)^{3/2}}}=1\quad \rightarrow C=\left({\frac {m}{2\pi k_{B}T}}\right)^{3/2}\end{aligned}}} Therefore, the Maxwell–Boltzmann speed distribution is: f (v) = (m 2 π k B T) 3 / 2 4 π v 2 exp (− m v 2 2 k B T) {\displaystyle f(v)=\left({\frac {m}{2\pi k_{B}T}}\right)^{3/2}4\pi v^{2}\exp \left(-{\frac {mv^{2}}{2k_{B}T}}\right)} Equilibrium thermal distributions for particles with integer spin (bosons), half integer spin (fermions), and classical (spinless) particles. Average occupancy ⟨ n ⟩ {\displaystyle \langle n\rangle } is shown versus energy ϵ {\displaystyle \epsilon } relative to the system chemical potential μ {\displaystyle \mu } , where T {\displaystyle T} is the system temperature, and k B {\displaystyle k_{B}} is the Boltzmann constant. Maxwell–Boltzmann statistics is used to derive the Maxwell–Boltzmann distribution of an ideal gas. However, it can also be used to extend that distribution to particles with a different energy–momentum relation, such as relativistic particles (resulting in Maxwell–Jüttner distribution), and to other than three-dimensional spaces. Maxwell–Boltzmann statistics is often described as the statistics of "distinguishable" classical particles. In other words, the configuration of particle A in state 1 and particle B in state 2 is different from the case in which particle B is in state 1 and particle A is in state 2. This assumption leads to the proper (Boltzmann) statistics of particles in the energy states, but yields non-physical results for the entropy, as embodied in the Gibbs paradox. At the same time, there are no real particles that have the characteristics required by Maxwell–Boltzmann statistics. Indeed, the Gibbs paradox is resolved if we treat all particles of a certain type (e.g., electrons, protons, photons, etc.) as principally indistinguishable. Once this assumption is made, the particle statistics change. The change in entropy in the entropy of mixing example may be viewed as an example of a non-extensive entropy resulting from the distinguishability of the two types of particles being mixed. Quantum particles are either bosons (following Bose–Einstein statistics) or fermions (subject to the Pauli exclusion principle, following instead Fermi–Dirac statistics). Both of these quantum statistics approach the Maxwell–Boltzmann statistics in the limit of high temperature and low particle density. Maxwell–Boltzmann statistics can be derived in various statistical mechanical thermodynamic ensembles:[1] The grand canonical ensemble, exactly. The canonical ensemble, exactly. The microcanonical ensemble, but only in the thermodynamic limit. In each case it is necessary to assume that the particles are non-interacting, and that multiple particles can occupy the same state and do so independently. This section may be too technical for most readers to understand. Please help improve it to make it understandable to non-experts, without removing the technical details. (December 2013) (Learn how and when to remove this message) Suppose we have a container with a huge number of very small particles all with identical physical characteristics (such as mass, charge, etc.). Let's refer to this as the system. Assume that though the particles have identical properties, they are distinguishable. For example, we might identify each particle by continually observing their trajectories, or by placing a marking on each one, e.g., drawing a different number on each one as is done with lottery balls. The particles are moving inside that container in all directions with great speed. Because the particles are speeding around, they possess some energy. The Maxwell–Boltzmann distribution is a mathematical function that describes about how many particles in the container have a certain energy. More precisely, the Maxwell–Boltzmann distribution gives the non-normalized probability (this means that the probabilities do not add up to 1) that the state corresponding to a particular energy is occupied. In general, there may be many particles with the same amount of energy ε {\displaystyle \varepsilon } . Let the number of particles with the same energy ε 1 {\displaystyle \varepsilon _{1}} be N 1 {\displaystyle N_{1}} , the number of particles possessing another energy ε 2 {\displaystyle \varepsilon _{2}} be N 2 {\displaystyle N_{2}} , and so forth for all the possible energies { ε i | i = 1 , 2 , 3 , … } . {\displaystyle \{\varepsilon _{i}\mid i=1,2,3,\ldots \}.} To describe this situation, we say that N i {\displaystyle N_{i}} is the occupation number of the energy level i . {\displaystyle i.} If we know all the occupation numbers { N i | i = 1 , 2 , 3 , … } , {\displaystyle \{N_{i}\mid i=1,2,3,\ldots \},} then we know the total energy of the system. However, because we can distinguish between which particles are occupying each energy level, the set of occupation numbers { N i | i = 1 , 2 , 3 , … } {\displaystyle \{N_{i}\mid i=1,2,3,\ldots \}} does not completely describe the state of the system. To completely describe the state of the system, or the microstate, we must specify exactly which particles are in each energy level. Thus when we count the number of possible states of the system, we must count each and every microstate, and not just the possible sets of occupation numbers. To begin with, assume that there is only one state at each energy level i {\displaystyle i} (there is no degeneracy). What follows next is a bit of combinatorial thinking which has little to do in accurately describing the reservoir of particles. For instance, let's say there is a total of k {\displaystyle k} boxes labelled a , b , … , k {\displaystyle a,b,\ldots ,k} . With the concept of combination, we could calculate how many ways there are to arrange N {\displaystyle N} into the set of boxes, where the order of balls within each box isn’t tracked. First, we select N a {\displaystyle N_{a}} balls from a total of N {\displaystyle N} balls to place into box a {\displaystyle a} , and continue to select for each box from the remaining balls, ensuring that every ball is placed in one of the boxes. The total number of ways that the balls can be arranged is W = N ! N a ! (N − N a) ! × (N − N a) ! N b ! (N − N a − N b) ! × (N − N a − N b) ! N c ! (N − N a − N b − N c) ! × ⋯ × (N − ⋯ − N ℓ) ! N k ! (N − ⋯ − N ℓ − N k) ! = N ! N a ! N b ! N c ! ⋯ N k ! (N − N a − ⋯ − N ℓ − N k) ! {\displaystyle {\begin{aligned}W&={\frac {N!}{N_{a}!{\cancel {(N-N_{a})!}}}}\times {\frac {\cancel {(N-N_{a})!}}{N_{b}!{\cancel {(N-N_{a}-N_{b})!}}}}\times {\frac {\cancel {(N-N_{a}-N_{b})!}}{N_{c}!{\cancel {(N-N_{a}-N_{b}-N_{c})!}}}}\times \cdots \times {\frac {\cancel {(N-\cdots -N_{\ell })!}}{N_{k}!(N-\cdots -N_{\ell }-N_{k})!}}\\[8pt]&={\frac {N!}{N_{a}!N_{b}!N_{c}!\cdots N_{k}!(N-N_{a}-\cdots -N_{\ell }-N_{k})!}}\end{aligned}}} As every ball has been placed into a box, (N − N a − N b − ⋯ − N k) ! = 0 ! = 1 {\displaystyle (N-N_{a}-N_{b}-\cdots -N_{k})!=0!=1} , and we simplify the expression as W = N ! ∏ ℓ = a , b , … k 1 N ℓ ! {\displaystyle W=N!\prod _{\ell =a,b,\ldots }^{k}{\frac {1}{N_{\ell }!}}} This is just the multinomial coefficient, the number of ways of arranging N items into k boxes, the l-th box holding Nl items, ignoring the permutation of items in each box. Now, consider the case where there is more than one way to put N i {\displaystyle N_{i}} particles in the box i {\displaystyle i} (i.e. taking the degeneracy problem into consideration). If the i {\displaystyle i} -th box has a "degeneracy" of g i {\displaystyle g_{i}} , that is, it has g i {\displaystyle g_{i}} "sub-boxes" (g i {\displaystyle g_{i}} boxes with the same energy ε i {\displaystyle \varepsilon _{i}} . These states/boxes with the same energy are called degenerate states.), such that any way of filling the i {\displaystyle i} -th box where the number in the sub-boxes is changed is a distinct way of filling the box, then the number of ways of filling the i-th box must be increased by the number of ways of distributing the N i {\displaystyle N_{i}} objects in the g i {\displaystyle g_{i}} "sub-boxes". The number of ways of placing N i {\displaystyle N_{i}} distinguishable objects in g i {\displaystyle g_{i}} "sub-boxes" is g i N i {\displaystyle g_{i}^{N_{i}}} (the first object can go into any of the g i {\displaystyle g_{i}} boxes, the second object can also go into any of the g i {\displaystyle g_{i}} boxes, and so on). Thus the number of ways W {\displaystyle W} that a total of N {\displaystyle N} particles can be classified into energy levels according to their energies, while each level i {\displaystyle i} having g i {\displaystyle g_{i}} distinct states such that the i-th level accommodates N i {\displaystyle N_{i}} particles is: W = N ! ∏ i g i N i N i ! {\displaystyle W=N!\prod _{i}{\frac {g_{i}^{N_{i}}}{N_{i}!}}} This is the form for W first derived by Boltzmann. Boltzmann's fundamental equation S = k ln W {\displaystyle S=k\,\ln W} relates the thermodynamic entropy S to the number of microstates W, where k is the Boltzmann constant. It was pointed out by Gibbs however, that the above expression for W does not yield an extensive entropy, and is therefore faulty. This problem is known as the Gibbs paradox. The problem is that the particles considered by the above equation are not indistinguishable. In other words, for two particles (A and B) in two energy sublevels the population represented by [A,B] is considered distinct from the population [B,A] while for indistinguishable particles, they are not. If we carry out the argument for indistinguishable particles, we are led to the Bose–Einstein expression for W: W = ∏ i (N i + g i − 1) ! N i ! (g i − 1) ! {\displaystyle W=\prod _{i}{\frac {(N_{i}+g_{i}-1)!}{N_{i}!(g_{i}-1)!}}} The Maxwell–Boltzmann distribution follows from this Bose–Einstein distribution for temperatures well above absolute zero, implying that g i ≫ 1 {\displaystyle g_{i}\gg 1} . The Maxwell–Boltzmann distribution also requires low density, implying that g i ≫ N i {\displaystyle g_{i}\gg N_{i}} . Under these conditions, we may use Stirling's approximation for the factorial: N ! ≈ N N e − N , {\displaystyle N!\approx N^{N}e^{-N},} to write: W ≈ ∏ i (N i + g i) N i + g i N i N i g i g i ≈ ∏ i g i N i (1 + N i / g i) g i N i N i {\displaystyle W\approx \prod _{i}{\frac {(N_{i}+g_{i})^{N_{i}+g_{i}}}{N_{i}^{N_{i}}g_{i}^{g_{i}}}}\approx \prod _{i}{\frac {g_{i}^{N_{i}}(1+N_{i}/g_{i})^{g_{i}}}{N_{i}^{N_{i}}}}} Using the fact that (1 + N i / g i) g i ≈ e N i {\displaystyle (1+N_{i}/g_{i})^{g_{i}}\approx e^{N_{i}}} for g i ≫ N i {\displaystyle g_{i}\gg N_{i}} we can again use Stirling's approximation to write: W ≈ ∏ i g i N i N i ! {\displaystyle W\approx \prod _{i}{\frac {g_{i}^{N_{i}}}{N_{i}!}}} This is essentially a division by N! of Boltzmann's original expression for W, and this correction is referred to as correct Boltzmann counting. We wish to find the N i {\displaystyle N_{i}} for which the function W {\displaystyle W} is maximized, while considering the constraint that there is a fixed number of particles (N = ∑ N i) {\textstyle \left(N=\sum N_{i}\right)} and a fixed energy (E = ∑ N i ε i) {\textstyle \left(E=\sum N_{i}\varepsilon _{i}\right)} in the container. The maxima of W {\displaystyle W} and ln (W) {\displaystyle \ln(W)} are achieved by the same values of N i {\displaystyle N_{i}} and, since it is easier to accomplish mathematically, we will maximize the latter function instead. We constrain our solution using Lagrange multipliers forming the function: f (N 1 , N 2 , … , N n) = ln (W) + α (N − ∑ N i) + β (E − ∑ N i ε i) {\displaystyle f(N_{1},N_{2},\ldots ,N_{n})=\textstyle \ln(W)+\alpha (N-\sum N_{i})+\beta (E-\sum N_{i}\varepsilon _{i})} ln W = ln [∏ i = 1 n g i N i N i !] ≈ ∑ i = 1 n (N i ln g i − N i ln N i + N i) {\displaystyle \ln W=\ln \left[\prod _{i=1}^{n}{\frac {g_{i}^{N_{i}}}{N_{i}!}}\right]\approx \sum _{i=1}^{n}\left(N_{i}\ln g_{i}-N_{i}\ln N_{i}+N_{i}\right)} Finally f (N 1 , N 2 , … , N n) = α N + β E + ∑ i = 1 n (N i ln g i − N i ln N i + N i − (α + β ε i) N i) {\displaystyle f(N_{1},N_{2},\ldots ,N_{n})=\alpha N+\beta E+\sum _{i=1}^{n}\left(N_{i}\ln g_{i}-N_{i}\ln N_{i}+N_{i}-(\alpha +\beta \varepsilon _{i})N_{i}\right)} In order to maximize the expression above we apply Fermat's theorem (stationary points), according to which local extrema, if exist, must be at critical points (partial derivatives vanish): ∂ f ∂ N i = ln g i − ln N i − (α + β ε i) = 0 {\displaystyle {\frac {\partial f}{\partial N_{i}}}=\ln g_{i}-\ln N_{i}-(\alpha +\beta \varepsilon _{i})=0} By solving the equations above (i = 1 … n {\displaystyle i=1\ldots n}) we arrive to an expression for N i {\displaystyle N_{i}} : N i = g i e α + β ε i {\displaystyle N_{i}={\frac {g_{i}}{e^{\alpha +\beta \varepsilon _{i}}}}} Substituting this expression for N i {\displaystyle N_{i}} into the equation for ln W {\displaystyle \ln W} and assuming that N ≫ 1 {\displaystyle N\gg 1} yields: ln W = (α + 1) N + β E {\displaystyle \ln W=(\alpha +1)N+\beta E\,} or, rearranging: E = ln W β − N β − α N β {\displaystyle E={\frac {\ln W}{\beta }}-{\frac {N}{\beta }}-{\frac {\alpha N}{\beta }}} Boltzmann realized that this is just an expression of the Euler-integrated fundamental equation of thermodynamics. Identifying E as the internal energy, the Euler-integrated fundamental equation states that : E = T S − P V + μ N {\displaystyle E=TS-PV+\mu N} where T is the temperature, P is pressure, V is volume, and μ is the chemical potential. Boltzmann's equation S = k ln W {\displaystyle S=k\ln W} is the realization that the entropy is proportional to ln W {\displaystyle \ln W} with the constant of proportionality being the Boltzmann constant. Using the ideal gas equation of state (PV = NkT), It follows immediately that β = 1 / k T {\displaystyle \beta =1/kT} and α = − μ / k T {\displaystyle \alpha =-\mu /kT} so that the populations may now be written: N i = g i e (ε i − μ) / (k T) {\displaystyle N_{i}={\frac {g_{i}}{e^{(\varepsilon _{i}-\mu)/(kT)}}}} Note that the above formula is sometimes written: N i = g i e ε i / k T / z {\displaystyle N_{i}={\frac {g_{i}}{e^{\varepsilon _{i}/kT}/z}}} where z = exp (μ / k T) {\displaystyle z=\exp(\mu /kT)} is the absolute activity. Alternatively, we may use the fact that ∑ i N i = N {\displaystyle \sum _{i}N_{i}=N} to obtain the population numbers as N i = N g i e − ε i / k T Z {\displaystyle N_{i}=N{\frac {g_{i}e^{-\varepsilon _{i}/kT}}{Z}}} where Z is the partition function defined by: Z = ∑ i g i e − ε i / k T {\displaystyle Z=\sum _{i}g_{i}e^{-\varepsilon _{i}/kT}} In an approximation where εi is considered to be a continuous variable, the Thomas–Fermi approximation yields a continuous degeneracy g proportional to ε {\displaystyle {\sqrt {\varepsilon }}} so that: ε e − ε / k T ∫ 0 ∞ ε e − ε / k T = ε e − ε / k T π 2 (k T) 3 / 2 = 2 ε e − ε / k T π (k T) 3 {\displaystyle {\frac {{\sqrt {\varepsilon }}\,e^{-\varepsilon /kT}}{\int _{0}^{\infty }{\sqrt {\varepsilon }}\,e^{-\varepsilon /kT}}}={\frac {{\sqrt {\varepsilon }}\,e^{-\varepsilon /kT}}{{\frac {\sqrt {\pi }}{2}}(kT)^{3/2}}}={\frac {2{\sqrt {\varepsilon }}\,e^{-\varepsilon /kT}}{\sqrt {\pi (kT)^{3}}}}} which is just the Maxwell–Boltzmann distribution for the energy. This section may be too technical for most readers to understand. Please help improve it to make it understandable to non-experts, without removing the technical details. (December 2013) (Learn how and when to remove this message) In the above discussion, the Boltzmann distribution function was obtained via directly analysing the multiplicities of a system. Alternatively, one can make use of the canonical ensemble. In a canonical ensemble, a system is in thermal contact with a reservoir. While energy is free to flow between the system and the reservoir, the reservoir is thought to have infinitely large heat capacity as to maintain constant temperature, T, for the combined system. In the present context, our system is assumed to have the energy levels ε i {\displaystyle \varepsilon _{i}} with degeneracies g i {\displaystyle g_{i}} . As before, we would like to calculate the probability that our system has energy ε i {\displaystyle \varepsilon _{i}} . If our system is in state s 1 {\displaystyle \;s_{1}} , then there would be a corresponding number of microstates available to the reservoir. Call this number Ω R (s 1) {\displaystyle \;\Omega _{R}(s_{1})} . By assumption, the combined system (of the system we are interested in and the reservoir) is isolated, so all microstates are equally probable. Therefore, for instance, if Ω R (s 1) = 2 Ω R (s 2) {\displaystyle \;\Omega _{R}(s_{1})=2\;\Omega _{R}(s_{2})} , we can conclude that our system is twice as likely to be in state s 1 {\displaystyle \;s_{1}} than s 2 {\displaystyle \;s_{2}} . In general, if P (s i) {\displaystyle \;P(s_{i})} is the probability that our system is in state s i {\displaystyle \;s_{i}} , P (s 1) P (s 2) = Ω R (s 1) Ω R (s 2) . {\displaystyle {\frac {P(s_{1})}{P(s_{2})}}={\frac {\Omega _{R}(s_{1})}{\Omega _{R}(s_{2})}}.} Since the entropy of the reservoir S R = k ln Ω R {\displaystyle \;S_{R}=k\ln \Omega _{R}} , the above becomes P (s 1) P (s 2) = e S R (s 1) / k e S R (s 2) / k = e (S R (s 1) − S R (s 2)) / k . {\displaystyle {\frac {P(s_{1})}{P(s_{2})}}={\frac {e^{S_{R}(s_{1})/k}}{e^{S_{R}(s_{2})/k}}}=e^{(S_{R}(s_{1})-S_{R}(s_{2}))/k}.} Next we recall the thermodynamic identity (from the first law of thermodynamics): d S R = 1 T (d U R + P d V R − μ d N R) . {\displaystyle dS_{R}={\frac {1}{T}}(dU_{R}+P\,dV_{R}-\mu \,dN_{R}).} In a canonical ensemble, there is no exchange of particles, so the d N R {\displaystyle dN_{R}} term is zero. Similarly, d V R = 0. {\displaystyle dV_{R}=0.} This gives S R (s 1) − S R (s 2) = 1 T (U R (s 1) − U R (s 2)) = − 1 T (E (s 1) − E (s 2)) , {\displaystyle S_{R}(s_{1})-S_{R}(s_{2})={\frac {1}{T}}(U_{R}(s_{1})-U_{R}(s_{2}))=-{\frac {1}{T}}(E(s_{1})-E(s_{2})),} where U R (s i) {\displaystyle U_{R}(s_{i})} and E (s i) {\displaystyle E(s_{i})} denote the energies of the reservoir and the system at s i {\displaystyle s_{i}} , respectively. For the second equality we have used the conservation of energy. Substituting into the first equation relating P (s 1) , P (s 2) {\displaystyle P(s_{1}),\;P(s_{2})} : P (s 1) P (s 2) = e − E (s 1) / k T e − E (s 2) / k T , {\displaystyle {\frac {P(s_{1})}{P(s_{2})}}={\frac {e^{-E(s_{1})/kT}}{e^{-E(s_{2})/kT}}},} which implies, for any state s of the system P (s) = 1 Z e − E (s) / k T , {\displaystyle P(s)={\frac {1}{Z}}e^{-E(s)/kT},} where Z is an appropriately chosen "constant" to make total probability 1. (Z is constant provided that the temperature T is invariant.) Z = ∑ s e − E (s) / k T , {\displaystyle Z=\sum _{s}e^{-E(s)/kT},} where the index s runs through all microstates of the system. Z is sometimes called the Boltzmann sum over states (or "Zustandssumme" in the original German). If we index the summation via the energy eigenvalues instead of all possible states, degeneracy must be taken into account. The probability of our system having energy ε i {\displaystyle \varepsilon _{i}} is simply the sum of the probabilities of all corresponding microstates: P (ε i) = 1 Z g i e − ε i / k T {\displaystyle P(\varepsilon _{i})={\frac {1}{Z}}g_{i}e^{-\varepsilon _{i}/kT}} where, with obvious modification, Z = ∑ j g j e − ε j / k T , {\displaystyle Z=\sum _{j}g_{j}e^{-\varepsilon _{j}/kT},} this is the same result as before. Comments on this derivation: Notice that in this formulation, the initial assumption "... suppose the system has total N particles..." is dispensed with. Indeed, the number of particles possessed by the system plays no role in arriving at the distribution. Rather, how many particles would occupy states with energy ε i {\displaystyle \varepsilon _{i}} follows as an easy consequence. What has been presented above is essentially a derivation of the canonical partition function. As one can see by comparing the definitions, the Boltzmann sum over states is equal to the canonical partition function. Exactly the same approach can be used to derive Fermi–Dirac and Bose–Einstein statistics. However, there one would replace the canonical ensemble with the grand canonical ensemble, since there is exchange of particles between the system and the reservoir. Also, the system one considers in those cases is a single particle state, not a particle. (In the above discussion, we could have assumed our system to be a single atom.) The Maxwell-Boltzmann distribution describes the probability of a particle occupying an energy state E in a classical system. It takes the following form: f MB,high (E) = exp (− E − E F k T) , for E ≫ E F f MB,low (E) = 1 − exp (E − E F k T) , for E ≪ E F {\displaystyle {\begin{aligned}f_{\text{MB,high}}(E)&=\exp \left(-{\frac {E-E_{F}}{kT}}\right),&{\text{for }}E\gg E_{F}\\f_{\text{MB,low}}(E)&=1-\exp \left({\frac {E-E_{F}}{kT}}\right),&{\text{for }}E\ll E_{F}\end{aligned}}} For a system of indistinguishable particles, we start with the canonical ensemble formalism. In a system with energy levels { E i } {\displaystyle \{E_{i}\}} , let n i {\displaystyle n_{i}} be the number of particles in state i. The total energy and particle number are: E total = ∑ i n i E i N = ∑ i n i {\displaystyle {\begin{aligned}E_{\text{total}}&=\sum _{i}n_{i}E_{i}\\N&=\sum _{i}n_{i}\end{aligned}}} For a specific configuration { n i } {\displaystyle \{n_{i}\}} , the probability in the canonical ensemble is: P ({ n i }) = 1 Z N N ! ∏ i n i ! ∏ i (e − β E i) n i {\displaystyle P(\{n_{i}\})={\frac {1}{Z_{N}}}{\frac {N!}{\prod _{i}n_{i}!}}\prod _{i}(e^{-\beta E_{i}})^{n_{i}}} The factor N ! ∏ i n i ! {\displaystyle {\frac {N!}{\prod _{i}n_{i}!}}} accounts for the number of ways to distribute N indistinguishable particles among the states. For Maxwell-Boltzmann statistics, we assume that the average occupation number of any state is much less than 1 (⟨ n i ⟩ ≪ 1 {\displaystyle \langle n_{i}\rangle \ll 1}), which leads to: ⟨ n i ⟩ ≈ e − β (E i − μ) {\displaystyle \langle n_{i}\rangle \approx e^{-\beta (E_{i}-\mu)}} where μ {\displaystyle \mu } is the chemical potential determined by ∑ i ⟨ n i ⟩ = N {\displaystyle \sum _{i}\langle n_{i}\rangle =N} . For energy states near the Fermi energy E F {\displaystyle E_{F}} , we can express μ ≈ E F {\displaystyle \mu \approx E_{F}} , giving: f MB (E) = e − (E − E F) / k T {\displaystyle f_{\text{MB}}(E)=e^{-(E-E_{F})/kT}} For high energies (E ≫ E F {\displaystyle E\gg E_{F}}), this directly gives: f MB,high (E) = e − (E − E F) / k T {\displaystyle f_{\text{MB,high}}(E)=e^{-(E-E_{F})/kT}} For low energies (E ≪ E F {\displaystyle E\ll E_{F}}), using the approximation e − x ≈ 1 − x {\displaystyle e^{-x}\approx 1-x} for small x: f MB,low (E) ≈ 1 − e (E − E F) / k T {\displaystyle f_{\text{MB,low}}(E)\approx 1-e^{(E-E_{F})/kT}} This is the derivation of the Maxwell-Boltzmann distribution in both energy regimes. Bose–Einstein statistics Fermi–Dirac statistics Boltzmann factor ^ For example, two simple point particles may have the same energy, but different momentum vectors. They may be distinguished from each other on this basis, and the degeneracy will be the number of possible ways that they can be so distinguished. ^ Tolman, R. C. (1938). The Principles of Statistical Mechanics. Dover Publications. ISBN 9780486638966. {{cite book}}: ISBN / Date incompatibility (help) Carter, Ashley H., "Classical and Statistical Thermodynamics", Prentice–Hall, Inc., 2001, New Jersey. Raj Pathria, "Statistical Mechanics", Butterworth–Heinemann, 1996. Retrieved from " Not to be confused with Maxwell–Boltzmann distribution. Statistical distribution used in many-particle mechanicsStatistical mechanics Thermodynamics Kinetic theory Particle statistics Spin–statistics theorem Indistinguishable particles Maxwell–Boltzmann Bose–Einstein Fermi–Dirac Parastatistics Anyonic statistics Braid statistics Thermodynamic ensembles NVE Microcanonical NVT Canonical µVT Grand canonical NPH Isoenthalpic–isobaric NPT Isothermal–isobaric Models Debye Einstein Ising Potts Potentials Internal energy Enthalpy Helmholtz free energy Gibbs free energy Grand potential / Landau free energy Scientists Maxwell Boltzmann Helmholtz Bose Gibbs Einstein Dirac Ehrenfest von Neumann Tolman Debye Fermi Synge Ising Landau vte Maxwell–Boltzmann statistics can be used to derive the Maxwell–Boltzmann distribution of particle speeds in an ideal gas. Shown: distribution of speeds for 106 oxygen molecules at -100, 20, and 600 °C. In statistical mechanics, Maxwell–Boltzmann statistics describes the distribution of classical material particles over various energy states in thermal equilibrium. It is applicable when the temperature is high enough or the particle density is low enough to render quantum effects negligible. The expected number of particles with energy ε i {\displaystyle \varepsilon _{i}} for Maxwell–Boltzmann statistics is ⟨ N i ⟩ = g i e (ε i − μ) / k T = N Z g i e − ε i / k T , {\displaystyle \langle N_{i}\rangle ={\frac {g_{i}}{e^{(\varepsilon _{i}-\mu)/kT}}}={\frac {N}{Z}}\,g_{i}e^{-\varepsilon _{i}/kT},} where: ε i {\displaystyle \varepsilon _{i}} is the energy of the i-th energy level, ⟨ N i ⟩ {\displaystyle \langle N_{i}\rangle } is the average number of particles in the set of states with energy ε i {\displaystyle \varepsilon _{i}} , g i {\displaystyle g_{i}} is the degeneracy of energy level i, that is, the number of states with energy ε i {\displaystyle \varepsilon _{i}} which may nevertheless be distinguished from each other by some other means,[nb 1] μ is the chemical potential, k is the Boltzmann constant, T is absolute temperature, N is the total number of particles: N = ∑ i N i , {\displaystyle N=\sum _{i}N_{i},} Z is the partition function: Z = ∑ i g i e − ε i / k T , {\displaystyle Z=\sum _{i}g_{i}e^{-\varepsilon _{i}/kT},} e is Euler's number Equivalently, the number of particles is sometimes expressed as ⟨ N i ⟩ = 1 e (ε i − μ) / k T = N Z e − ε i / k T , {\displaystyle \langle N_{i}\rangle ={\frac {1}{e^{(\varepsilon _{i}-\mu)/kT}}}={\frac {N}{Z}}\,e^{-\varepsilon _{i}/kT},} where the index i now specifies a particular state rather than the set of all states with energy ε i {\displaystyle \varepsilon _{i}} , and Z = ∑ i e − ε i / k T {\textstyle Z=\sum _{i}e^{-\varepsilon _{i}/kT}} . Further information: Maxwell–Boltzmann distribution Maxwell–Boltzmann statistics grew out of the Maxwell–Boltzmann distribution, most likely as a distillation of the underlying technique.[dubious – discuss] The distribution was first derived by Maxwell in 1860 on heuristic grounds. Boltzmann later, in the 1870s, carried out significant investigations into the physical origins of this distribution. The distribution can be derived on the ground that it maximizes the entropy of the system. Maxwell–Boltzmann distribution and Maxwell–Boltzmann statistics are closely related. Maxwell–Boltzmann statistics is a more general principle in statistical mechanics that describes the probability of a classical particle being in a particular energy state: P i = e − E i / k B T Z {\displaystyle P_{i}={\frac {e^{-E_{i}/k_{B}T}}{Z}}} where: Z {\displaystyle Z} is the partition function: Z = ∑ i e − E i / k B T {\displaystyle Z=\sum _{i}e^{-E_{i}/k_{B}T}} , E i {\displaystyle E_{i}} is the energy of state i {\displaystyle i} , k B {\displaystyle k_{B}} is Boltzmann's constant, T {\displaystyle T} is the absolute temperature. Maxwell–Boltzmann distribution is a specific application of Maxwell–Boltzmann statistics to the kinetic energies of gas particles. The distribution of velocities (or speeds) of particles in an ideal gas follows from the statistical assumption that the energy levels of a gas molecule are given by its kinetic energy: f (v) = (m 2 π k B T) 3 / 2 4 π v 2 e − m v 2 2 k B T {\displaystyle f(v)=\left({\frac {m}{2\pi k_{B}T}}\right)^{3/2}4\pi v^{2}e^{-{\frac {mv^{2}}{2k_{B}T}}}} where: f (v) {\displaystyle f(v)} is the probability density function of particle speeds, m {\displaystyle m} is the mass of a particle, k B {\displaystyle k_{B}} is Boltzmann's constant, T {\displaystyle T} is the absolute temperature, v {\displaystyle v} is the speed of the particle. We can deduce the Maxwell–Boltzmann distribution from Maxwell–Boltzmann statistics, starting with the Maxwell-Boltzmann probability for energy states and substituting the kinetic energy E = 1 2 m v 2 {\displaystyle E={\frac {1}{2}}mv^{2}} to express the probability in terms of velocity: P (E) = 1 Z exp (− E k B T) → P (v) = 1 Z exp (− m v 2 2 k B T) {\displaystyle {\begin{aligned}P(E)&={\frac {1}{Z}}~\exp \left({\frac {-E}{k_{B}T}}\right)\\\rightarrow P(v)&={\frac {1}{Z}}~\exp \left({\frac {-mv^{2}}{2k_{B}T}}\right)\end{aligned}}} In 3D, this is proportional to the surface area of a sphere, 4 π v 2 {\displaystyle 4\pi v^{2}} . Thus, the probability density function (PDF) for speed v {\displaystyle v} becomes: f (v) = C ⋅ 4 π v 2 exp (− m v 2 2 k B T) {\displaystyle f(v)=C\cdot 4\pi v^{2}\exp \left(-{\frac {mv^{2}}{2k_{B}T}}\right)} To find the normalization constant C {\displaystyle C} , we require the integral of the probability density function over all possible speeds to be unity: ∫ 0 ∞ f (v) d v = 1 → C ∫ 0 ∞ 4 π v 2 exp (− m v 2 2 k B T) d v = 1 {\displaystyle {\begin{aligned}\int _{0}^{\infty }f(v)dv&=1\\\rightarrow C\int _{0}^{\infty }4\pi v^{2}\exp \left(-{\frac {mv^{2}}{2k_{B}T}}\right)dv&=1\end{aligned}}} Evaluating the integral using the known result ∫ 0 ∞ v 2 e − a v 2 d v = π 4 a 3 / 2 {\displaystyle \int _{0}^{\infty }v^{2}e^{-av^{2}}dv={\frac {\sqrt {\pi }}{4a^{3/2}}}} , with a = m 2 k B T {\displaystyle a={\frac {m}{2k_{B}T}}} , we obtain: C ⋅ 4 π ⋅ π 4 (m 2 k B T) 3 / 2 = 1 → C = (m 2 π k B T) 3 / 2 {\displaystyle {\begin{aligned}C\cdot 4\pi \cdot {\frac {\sqrt {\pi }}{4\left({\frac {m}{2k_{B}T}}\right)^{3/2}}}=1\quad \rightarrow C=\left({\frac {m}{2\pi k_{B}T}}\right)^{3/2}\end{aligned}}} Therefore, the Maxwell–Boltzmann speed distribution is: f (v) = (m 2 π k B T) 3 / 2 4 π v 2 exp (− m v 2 2 k B T) {\displaystyle f(v)=\left({\frac {m}{2\pi k_{B}T}}\right)^{3/2}4\pi v^{2}\exp \left(-{\frac {mv^{2}}{2k_{B}T}}\right)} Equilibrium thermal distributions for particles with integer spin (bosons), half integer spin (fermions), and classical (spinless) particles. Average occupancy ⟨ n ⟩ {\displaystyle \langle n\rangle } is shown versus energy ϵ {\displaystyle \epsilon } relative to the system chemical potential μ {\displaystyle \mu } , where T {\displaystyle T} is the system temperature, and k B {\displaystyle k_{B}} is the Boltzmann constant. Maxwell–Boltzmann statistics is used to derive the Maxwell–Boltzmann distribution of an ideal gas. However, it can also be used to extend that distribution to particles with a different energy–momentum relation, such as relativistic particles (resulting in Maxwell–Jüttner distribution), and to other than three-dimensional spaces. Maxwell–Boltzmann statistics is often described as the statistics of "distinguishable" classical particles. In other words, the configuration of particle A in state 1 and particle B in state 2 is different from the case in which particle B is in state 1 and particle A is in state 2. This assumption leads to the proper (Boltzmann) statistics of particles in the energy states, but yields non-physical results for the entropy, as embodied in the Gibbs paradox. At the same time, there are no real particles that have the characteristics required by Maxwell–Boltzmann statistics. Indeed, the Gibbs paradox is resolved if we treat all particles of a certain type (e.g., electrons, protons, photons, etc.) as principally indistinguishable. Once this assumption is made, the particle statistics change. The change in entropy in the entropy of mixing example may be viewed as an example of a non-extensive entropy resulting from the distinguishability of the two types of particles being mixed. Quantum particles are either bosons (following Bose–Einstein statistics) or fermions (subject to the Pauli exclusion principle, following instead Fermi–Dirac statistics). Both of these quantum statistics approach the Maxwell–Boltzmann statistics in the limit of high temperature and low particle density. Maxwell–Boltzmann statistics can be derived in various statistical mechanical thermodynamic ensembles:[1] The grand canonical ensemble, exactly. The canonical ensemble, exactly. The microcanonical ensemble, but only in the thermodynamic limit. In each case it is necessary to assume that the particles are non-interacting, and that multiple particles can occupy the same state and do so independently. This section may be too technical for most readers to understand. Please help improve it to make it understandable to non-experts, without removing the technical details. (December 2013) (Learn how and when to remove this message) Suppose we have a container with a huge number of very small particles all with identical physical characteristics (such as mass, charge, etc.). Let's refer to this as the system. Assume that though the particles have identical properties, they are distinguishable. For example, we might identify each particle by continually observing their trajectories, or by placing a marking on each one, e.g., drawing a different number on each one as is done with lottery balls. The particles are moving inside that container in all directions with great speed. Because the particles are speeding around, they possess some energy. The Maxwell–Boltzmann distribution is a mathematical function that describes about how many particles in the container have a certain energy. More precisely, the Maxwell–Boltzmann distribution gives the non-normalized probability (this means that the probabilities do not add up to 1) that the state corresponding to a particular energy is occupied. In general, there may be many particles with the same amount of energy ε {\displaystyle \varepsilon } . Let the number of particles with the same energy ε 1 {\displaystyle \varepsilon _{1}} be N 1 {\displaystyle N_{1}} , the number of particles possessing another energy ε 2 {\displaystyle \varepsilon _{2}} be N 2 {\displaystyle N_{2}} , and so forth for all the possible energies { ε i | i = 1 , 2 , 3 , … } . {\displaystyle \{\varepsilon _{i}\mid i=1,2,3,\ldots \}.} To describe this situation, we say that N i {\displaystyle N_{i}} is the occupation number of the energy level i . {\displaystyle i.} If we know all the occupation numbers { N i | i = 1 , 2 , 3 , … } , {\displaystyle \{N_{i}\mid i=1,2,3,\ldots \},} then we know the total energy of the system. However, because we can distinguish between which particles are occupying each energy level, the set of occupation numbers { N i | i = 1 , 2 , 3 , … } {\displaystyle \{N_{i}\mid i=1,2,3,\ldots \}} does not completely describe the state of the system. To completely describe the state of the system, or the microstate, we must specify exactly which particles are in each energy level. Thus when we count the number of possible states of the system, we must count each and every microstate, and not just the possible sets of occupation numbers. To begin with, assume that there is only one state at each energy level i {\displaystyle i} (there is no degeneracy). What follows next is a bit of combinatorial thinking which has little to do in accurately describing the reservoir of particles. For instance, let's say there is a total of k {\displaystyle k} boxes labelled a , b , … , k {\displaystyle a,b,\ldots ,k} . With the concept of combination, we could calculate how many ways there are to arrange N {\displaystyle N} into the set of boxes, where the order of balls within each box isn’t tracked. First, we select N a {\displaystyle N_{a}} balls from a total of N {\displaystyle N} balls to place into box a {\displaystyle a} , and continue to select for each box from the remaining balls, ensuring that every ball is placed in one of the boxes. The total number of ways that the balls can be arranged is W = N ! N a ! (N − N a) ! × (N − N a) ! N b ! (N − N a − N b) ! × (N − N a − N b) ! N c ! (N − N a − N b − N c) ! × ⋯ × (N − ⋯ − N ℓ) ! N k ! (N − ⋯ − N ℓ − N k) ! = N ! N a ! N b ! N c ! ⋯ N k ! (N − N a − ⋯ − N ℓ − N k) ! {\displaystyle {\begin{aligned}W&={\frac {N!}{N_{a}!{\cancel {(N-N_{a})!}}}}\times {\frac {\cancel {(N-N_{a})!}}{N_{b}!{\cancel {(N-N_{a}-N_{b})!}}}}\times {\frac {\cancel {(N-N_{a}-N_{b})!}}{N_{c}!{\cancel {(N-N_{a}-N_{b}-N_{c})!}}}}\times \cdots \times {\frac {\cancel {(N-\cdots -N_{\ell })!}}{N_{k}!(N-\cdots -N_{\ell }-N_{k})!}}\\[8pt]&={\frac {N!}{N_{a}!N_{b}!N_{c}!\cdots N_{k}!(N-N_{a}-\cdots -N_{\ell }-N_{k})!}}\end{aligned}}} As every ball has been placed into a box, (N − N a − N b − ⋯ − N k) ! = 0 ! = 1 {\displaystyle (N-N_{a}-N_{b}-\cdots -N_{k})!=0!=1} , and we simplify the expression as W = N ! ∏ ℓ = a , b , … k 1 N ℓ ! {\displaystyle W=N!\prod _{\ell =a,b,\ldots }^{k}{\frac {1}{N_{\ell }!}}} This is just the multinomial coefficient, the number of ways of arranging N items into k boxes, the l-th box holding Nl items, ignoring the permutation of items in each box. Now, consider the case where there is more than one way to put N i {\displaystyle N_{i}} particles in the box i {\displaystyle i} (i.e. taking the degeneracy problem into consideration). If the i {\displaystyle i} -th box has a "degeneracy" of g i {\displaystyle g_{i}} , that is, it has g i {\displaystyle g_{i}} "sub-boxes" (g i {\displaystyle g_{i}} boxes with the same energy ε i {\displaystyle \varepsilon _{i}} . These states/boxes with the same energy are called degenerate states.), such that any way of filling the i {\displaystyle i} -th box where the number in the sub-boxes is changed is a distinct way of filling the box, then the number of ways of filling the i-th box must be increased by the number of ways of distributing the N i {\displaystyle N_{i}} objects in the g i {\displaystyle g_{i}} "sub-boxes". The number of ways of placing N i {\displaystyle N_{i}} distinguishable objects in g i {\displaystyle g_{i}} "sub-boxes" is g i N i {\displaystyle g_{i}^{N_{i}}} (the first object can go into any of the g i {\displaystyle g_{i}} boxes, the second object can also go into any of the g i {\displaystyle g_{i}} boxes, and so on). Thus the number of ways W {\displaystyle W} that a total of N {\displaystyle N} particles can be classified into energy levels according to their energies, while each level i {\displaystyle i} having g i {\displaystyle g_{i}} distinct states such that the i-th level accommodates N i {\displaystyle N_{i}} particles is: W = N ! ∏ i g i N i N i ! {\displaystyle W=N!\prod _{i}{\frac {g_{i}^{N_{i}}}{N_{i}!}}} This is the form for W first derived by Boltzmann. Boltzmann's fundamental equation S = k ln W {\displaystyle S=k\,\ln W} relates the thermodynamic entropy S to the number of microstates W, where k is the Boltzmann constant. It was pointed out by Gibbs however, that the above expression for W does not yield an extensive entropy, and is therefore faulty. This problem is known as the Gibbs paradox. The problem is that the particles considered by the above equation are not indistinguishable. In other words, for two particles (A and B) in two energy sublevels the population represented by [A,B] is considered distinct from the population [B,A] while for indistinguishable particles, they are not. If we carry out the argument for indistinguishable particles, we are led to the Bose–Einstein expression for W: W = ∏ i (N i + g i − 1) ! N i ! (g i − 1) ! {\displaystyle W=\prod _{i}{\frac {(N_{i}+g_{i}-1)!}{N_{i}!(g_{i}-1)!}}} The Maxwell–Boltzmann distribution follows from this Bose–Einstein distribution for temperatures well above absolute zero, implying that g i ≫ 1 {\displaystyle g_{i}\gg 1} . The Maxwell–Boltzmann distribution also requires low density, implying that g i ≫ N i {\displaystyle g_{i}\gg N_{i}} . Under these conditions, we may use Stirling's approximation for the factorial: N ! ≈ N N e − N , {\displaystyle N!\approx N^{N}e^{-N},} to write: W ≈ ∏ i (N i + g i) N i + g i N i N i g i g i ≈ ∏ i g i N i (1 + N i / g i) g i N i N i {\displaystyle W\approx \prod _{i}{\frac {(N_{i}+g_{i})^{N_{i}+g_{i}}}{N_{i}^{N_{i}}g_{i}^{g_{i}}}}\approx \prod _{i}{\frac {g_{i}^{N_{i}}(1+N_{i}/g_{i})^{g_{i}}}{N_{i}^{N_{i}}}}} Using the fact that (1 + N i / g i) g i ≈ e N i {\displaystyle (1+N_{i}/g_{i})^{g_{i}}\approx e^{N_{i}}} for g i ≫ N i {\displaystyle g_{i}\gg N_{i}} we can again use Stirling's approximation to write: W ≈ ∏ i g i N i N i ! {\displaystyle W\approx \prod _{i}{\frac {g_{i}^{N_{i}}}{N_{i}!}}} This is essentially a division by N! of Boltzmann's original expression for W, and this correction is referred to as correct Boltzmann counting. We wish to find the N i {\displaystyle N_{i}} for which the function W {\displaystyle W} is maximized, while considering the constraint that there is a fixed number of particles (N = ∑ N i) {\textstyle \left(N=\sum N_{i}\right)} and a fixed energy (E = ∑ N i ε i) {\textstyle \left(E=\sum N_{i}\varepsilon _{i}\right)} in the container. The maxima of W {\displaystyle W} and ln (W) {\displaystyle \ln(W)} are achieved by the same values of N i {\displaystyle N_{i}} and, since it is easier to accomplish mathematically, we will maximize the latter function instead. We constrain our solution using Lagrange multipliers forming the function: f (N 1 , N 2 , … , N n) = ln (W) + α (N − ∑ N i) + β (E − ∑ N i ε i) {\displaystyle f(N_{1},N_{2},\ldots ,N_{n})=\textstyle \ln(W)+\alpha (N-\sum N_{i})+\beta (E-\sum N_{i}\varepsilon _{i})} ln W = ln [∏ i = 1 n g i N i N i !] ≈ ∑ i = 1 n (N i ln g i − N i ln N i + N i) {\displaystyle \ln W=\ln \left[\prod _{i=1}^{n}{\frac {g_{i}^{N_{i}}}{N_{i}!}}\right]\approx \sum _{i=1}^{n}\left(N_{i}\ln g_{i}-N_{i}\ln N_{i}+N_{i}\right)} Finally f (N 1 , N 2 , … , N n) = α N + β E + ∑ i = 1 n (N i ln g i − N i ln N i + N i − (α + β ε i) N i) {\displaystyle f(N_{1},N_{2},\ldots ,N_{n})=\alpha N+\beta E+\sum _{i=1}^{n}\left(N_{i}\ln g_{i}-N_{i}\ln N_{i}+N_{i}-(\alpha +\beta \varepsilon _{i})N_{i}\right)} In order to maximize the expression above we apply Fermat's theorem (stationary points), according to which local extrema, if exist, must be at critical points (partial derivatives vanish): ∂ f ∂ N i = ln g i − ln N i − (α + β ε i) = 0 {\displaystyle {\frac {\partial f}{\partial N_{i}}}=\ln g_{i}-\ln N_{i}-(\alpha +\beta \varepsilon _{i})=0} By solving the equations above (i = 1 … n {\displaystyle i=1\ldots n}) we arrive to an expression for N i {\displaystyle N_{i}} : N i = g i e α + β ε i {\displaystyle N_{i}={\frac {g_{i}}{e^{\alpha +\beta \varepsilon _{i}}}}} Substituting this expression for N i {\displaystyle N_{i}} into the equation for ln W {\displaystyle \ln W} and assuming that N ≫ 1 {\displaystyle N\gg 1} yields: ln W = (α + 1) N + β E {\displaystyle \ln W=(\alpha +1)N+\beta E\,} or, rearranging: E = ln W β − N β − α N β {\displaystyle E={\frac {\ln W}{\beta }}-{\frac {N}{\beta }}-{\frac {\alpha N}{\beta }}} Boltzmann realized that this is just an expression of the Euler-integrated fundamental equation of thermodynamics. Identifying E as the internal energy, the Euler-integrated fundamental equation states that : E = T S − P V + μ N {\displaystyle E=TS-PV+\mu N} where T is the temperature, P is pressure, V is volume, and μ is the chemical potential. Boltzmann's equation S = k ln W {\displaystyle S=k\ln W} is the realization that the entropy is proportional to ln W {\displaystyle \ln W} with the constant of proportionality being the Boltzmann constant. Using the ideal gas equation of state (PV = NkT), It follows immediately that β = 1 / k T {\displaystyle \beta =1/kT} and α = − μ / k T {\displaystyle \alpha =-\mu /kT} so that the populations may now be written: N i = g i e (ε i − μ) / (k T) {\displaystyle N_{i}={\frac {g_{i}}{e^{(\varepsilon _{i}-\mu)/(kT)}}}} Note that the above formula is sometimes written: N i = g i e ε i / k T / z {\displaystyle N_{i}={\frac {g_{i}}{e^{\varepsilon _{i}/kT}/z}}} where z = exp (μ / k T) {\displaystyle z=\exp(\mu /kT)} is the absolute activity. Alternatively, we may use the fact that ∑ i N i = N {\displaystyle \sum _{i}N_{i}=N} to obtain the population numbers as N i = N g i e − ε i / k T Z {\displaystyle N_{i}=N{\frac {g_{i}e^{-\varepsilon _{i}/kT}}{Z}}} where Z is the partition function defined by: Z = ∑ i g i e − ε i / k T {\displaystyle Z=\sum _{i}g_{i}e^{-\varepsilon _{i}/kT}} In an approximation where εi is considered to be a continuous variable, the Thomas–Fermi approximation yields a continuous degeneracy g proportional to ε {\displaystyle {\sqrt {\varepsilon }}} so that: ε e − ε / k T ∫ 0 ∞ ε e − ε / k T = ε e − ε / k T π 2 (k T) 3 / 2 = 2 ε e − ε / k T π (k T) 3 {\displaystyle {\frac {{\sqrt {\varepsilon }}\,e^{-\varepsilon /kT}}{\int _{0}^{\infty }{\sqrt {\varepsilon }}\,e^{-\varepsilon /kT}}}={\frac {{\sqrt {\varepsilon }}\,e^{-\varepsilon /kT}}{{\frac {\sqrt {\pi }}{2}}(kT)^{3/2}}}={\frac {2{\sqrt {\varepsilon }}\,e^{-\varepsilon /kT}}{\sqrt {\pi (kT)^{3}}}}} which is just the Maxwell–Boltzmann distribution for the energy. This section may be too technical for most readers to understand. Please help improve it to make it understandable to non-experts, without removing the technical details. (December 2013) (Learn how and when to remove this message) In the above discussion, the Boltzmann distribution function was obtained via directly analysing the multiplicities of a system. Alternatively, one can make use of the canonical ensemble. In a canonical ensemble, a system is in thermal contact with a reservoir. While energy is free to flow between the system and the reservoir, the reservoir is thought to have infinitely large heat capacity as to maintain constant temperature, T, for the combined system. In the present context, our system is assumed to have the energy levels ε i {\displaystyle \varepsilon _{i}} with degeneracies g i {\displaystyle g_{i}} . As before, we would like to calculate the probability that our system has energy ε i {\displaystyle \varepsilon _{i}} . If our system is in state s 1 {\displaystyle \;s_{1}} , then there would be a corresponding number of microstates available to the reservoir. Call this number Ω R (s 1) {\displaystyle \;\Omega _{R}(s_{1})} . By assumption, the combined system (of the system we are interested in and the reservoir) is isolated, so all microstates are equally probable. Therefore, for instance, if Ω R (s 1) = 2 Ω R (s 2) {\displaystyle \;\Omega _{R}(s_{1})=2\;\Omega _{R}(s_{2})} , we can conclude that our system is twice as likely to be in state s 1 {\displaystyle \;s_{1}} than s 2 {\displaystyle \;s_{2}} . In general, if P (s i) {\displaystyle \;P(s_{i})} is the probability that our system is in state s i {\displaystyle \;s_{i}} , P (s 1) P (s 2) = Ω R (s 1) Ω R (s 2) . {\displaystyle {\frac {P(s_{1})}{P(s_{2})}}={\frac {\Omega _{R}(s_{1})}{\Omega _{R}(s_{2})}}.} Since the entropy of the reservoir S R = k ln Ω R {\displaystyle \;S_{R}=k\ln \Omega _{R}} , the above becomes P (s 1) P (s 2) = e S R (s 1) / k e S R (s 2) / k = e (S R (s 1) − S R (s 2)) / k . {\displaystyle {\frac {P(s_{1})}{P(s_{2})}}={\frac {e^{S_{R}(s_{1})/k}}{e^{S_{R}(s_{2})/k}}}=e^{(S_{R}(s_{1})-S_{R}(s_{2}))/k}.} Next we recall the thermodynamic identity (from the first law of thermodynamics): d S R = 1 T (d U R + P d V R − μ d N R) . {\displaystyle dS_{R}={\frac {1}{T}}(dU_{R}+P\,dV_{R}-\mu \,dN_{R}).} In a canonical ensemble, there is no exchange of particles, so the d N R {\displaystyle dN_{R}} term is zero. Similarly, d V R = 0. {\displaystyle dV_{R}=0.} This gives S R (s 1) − S R (s 2) = 1 T (U R (s 1) − U R (s 2)) = − 1 T (E (s 1) − E (s 2)) , {\displaystyle S_{R}(s_{1})-S_{R}(s_{2})={\frac {1}{T}}(U_{R}(s_{1})-U_{R}(s_{2}))=-{\frac {1}{T}}(E(s_{1})-E(s_{2})),} where U R (s i) {\displaystyle U_{R}(s_{i})} and E (s i) {\displaystyle E(s_{i})} denote the energies of the reservoir and the system at s i {\displaystyle s_{i}} , respectively. For the second equality we have used the conservation of energy. Substituting into the first equation relating P (s 1) , P (s 2) {\displaystyle P(s_{1}),\;P(s_{2})} : P (s 1) P (s 2) = e − E (s 1) / k T e − E (s 2) / k T , {\displaystyle {\frac {P(s_{1})}{P(s_{2})}}={\frac {e^{-E(s_{1})/kT}}{e^{-E(s_{2})/kT}}},} which implies, for any state s of the system P (s) = 1 Z e − E (s) / k T , {\displaystyle P(s)={\frac {1}{Z}}e^{-E(s)/kT},} where Z is an appropriately chosen "constant" to make total probability 1. (Z is constant provided that the temperature T is invariant.) Z = ∑ s e − E (s) / k T , {\displaystyle Z=\sum _{s}e^{-E(s)/kT},} where the index s runs through all microstates of the system. Z is sometimes called the Boltzmann sum over states (or "Zustandssumme" in the original German). If we index the summation via the energy eigenvalues instead of all possible states, degeneracy must be taken into account. The probability of our system having energy ε i {\displaystyle \varepsilon _{i}} is simply the sum of the probabilities of all corresponding microstates: P (ε i) = 1 Z g i e − ε i / k T {\displaystyle P(\varepsilon _{i})={\frac {1}{Z}}g_{i}e^{-\varepsilon _{i}/kT}} where, with obvious modification, Z = ∑ j g j e − ε j / k T , {\displaystyle Z=\sum _{j}g_{j}e^{-\varepsilon _{j}/kT},} this is the same result as before. Comments on this derivation: Notice that in this formulation, the initial assumption "... suppose the system has total N particles..." is dispensed with. Indeed, the number of particles possessed by the system plays no role in arriving at the distribution. Rather, how many particles would occupy states with energy ε i {\displaystyle \varepsilon _{i}} follows as an easy consequence. What has been presented above is essentially a derivation of the canonical partition function. As one can see by comparing the definitions, the Boltzmann sum over states is equal to the canonical partition function. Exactly the same approach can be used to derive Fermi–Dirac and Bose–Einstein statistics. However, there one would replace the canonical ensemble with the grand canonical ensemble, since there is exchange of particles between the system and the reservoir. Also, the system one considers in those cases is a single particle state, not a particle. (In the above discussion, we could have assumed our system to be a single atom.) The Maxwell-Boltzmann distribution describes the probability of a particle occupying an energy state E in a classical system. It takes the following form: f MB,high (E) = exp (− E − E F k T) , for E ≫ E F f MB,low (E) = 1 − exp (E − E F k T) , for E ≪ E F {\displaystyle {\begin{aligned}f_{\text{MB,high}}(E)&=\exp \left(-{\frac {E-E_{F}}{kT}}\right),&{\text{for }}E\gg E_{F}\\f_{\text{MB,low}}(E)&=1-\exp \left({\frac {E-E_{F}}{kT}}\right),&{\text{for }}E\ll E_{F}\end{aligned}}} For a system of indistinguishable particles, we start with the canonical ensemble formalism. In a system with energy levels { E i } {\displaystyle \{E_{i}\}} , let n i {\displaystyle n_{i}} be the number of particles in state i. The total energy and particle number are: E total = ∑ i n i E i N = ∑ i n i {\displaystyle {\begin{aligned}E_{\text{total}}&=\sum _{i}n_{i}E_{i}\\N&=\sum _{i}n_{i}\end{aligned}}} For a specific configuration { n i } {\displaystyle \{n_{i}\}} , the probability in the canonical ensemble is: P ({ n i }) = 1 Z N N ! ∏ i n i ! ∏ i (e − β E i) n i {\displaystyle P(\{n_{i}\})={\frac {1}{Z_{N}}}{\frac {N!}{\prod _{i}n_{i}!}}\prod _{i}(e^{-\beta E_{i}})^{n_{i}}} The factor N ! ∏ i n i ! {\displaystyle {\frac {N!}{\prod _{i}n_{i}!}}} accounts for the number of ways to distribute N indistinguishable particles among the states. For Maxwell-Boltzmann statistics, we assume that the average occupation number of any state is much less than 1 (⟨ n i ⟩ ≪ 1 {\displaystyle \langle n_{i}\rangle \ll 1}), which leads to: ⟨ n i ⟩ ≈ e − β (E i − μ) {\displaystyle \langle n_{i}\rangle \approx e^{-\beta (E_{i}-\mu)}} where μ {\displaystyle \mu } is the chemical potential determined by ∑ i ⟨ n i ⟩ = N {\displaystyle \sum _{i}\langle n_{i}\rangle =N} . For energy states near the Fermi energy E F {\displaystyle E_{F}} , we can express μ ≈ E F {\displaystyle \mu \approx E_{F}} , giving: f MB (E) = e − (E − E F) / k T {\displaystyle f_{\text{MB}}(E)=e^{-(E-E_{F})/kT}} For high energies (E ≫ E F {\displaystyle E\gg E_{F}}), this directly gives: f MB,high (E) = e − (E − E F) / k T {\displaystyle f_{\text{MB,high}}(E)=e^{-(E-E_{F})/kT}} For low energies (E ≪ E F {\displaystyle E\ll E_{F}}), using the approximation e − x ≈ 1 − x {\displaystyle e^{-x}\approx 1-x} for small x: f MB,low (E) ≈ 1 − e (E − E F) / k T {\displaystyle f_{\text{MB,low}}(E)\approx 1-e^{(E-E_{F})/kT}} This is the derivation of the Maxwell-Boltzmann distribution in both energy regimes. Bose–Einstein statistics Fermi–Dirac statistics Boltzmann factor ^ For example, two simple point particles may have the same energy, but different momentum vectors. They may be distinguished from each other on this basis, and the degeneracy will be the number of possible ways that they can be so distinguished. ^ Tolman, R. C. (1938). The Principles of Statistical Mechanics. Dover Publications.

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