

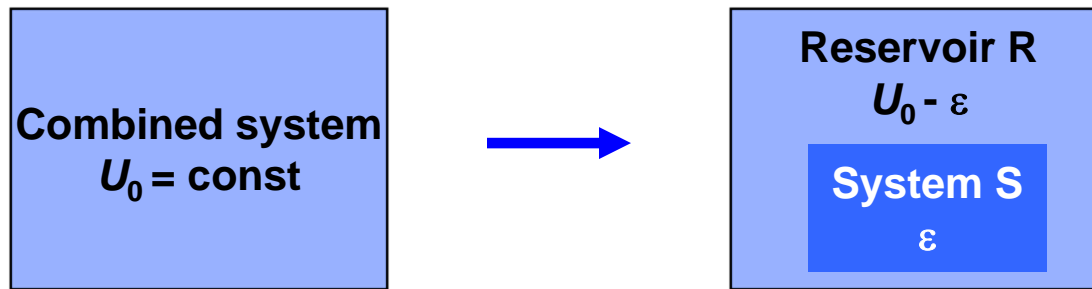
Lecture 19. Boltzmann Statistics (Ch. 6)

We have followed the following logic:

1. Statistical treatment of isolated systems: multiplicity \Rightarrow entropy \Rightarrow the 2nd Law.
2. Thermodynamic treatment of systems in contact with the heat reservoir \Rightarrow the minimum free energy principle. However, the link between **G** and the process of counting of accessible microstates was not straightforward.

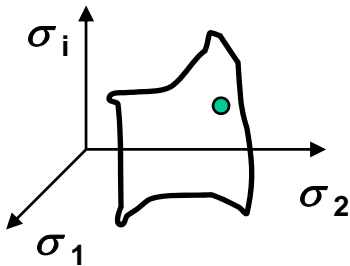
Now we want to learn how to “statistically” treat a system in contact with a heat bath.

The fundamental assumption states that a closed (isolated) system visits every one of its microstates with equal frequency: all allowed states of the system are equally probable. This statement applies to the combined system (the system of interest + the reservoir). ***We wish to translate this statement into a statement that applies to the system of interest only.*** Thus, the question: ***how often does the system visit each of its microstates being in the thermal equilibrium with the reservoir?*** The only information we have about the reservoir is that it is at the temperature ***T***.



a combined (isolated) system = a heat reservoir and a system in thermal contact

The Fundamental Assumption for an Isolated System



Isolated \Rightarrow the energy is conserved. The ensemble of all equi-energetic states \Rightarrow **a microcanonical ensemble**

The ergodic hypothesis: an isolated system in thermal equilibrium, evolving in time, will pass through all the **accessible** microstates at the same recurrence rate, i.e. **all accessible microstates are equally probable**.

The average over long times will equal the average over the ensemble of all equi-energetic microstates: if we take a snapshot of a system with N microstates, we will find the system in **any** of these microstates with the **same** probability.

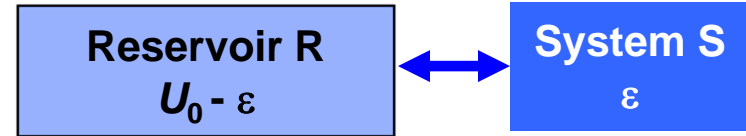
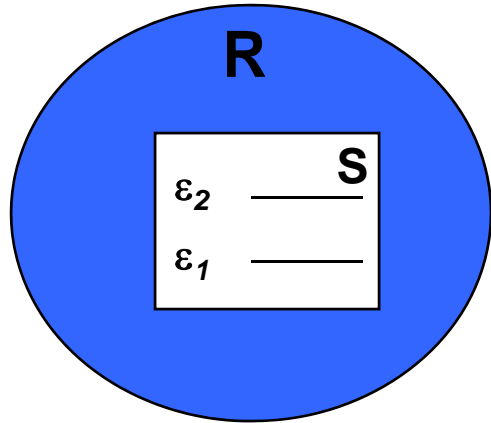
$$\begin{aligned} &\text{Probability of a particular microstate of a microcanonical ensemble} \\ &= 1 / (\# \text{ of all accessible microstates}) \end{aligned}$$

The probability of a certain **macrostate** is determined by how many microstates correspond to this macrostate – **the multiplicity of a given macrostate** Ω

$$\begin{aligned} &\text{Probability of a particular macrostate} \\ &= (\Omega \text{ of a particular macrostate}) / (\# \text{ of all accessible microstates}) \end{aligned}$$

Note that the assumption that a system is **isolated** is important. If a system is **coupled** to a heat reservoir and is able to exchange energy, in order to replace the system's trajectory by an ensemble, we must determine the relative occurrence of states with **different** energies.

Systems in Contact with the Reservoir



The system – any ***small macroscopic*** or ***microscopic*** object. If the interactions between the system and the reservoir are weak, we can assume that the spectrum of energy levels of a weakly-interacting system is the same as that for an isolated system.

Example: a two-level system in thermal contact with a heat bath.

We ask the following question: ***under conditions of equilibrium between the system and reservoir***, what is the probability $P(\epsilon_k)$ of finding the system **S** in a particular quantum state **k** of energy ϵ_k ? We assume weak interaction between **R** and **S** so that their energies are additive. The energy conservation in the isolated system “system+reservoir”:

$$U_0 = U_R + U_S = \text{const}$$

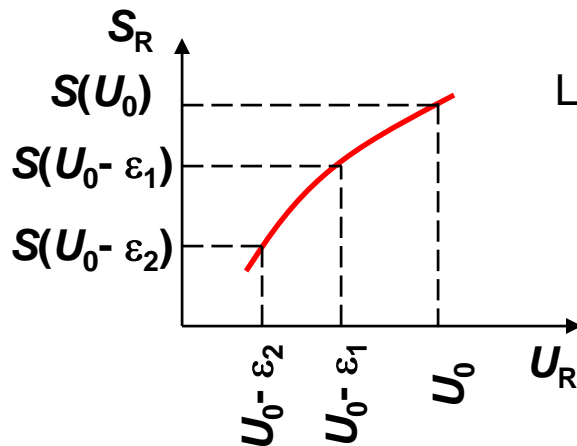
According to the fundamental assumption of thermodynamics, all the states of the combined (***isolated***) system “**R+S**” are ***equally probable***. By specifying the ***microstate*** of the system **k**, we have reduced Ω_S to 1 and S_S to 0. Thus, the probability of occurrence of a situation where the system is in state **k** is proportional to the number of states accessible to **the reservoir R**. The total multiplicity:

$$\Omega(\epsilon_k, U_0 - \epsilon_k) = \Omega_S(\epsilon_k) \times \Omega_R(U_0 - \epsilon_k) = 1 \times \Omega_R(U_0 - \epsilon_k) = \Omega_R(U_0 - \epsilon_k)$$

Systems in Contact with the Reservoir (cont.)

The ratio of the probability that the system is in quantum state 1 at energy ε_1 to the probability that the system is in quantum state 2 at energy ε_2 is:

$$\frac{P_S(\varepsilon_1)}{P_S(\varepsilon_2)} = \frac{\Omega_R(U_0 - \varepsilon_1)}{\Omega_R(U_0 - \varepsilon_2)} = \frac{\exp[S_R(U_0 - \varepsilon_1)/k_B]}{\exp[S_R(U_0 - \varepsilon_2)/k_B]} = \exp\left[\frac{S_R(U_0 - \varepsilon_1) - S_R(U_0 - \varepsilon_2)}{k_B}\right] = \exp\left(\frac{\Delta S_R}{k_B}\right)$$



Let's now use the fact that \mathbf{S} is much smaller than \mathbf{R} ($U_S = \varepsilon_k \ll U_R$).

Also, we'll consider the case of fixed volume and number of particles (the latter limitation will be removed later, when we'll allow the system to exchange particles with the heat bath)

$$dS_R = \frac{1}{T_R} (dU_R + P dV_R - \mu dN_R)$$

\swarrow \searrow
 0

(Pr. 6.9 addresses the case when the 2nd is not negligible)

$$S_R(U) \approx S_R(U_0) + \left[\frac{\partial S_R}{\partial U_R}(U_0) \right]_{V,N} (U - U_0)$$

$$S_R(U_0 - \varepsilon_i) \approx S_R(U_0) - \varepsilon_i \left[\frac{dS_R}{dU_R}(U_0) \right]_{V,N}$$

$$\Delta S_R = \left(\frac{\partial S_R}{\partial U_R}(U_0) \right)_{V,N} \varepsilon_2 - \left(\frac{\partial S_R}{\partial U_R}(U_0) \right)_{V,N} \varepsilon_1 = \left[\left(\frac{\partial S_R}{\partial U_R}(U_0) \right)_{V,N} \right] = \frac{1}{T_R} = -\frac{\varepsilon_1 - \varepsilon_2}{T_R}$$

Boltzmann Factor

$$\frac{P_S(\varepsilon_1)}{P_S(\varepsilon_2)} = \exp\left(\frac{\Delta S_R}{k_B}\right) = \exp\left(-\frac{\varepsilon_1 - \varepsilon_2}{k_B T}\right)$$

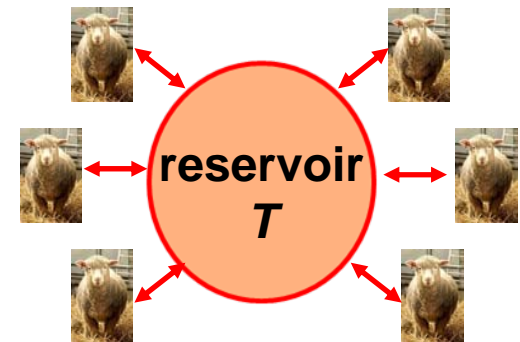
T is the characteristic of the **heat reservoir**

$\exp(-\varepsilon_k/k_B T)$ is called the **Boltzmann factor**

$$\frac{P_S(\varepsilon_1)}{P_S(\varepsilon_2)} = \frac{\exp\left(-\frac{\varepsilon_1}{k_B T}\right)}{\exp\left(-\frac{\varepsilon_2}{k_B T}\right)}$$

This result shows that we do not have to know anything about the reservoir except that it maintains a constant temperature T !

The corresponding probability distribution is known as the **canonical distribution**. An ensemble of identical systems all of which are in contact with the same heat reservoir and distributed over states in accordance with the Boltzmann distribution is called a **canonical ensemble**.



The fundamental assumption for an isolated system has been transformed into the following statement for the system of interest which is in thermal equilibrium with the thermal reservoir: **the system visits each microstate with a frequency proportional to the Boltzmann factor**.

Apparently, this is what the system actually does, but from the macroscopic point of view of thermodynamics, it appears as if the system is trying to minimize its free energy. Or conversely, this is what the system has to do in order to minimize its free energy.

One of the most useful equations in TD+SP...

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \exp\left(\frac{\Delta S_R}{k_B}\right) = \exp\left(-\frac{\varepsilon_1 - \varepsilon_2}{k_B T}\right)$$

Firstly, notice that only the energy difference $\Delta\varepsilon = \varepsilon_i - \varepsilon_j$ comes into the result so that provided that both energies are measured from the same origin it does not matter what that origin is.

Secondly, what matters in determining the ratio of the occupation numbers is the ratio of the energy difference $\Delta\varepsilon$ to $k_B T$. Suppose that $\varepsilon_i = k_B T$ and $\varepsilon_j = 10k_B T$. Then $(\varepsilon_i - \varepsilon_j) / k_B T = -9$, and

$$\frac{P(\varepsilon_i)}{P(\varepsilon_j)} = e^9 \approx 8000$$

The lowest energy level ε_0 available to a system (e.g., a molecule) is referred to as the “ground state”. If we measure all energies relative to ε_0 and n_0 is the number of molecules in this state, then the number of molecules with energy $\varepsilon > \varepsilon_0$

$$\frac{n(\varepsilon)}{n_0} = \exp\left(-\frac{\varepsilon}{k_B T}\right)$$

Problem 6.13. At very high temperature (as in the very early universe), the proton and the neutron can be thought of as two different states of the same particle, called the “nucleon”. Since the neutron’s mass is higher than the proton’s by $\Delta m = 2.3 \cdot 10^{-30}$ kg, its energy is higher by Δmc^2 . What was the ratio of the number of protons to the number of neutrons at $T = 10^{11}$ K?

$$\frac{P(n)}{P(p)} = \frac{\exp\left(-\frac{m_n c^2}{k_B T}\right)}{\exp\left(-\frac{m_p c^2}{k_B T}\right)} = \exp\left(-\frac{\Delta mc^2}{k_B T}\right) = \exp\left(-\frac{2.3 \cdot 10^{-30} \text{ kg} \times (3 \cdot 10^8 \text{ m/s})^2}{1.38 \cdot 10^{-23} \text{ J/K} \times 10^{11} \text{ K}}\right) = 0.86$$

More problems

Problem 6.14. Use Boltzmann factors to derive the exponential formula for the density of an isothermal atmosphere.

The system is a single air molecule, with two states: 1 at the sea level ($\mathbf{z} = \mathbf{0}$), 2 – at a height \mathbf{z} . The energies of these two states differ only by the potential energy \mathbf{mgz} (the temperature \mathbf{T} does not vary with \mathbf{z}):

$$\frac{P(\varepsilon_2)}{P(\varepsilon_1)} = \frac{\exp\left(-\frac{\varepsilon_2}{k_B T}\right)}{\exp\left(-\frac{\varepsilon_1}{k_B T}\right)} = \frac{\exp\left(-\frac{\varepsilon_1 + mgz}{k_B T}\right)}{\exp\left(-\frac{\varepsilon_1}{k_B T}\right)} = \exp\left(-\frac{mgz}{k_B T}\right) \quad \rho(z) = \rho_0 \exp\left(-\frac{mgz}{k_B T}\right)$$

At home:

A system of particles are placed in a uniform field at $\mathbf{T}=280\text{K}$. The particle concentrations measured at two points along the field line 3 cm apart differ by a factor of 2. Find the force \mathbf{F} acting on the particles.

Answer: $\mathbf{F} = 0.9 \cdot 10^{-19} \text{ N}$

A mixture of two gases with the molecular masses $\mathbf{m_1}$ and $\mathbf{m_2}$ ($\mathbf{m_2} > \mathbf{m_1}$) is placed in a very tall container. The container is in a uniform gravitational field, the acceleration of free fall, \mathbf{g} , is given. Near the bottom of the container, the concentrations of these two types of molecules are $\mathbf{n_1}$ and $\mathbf{n_2}$ respectively ($\mathbf{n_2} > \mathbf{n_1}$) . Find the height from the bottom where these two concentrations become equal.

Answer:
$$h = \frac{k_B T \ln(n_2 / n_1)}{(m_2 - m_1)g}$$

The Partition Function

For the absolute values of probability (rather than the ratio of probabilities), we need an explicit formula for the normalizing factor $1/Z$:

$$P(\varepsilon_i) = \frac{1}{Z} \exp\left(-\frac{\varepsilon_i}{k_B T}\right) = \frac{1}{Z} \exp(-\beta \varepsilon_i)$$

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

- we will often use this notation

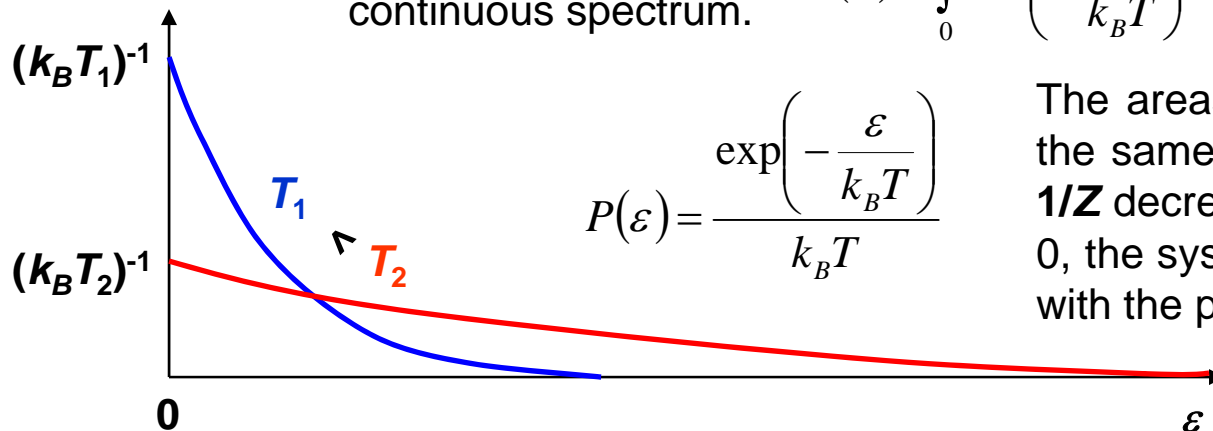
The quantity **Z , the partition function**, can be found from the **normalization condition** - the total probability to find the system in **all** allowed quantum states is 1:

$$1 = \sum_i P(\varepsilon_i) = \sum_i \frac{1}{Z} \exp(-\beta \varepsilon_i) \quad \text{or} \quad Z(T, V, N) = \sum_i \exp(-\beta \varepsilon_i) \quad \text{The } Z_{ustands\textit{summe}} \text{ in German}$$

The partition function **Z** is called “function” because it depends on **T** , the spectrum (thus, **V**), etc.

Example: a single particle, continuous spectrum.

$$Z(T) = \int_0^{\infty} \exp\left(-\frac{\varepsilon}{k_B T}\right) d\varepsilon = k_B T \int_0^{\infty} \exp(-x) dx = k_B T$$



The areas under these curves must be the same (=1). Thus, with increasing **T** , **$1/Z$** decreases, and **Z** increases. At **$T = 0$** , the system is in its ground state ($\varepsilon=0$) with the probability =1.

Average Values in a Canonical Ensemble

We have developed the tools that permit us to calculate the **average value** of different physical quantities for a canonical ensemble of identical systems. In general, if the systems in an ensemble are distributed over their accessible states in accordance with the distribution $P(\varepsilon_i)$, the **average value** of some quantity $x(\varepsilon_i)$ can be found as:

$$\bar{x} = \langle x(\varepsilon_i) \rangle = \sum_i x_i(\varepsilon_i) P(\varepsilon_i)$$

In particular, for a canonical ensemble: $\langle x(\varepsilon_i) \rangle = \frac{1}{Z(T, V, N)} \sum_i x_i(\varepsilon_i) \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$

Let's apply this result to the **average (mean) energy** of the systems in a canonical ensemble (the average of the energies of the visited microstates according to the frequency of visits):

$$\langle U \rangle = \sum_i \varepsilon_i P(\varepsilon_i) = \sum_i \varepsilon_i \frac{1}{Z} \exp(-\beta \varepsilon_i) = \frac{1}{Z} \sum_i \varepsilon_i \exp(-\beta \varepsilon_i)$$

The average values are additive. The average total energy U_{tot} of N identical systems is:

$$U_{tot} = N \langle U \rangle$$

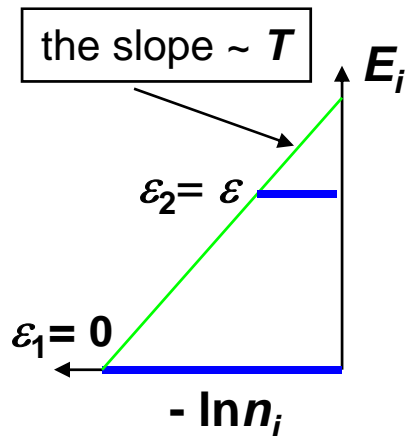
Another useful representation for the average energy (Pr. 6.16):

$$\sum_i \varepsilon_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right) = \left[\frac{1}{k_B T} \equiv \beta \right] = -\frac{\partial}{\partial \beta} \sum_i \exp(-\varepsilon_i \beta) = -\frac{\partial}{\partial \beta} Z$$

$$\langle U \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z = k_B T^2 \frac{\partial}{\partial T} (\ln Z)$$

thus, if we know $Z=Z(T, V, N)$, we know the average energy!

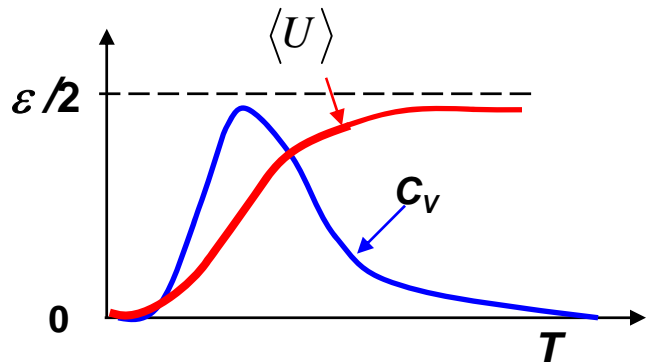
Example: energy and heat capacity of a two-level system



The partition function:
$$Z = \exp\left(-\frac{0}{k_B T}\right) + \exp\left(-\frac{\varepsilon}{k_B T}\right) = 1 + \exp\left(-\frac{\varepsilon}{k_B T}\right)$$

The average energy:

$$\langle U \rangle = \frac{1}{Z(T)} \left[0 \times \exp\left(-\frac{0}{k_B T}\right) + \varepsilon \times \exp\left(-\frac{\varepsilon}{k_B T}\right) \right] = \frac{\varepsilon}{1 + \exp\left(\frac{\varepsilon}{k_B T}\right)}$$



(check that the same result follows from $\langle U \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$)

The heat capacity at constant volume:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = \frac{\partial}{\partial T} \left[\frac{\varepsilon}{1 + \exp(\varepsilon / k_B T)} \right] = \frac{k_B (\varepsilon / k_B T)^2 \exp(\varepsilon / k_B T)}{[1 + \exp(\varepsilon / k_B T)]^2}$$

Partition Function and Helmholtz Free Energy

Now we can relate \mathbf{F} to \mathbf{Z} : $\langle U \rangle = F + TS = F - T \frac{\partial F}{\partial T} = T^2 \left(\frac{F}{T^2} - \frac{1}{T} \frac{\partial F}{\partial T} \right) = k_B T^2 \frac{\partial}{\partial T} \left(\frac{-F}{k_B T} \right)$

Comparing this with the expression for the average energy:

$$Z = \exp \left(- \frac{F}{k_B T} \right) = \exp(-\beta F)$$

This equation provides the connection between the microscopic world which we specified with microstates and the macroscopic world which we described with \mathbf{F} .

If we know $\mathbf{Z}=\mathbf{Z}(T,V,N)$, we know everything we want to know about the thermal behavior of a system. We can compute all the thermodynamic properties:

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = k_B \ln Z + k_B T \left(\frac{\partial \ln Z}{\partial T} \right)_{V,N}$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N}$$

$$\mu = - \left(\frac{\partial F}{\partial N} \right)_{T,V} = k_B T \left(\frac{\partial \ln Z}{\partial N} \right)_{T,V}$$

Microcanonical \Leftrightarrow Canonical

Our description of the microcanonical and canonical ensembles was based on counting the number of accessible microstates. Let's compare these two cases:

microcanonical ensemble

For an isolated system, the multiplicity Ω provides the number of accessible microstates. The constraint in calculating the states: **$U, V, N - \text{const}$**

For a fixed **U** , the mean temperature **T** is specified, but **T** can fluctuate.

$P_n = \frac{1}{\Omega}$ - the probability of finding a system in one of the accessible states

$$S(U, V, N) = k_B \ln \Omega$$

- in equilibrium, **S** reaches a maximum

canonical ensemble

For a system in thermal contact with reservoir, the partition function **Z** provides the # of accessible microstates. The constraint: **$T, V, N - \text{const}$**

For a fixed **T** , the mean energy **U** is specified, but **U** can fluctuate.

$P_n = \frac{1}{Z} e^{-\frac{E_n}{k_B T}}$ - the probability of finding a system in one of these states

$$F(T, V, N) = -k_B T \ln Z$$

- in equilibrium, **F** reaches a minimum

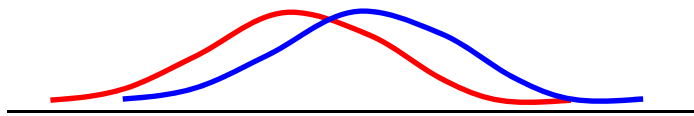
For the canonical ensemble, the role of **Z** is similar to that of the multiplicity Ω for the microcanonical ensemble. This equation gives ***the fundamental relation between statistical mechanics and thermodynamics*** for given values of **T, V** , and **N** , just as **$S = k_B \ln \Omega$** gives the fundamental relation between statistical mechanics and thermodynamics for given values of **U, V** , and **N** .

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{U,N} \quad \frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{U,V}$$

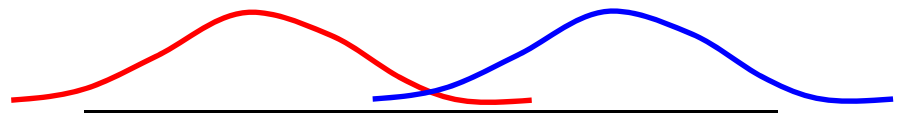
$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} \quad P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} \quad \mu = - \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

Boltzmann Statistics: classical (low-density) limit

We have developed the formalism for calculating the thermodynamic properties of the systems whose particles can occupy particular quantum states **regardless** of the other particles (**classical** systems). In other words, we ignored all kind of interactions between the particles. However, the occupation numbers are not free from the rule of quantum mechanics. In quantum mechanics, even if the particles do not interact through forces, they still might participate in the so-called **exchange interaction** which is dependent on the spin of interacting particles (this is related to the principle of indistinguishability of elementary particles, we'll consider bosons and fermions in Lecture 23). This type of interactions becomes important if the particles are in the same quantum state (the same set of quantum numbers), and their wave functions **overlap** in space:



strong exchange interaction



weak exchange interaction

the de Broglie wavelength $\lambda \leftrightarrow (n)^{1/3}$ the average distance btw particles

$$\lambda = \frac{h}{p} \sim \frac{h}{\sqrt{k_B T m}} \quad (\text{for } \text{N}_2 \text{ molecule, } \lambda \sim 10^{-11} \text{ m at RT})$$

$$\boxed{\frac{h(n)^{1/3}}{\sqrt{k_B T m}} \ll 1} \quad \text{Boltzmann statistics applies}$$

Violations of the Boltzmann statistics are observed if the the density of particles is very large (neutron stars), or particles are very light (electrons in metals, photons), or they are at very low temperatures (liquid helium),

However, **in the limit of small density of particles**, the distinctions between Boltzmann, Fermi, and Bose-Einstein statistics vanish.

Degenerate Energy Levels

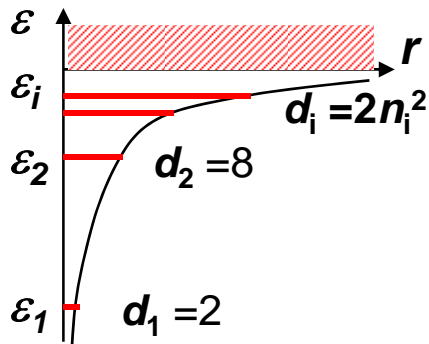
If **several** quantum states of the system (different sets of quantum numbers) correspond to the **same** energy level, this level is called **degenerate**. The probability to find the system in one of these degenerate states is the same for all the degenerate states. Thus, the total probability to find the system in a state with energy ε_i is

$$P(\varepsilon_i) = d_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \quad \text{where } d_i \text{ is the degree of degeneracy.}$$

Taking the degeneracy of energy levels into account, the partition function should be modified:

$$Z = \sum_i d_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$$

Example: The energy levels of an electron in the hydrogen atom: $\varepsilon(n_i) = -\frac{13.6 \text{ eV}}{n_i^2}$



(for a continuous spectrum, we need another approach)

where $n_i = 1, 2, \dots$ is the principle quantum number (these levels are obtained by solving the Schrödinger equation for the Coulomb potential). In addition to n_i , the states of the electron in the H atom are characterized with three other quantum numbers: the orbital quantum number $l_{i \max} = 0, 1, \dots, n_i - 1$, the projection of the orbital momentum $m_{li} = -l_i, -l_i + 1, \dots, 0, l_i - 1, l_i$, and the projection of spin $s_i = \pm 1/2$. In the absence of the external magnetic field, all electron states with the same n_i are degenerate (the property of Coulomb potential). The degree of degeneracy in this case:

$$d_i = 2 \sum_{l_{\min}=0}^{l_{\max}=n_i-1} [2l_i + 1] = n_i \frac{1 + 2(n_i - 1) + 1}{2} = 2n_i^2$$

Problem (final 2005, partition function)

Consider a system of distinguishable particles with five microstates with energies **0**, ε , ε , ε , and **2ε** ($\varepsilon = 1 \text{ eV}$) in equilibrium with a reservoir at temperature **$T=0.5 \text{ eV}$** .

1. Find the partition function of the system.
2. Find the average energy of a particle.
3. What is the average energy of 10 such particles?

$$Z_1 = 1 + 3 \exp\left(-\frac{\varepsilon}{k_B T}\right) + \exp\left(-\frac{2\varepsilon}{k_B T}\right) = 1 + 0.406 + 0.018 = 1.424$$

the average energy of a single particle:

$$\langle \varepsilon \rangle = \sum_i \varepsilon_i P(\varepsilon_i) = \frac{\varepsilon \times 3 \exp\left(-\frac{\varepsilon}{k_B T}\right) + 2\varepsilon \times \exp\left(-\frac{2\varepsilon}{k_B T}\right)}{1 + 3 \exp\left(-\frac{\varepsilon}{k_B T}\right) + \exp\left(-\frac{2\varepsilon}{k_B T}\right)} = 1 \text{ eV} \times \frac{0.406 + 0.036}{1.424} = 0.310 \text{ eV}$$

the same
result you'd
get from this:

$$\langle \varepsilon \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{3 \times \exp(-\beta\varepsilon) \times (-\varepsilon) + \exp(-2\beta\varepsilon) \times (-2\varepsilon)}{1 + 3 \exp(-\beta\varepsilon) + \exp(-2\beta\varepsilon)}$$

the average energy of **$N = 10$** such particles:

$$U_{10} = N \langle U \rangle = 10 \times 0.310 \text{ eV} = 3.1 \text{ eV}$$

Problem 1 (partition function, average energy)

Consider a system of N particles with only 3 possible energy levels separated by ε (let the ground state energy be 0). The system occupies a fixed volume V and is in thermal equilibrium with a reservoir at temperature T . Ignore interactions between particles and assume that Boltzmann statistics applies.

- (2) What is the partition function for a single particle in the system?
- (5) What is the average energy per particle?
- (5) What is probability that the 2ε level is occupied in the high temperature limit, $k_B T \gg \varepsilon$? Explain your answer on physical grounds.
- (5) What is the average energy per particle in the high temperature limit, $k_B T \gg \varepsilon$?
- (3) At what temperature is the ground state 1.1 times as likely to be occupied as the 2ε level?
- (25) Find the heat capacity of the system, C_V , analyze the low- T ($k_B T \ll \varepsilon$) and high- T ($k_B T \gg \varepsilon$) limits, and sketch C_V as a function of T . Explain your answer on physical grounds.

$$(a) \quad Z = \sum_i d_i \exp(-\beta \varepsilon_i) = 1 + e^{-\beta \varepsilon} + e^{-2\beta \varepsilon}$$

$$(b) \quad \langle \varepsilon \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{(-\varepsilon)e^{-\beta \varepsilon} + (-2\varepsilon)e^{-2\beta \varepsilon}}{1 + e^{-\beta \varepsilon} + e^{-2\beta \varepsilon}} = \varepsilon \frac{e^{-\beta \varepsilon} + 2e^{-2\beta \varepsilon}}{1 + e^{-\beta \varepsilon} + e^{-2\beta \varepsilon}}$$

$$(c) \quad P = \frac{e^{-2\beta \varepsilon}}{1 + e^{-\beta \varepsilon} + e^{-2\beta \varepsilon}} \approx \frac{1 - 2\beta \varepsilon}{1 + 1 - \beta \varepsilon + 1 - 2\beta \varepsilon} \approx \frac{1}{3} \quad \text{all 3 levels are populated with the same probability}$$

$$(d) \quad \langle \varepsilon \rangle = \varepsilon \frac{e^{-\beta \varepsilon} + 2e^{-2\beta \varepsilon}}{1 + e^{-\beta \varepsilon} + e^{-2\beta \varepsilon}} \approx \varepsilon \frac{1 + 2}{1 + 1 + 1} = \varepsilon$$

Problem 1 (partition function, average energy)

$$(e) \quad \exp(-2\beta\varepsilon) = \frac{1}{1.1} \quad 2\beta\varepsilon = \ln 1.1 \quad T = \frac{2\varepsilon}{k_B \ln 1.1}$$

$$(f) \quad C_V = \frac{dU}{dT} = N \frac{d\langle \varepsilon \rangle}{dT} = N \frac{d\langle \varepsilon \rangle}{d\beta} \frac{d\beta}{dT}$$

$$= N\varepsilon \left(-\frac{1}{k_B T^2} \right) \left\{ \frac{(-\varepsilon)e^{-\beta\varepsilon} + (-2\varepsilon)2e^{-2\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}} - \frac{(e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon})[(-\varepsilon)e^{-\beta\varepsilon} + (-2\varepsilon)e^{-2\beta\varepsilon}]}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \right\}$$

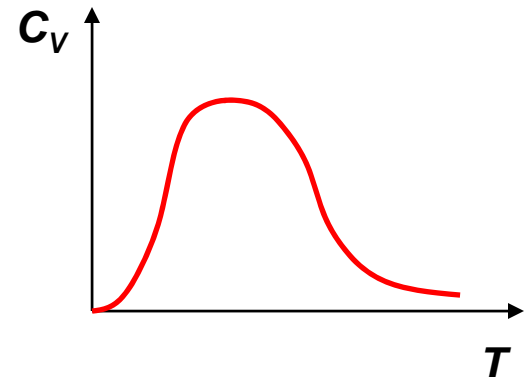
$$= \left(\frac{N\varepsilon^2}{k_B T^2} \right) \left\{ \frac{[e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon}][1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}] - (e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon})(e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon})}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \right\}$$

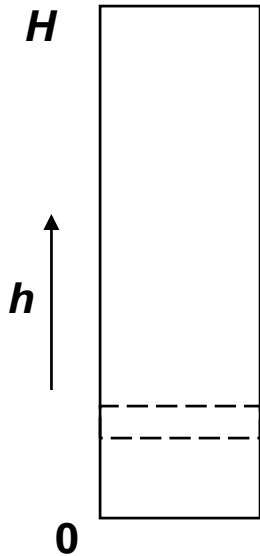
$$= \frac{N\varepsilon^2}{k_B T^2} \left\{ \frac{e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon} + e^{-2\beta\varepsilon} + 4e^{-3\beta\varepsilon} + e^{-3\beta\varepsilon} + 4e^{-4\beta\varepsilon} - e^{-2\beta\varepsilon} - 4e^{-3\beta\varepsilon} - 4e^{-4\beta\varepsilon}}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \right\}$$

$$= \frac{N\varepsilon^2}{k_B T^2} \frac{e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2}$$

Low T ($\beta \gg \varepsilon$): $C_V = \frac{N\varepsilon^2}{k_B T^2} \frac{e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \approx \frac{N\varepsilon^2}{k_B T^2} e^{-\frac{\varepsilon}{k_B T}}$

high T ($\beta \ll \varepsilon$): $C_V = \frac{N\varepsilon^2}{k_B T^2} \frac{e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \approx \frac{2}{3} \frac{N\varepsilon^2}{k_B T^2}$





Problem (the average values)

A gas is placed in a very tall container at the temperature T . The container is in a uniform gravitational field, the acceleration of free fall, g , is given. Find the average potential energy of the molecules.

of molecules within dh : $dN(h \leftrightarrow h + dh) = n_0 \exp\left(-\frac{mgh}{k_B T}\right) (area) dh$

$$\langle U \rangle = \frac{\int_0^H mgh \times n_0 \exp\left(-\frac{mgh}{k_B T}\right) (area) dh}{\int_0^H n_0 \exp\left(-\frac{mgh}{k_B T}\right) (area) dh} = \left[\frac{mgh}{k_B T} = y \right] = \frac{\int_0^{\frac{mgH}{k_B T}} (k_B T) y \times \exp(-y) \times \frac{k_B T}{mg} dy}{\int_0^{\frac{mgH}{k_B T}} \exp(-y) \times \frac{k_B T}{mg} dy} = k_B T \times \frac{\int_0^{\frac{mgH}{k_B T}} y \times \exp(-y) dy}{\int_0^{\frac{mgH}{k_B T}} \exp(-y) dy}$$

$$\int_0^A y \times \exp(-y) dy \rightarrow \frac{d}{dy} [y \times \exp(-y)] = \exp(-y) - y \times \exp(-y) \quad \left| \int_0^A dy \right.$$

$$[y \times \exp(-y)]_0^A = \int_0^A \exp(-y) dy - \int_0^A y \times \exp(-y) dy \quad \int_0^A y \times \exp(-y) dy = -A \times \exp(-A) + 1 - \exp(-A)$$

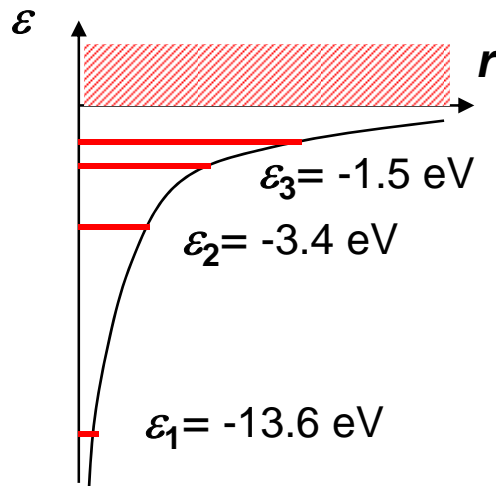
$$\int_0^A \exp(-y) dy = -\exp(-A) + 1$$

For a **very tall** container ($mgH/k_B T \rightarrow \infty$):

$$\boxed{\langle U \rangle = k_B T}$$

Partition Function for a Hydrogen Atom (Pr. 6.9)

Any reference energy can be chosen. Let's choose $\varepsilon = 0$ in the ground state: $\varepsilon_1=0$, $\varepsilon_2=10.2$ eV, $\varepsilon_3=12.1$ eV, etc. The partition function:



$$Z = \sum_i d_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right) = \sum_i 2n_i^2 \exp\left[-\frac{13.6 \text{ eV} \left(1 - 1/n_i^2\right)}{k_B T}\right]$$

(a) Estimate the partition function for a hydrogen atom at $T = 5800\text{K}$ ($= 0.5$ eV) by taking into account only three lowest energy states.

- we can forget about the spin degeneracy – **it is the same for all the levels** – the only factor that matters is n^2

$$Z = \exp\left(-\frac{\varepsilon_1}{k_B T}\right) + 4 \times \exp\left(-\frac{\varepsilon_2}{k_B T}\right) + 9 \times \exp\left(-\frac{\varepsilon_3}{k_B T}\right) = e^0 + 4 \times e^{-20.4} + 9 \times e^{-24.2} = 1 + 5.5 \cdot 10^{-9} + 2.8 \cdot 10^{-10} \approx 1$$

However, if we take into account **all discrete levels**, the full partition function **diverges**:

$$Z = \sum_{n=1}^{\infty} n^2 \exp\left[-\frac{13.6 \left(1 - \frac{1}{n^2}\right)}{k_B T}\right] > \exp\left(-\frac{13.6}{k_B T}\right) \sum_{n=1}^{\infty} n^2 = \infty$$

Partition Function for a Hydrogen Atom (cont.)

Intuitively, only the lowest levels should matter at $\epsilon \gg k_B T$. To resolve this paradox, let's go back to our assumptions: we neglected the term PdV in

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

If we keep this term, then

$$\text{New Boltzmann factor} = \exp\left(-\frac{E + PV}{k_B T}\right)$$

For a H atom in its ground state, $V \sim (0.1 \text{ nm})^3$, and at the atmospheric pressure, $PV \sim 10^{-6} \text{ eV}$ (negligible correction). However, this volume increases as n^3 (the Bohr radius grows as n), and for $n=100$, PV is already $\sim 1 \text{ eV}$. The PV terms cause the Boltzmann factors to decrease exponentially, and this rehabilitates our physical intuition: the correct partition function will be dominated by just a few lowest energy levels.