Boltzmann Distribution

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Note: Difference of Notations

Note that these notes use different notations from our main notes and Kittel and Krömer (but these notations are those of Reif and are also often used in the literature)

Number of states = $\Omega$ instead of $g$

\[
\beta = \frac{1}{\tau} = \frac{1}{k_B T}
\]

\[
\alpha = -\frac{\mu}{\tau} = -\frac{\mu}{k_B T}
\]
Canonical distribution and Boltzmann factor

**Isolated system:**
The physical information about a system only restrains the number of states in the representative statistical ensemble. For an isolated system which is a situation of fundamental importance the energy of a system remains constant. Even if a System A is not isolated and can interact with another system A´ then we can consider A+A´as an isolated system.

Suppose that volume ($V$) is the only relevant external parameter of a system and we know that the constant energy of the system lies between $E$ and $E+\delta E$. If the energy of the system in state $r$ is denoted by $E_r$ the probability of finding the system in state $r$ is given by (fundamental statistical postulate):

$$P_r = \begin{cases} C & \text{if } E<E_r<E+\delta E \\ 0 & \text{otherwise} \end{cases}$$

And $\Sigma P_r=1$ if summed over all the states between $E$ and $E+\delta E$.

**Microcanonical ensemble**

**System in contact with a heat reservoir:**
We consider the case of a small system $A$ in contact with a heat reservoir $A´$. Under equilibrium what is the probability to find the system $A$ in any particular state $r$ with energy $E_r$?

$E_r$ not necessarily constant but $E_r+E'=E$ therefore

$$P_r = C'\Omega'(E-E_r)$$

$\sum P_r=1$

What if $A´>>A$:

$$\ln \Omega'(E-E_r) = \ln \Omega'(E) - \left[ \frac{\partial \ln \Omega'}{\partial E'} \right] E_r \ldots$$

Evaluated at $E$ but:

$$\frac{\partial \ln \Omega'}{\partial E'} \equiv \beta = (kT)^{-1}$$

$$\Rightarrow \ln \Omega'(E-E_r) = \ln \Omega'(E) - \beta E_r \Rightarrow \Omega'(E-E_r) = \Omega'(E)e^{-\beta E_r} \Omega'(E) = \text{cte} \Rightarrow P_r = Ce^{-\beta E_r} \Rightarrow C^{-1} = \sum_r e^{-\beta E_r} \Rightarrow$$

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

$e^{-\beta E}$ is called Boltzmann factor the corresponding probability distribution is called canonical distribution. Canonical ensemble is an ensemble representing a system in contact with a heat reservoir.
Example: Paramagnetism

Consider a substance with $N_0$ magnetic atoms per volume is placed in an external magnetic field $H$.
Assume that each atom has spin 1/2 due to its unpaired electron and magnetic moment $\mu$. From quantum mechanics the magnetic moment of each atom can point either parallel or antiparallel to $H$. If $T$ is constant what is the mean value for $\mu$?

Lets divide the system into a single atom in equilibrium with the rest. We note state (+) if atom’s $\mu$ is parallel with $H$ and state (-) if antiparallel.

State +: $\epsilon_+ = -\mu H \Rightarrow P_+ = Ce^{-\beta H} = Ce^{\beta H}$
State -: $\epsilon_+ = \mu H \Rightarrow P_+ = Ce^{-\beta H}$

As the ratio between the magnetic energy and the thermal energy.

Intuitively if $y<<1$ then the $P_+$ and $P_-$ are similar and we expect $\mu = 0$ but if $y>>1$ then $P_+=0$ and we expect that $\mu = \mu$

$\mu = \frac{P_+}{P_+ + P_-} = \mu e^{\beta H} e^{-\beta H} = \mu \tanh(y)$

$y << 1 \Rightarrow \tanh(y) = \left(\frac{1 + y + \ldots}{2}\right) - \left(\frac{1 - y - \ldots}{2}\right) = y \Rightarrow \mu = \frac{\mu^2 H}{kT}$

$y >> 1 \Rightarrow e^y >> e^{-y} \Rightarrow \tanh(y) = 1 \Rightarrow \mu = \mu$

Magnetization: $\vec{M}_0 = N_0 \mu$

$\vec{M}_0 = \chi H; \chi = \frac{N_0 \mu^2}{kT}$

The fact that at high $T$, $\chi \propto 1/T$ is known as the Curie’s law.

On the other hand at low $T$, $M_0 \to N_0 \mu$. 
System with specified mean energy

Another situation of physical interest is that where a system $A$ consists of a fixed number $N$ of particles in a given volume $V$, but where the only information available about the energy is its mean energy. Very common situation! As the measure of macroscopic work done or heat transfer leads only to an estimate of the mean energy.

A system $A$ with specified mean energy is also described by a canonical distribution.

Denote the energy of the system $A$ in state $r$ by $E_r$. Suppose that the statistical ensemble consists of a very large number $a$ of such systems $a_r$ of which are in state $r$. Then the information available to us is that:

$$\frac{1}{a} \sum_s a_s E_s = \bar{E} \Rightarrow \sum_s a_s E_s = a\bar{E}$$

If a system in the ensemble is in the state $r$, the remaining $(a-1)$ systems must then have the combined energy $E' = a\bar{E} - E_r$. These $(a-1)$ systems can be distributed over some very large number $\Omega(E')$ of accessible states if their combined energy is $E'$. But $E_r << a\bar{E}$. The mathematical problem is exactly the same as that of $T = \text{cte}$.

Again one obtains: $P_r \propto e^{-\beta E_r}$

$$\sum_r E_r e^{-\beta E_r} \frac{r}{\sum_r e^{-\beta E_r}} = \bar{E}$$

Here one needs to calculate $\beta$ from $\bar{E}$. 
Calculating the mean values (measurable quantities) from partition function

\[ \bar{E} = \sum_r E_r P_r \quad \text{And} \quad P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \quad \text{then} \quad \bar{E} = \sum_r E_r e^{-\beta E_r} = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \]

Lets define:

\[ Z \equiv \sum_r e^{-\beta E_r} \]

\[ \sum_r E_r e^{-\beta E_r} = -\sum_r \frac{\partial}{\partial \beta} (e^{-\beta E_r}) = -\frac{\partial Z}{\partial \beta} \Rightarrow \bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln(Z)}{\partial \beta} \]

The quantity \( Z \) is called “sum over states” or the “partition function”. (\( Z \) from German “Zustandsumme”)

\[ (\Delta E)^2 \equiv (E - \bar{E})^2 = E^2 - \bar{E}^2 \]

\[ \bar{E}^2 = \frac{\sum_r E_r^2 e^{-\beta E_r}}{Z} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 = -\frac{\partial E}{\partial \beta} + \bar{E}^2 \]

\[ \Rightarrow \quad (\Delta E)^2 = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln(Z)}{\partial \beta^2} \]
Suppose that the system is characterized by a single external parameter $x$. Consider a quasi-static change of the external parameter to $x+dx$. In this process the energy of the system in state $r$ changes by the amount:

$$ \Delta_x E_r = \frac{\partial E_r}{\partial x} \, dx $$

The macroscopic work done by the system then is:

$$ dW = \sum_r e^{-\beta E_r} \left( -\frac{\partial E_r}{\partial x} \, dx \right) / \sum_r e^{-\beta E_r} $$

$$ \sum e^{-\beta E_r} \frac{\partial E_r}{\partial \beta} = -\frac{1}{\beta} \frac{\partial}{\partial x} \left( \sum e^{-\beta E_r} \right) = -\frac{1}{\beta} \frac{\partial Z}{\partial x} $$

Generalized force $\overline{X}$ corresponding to variable $x = \frac{\partial E}{\partial x}$ so that $dW = \overline{X} dx$

$$ \Rightarrow \overline{X} = \frac{1}{\beta} \frac{\partial \ln(Z)}{\partial x} $$

For example if $x=V$ the volume the generalized force is pressure and

$$ \overline{p} = \frac{1}{\beta} \frac{\partial \ln(Z)}{\partial V} \quad \overline{p} \text{ is } \overline{p}(T,V) \text{ so this equation directly gives the equation of state} $$
Connection with thermodynamics

All the important physical quantities can be expressed completely in terms of \( \ln(Z) \). As both \( \overrightarrow{dW} \) and \( \overrightarrow{E} \) are expressible in terms of \( Z \), we might be able to find their relation (second law of thermodynamics):

**Note that** \( Z \) **is a function of both** \( \beta \) **and external parameter** \( x \) (e.g V) **then** \( Z=Z(\beta,x) \):

\[
d\ln(Z) = \frac{\partial \ln(Z)}{\partial x} dx + \frac{\partial \ln(Z)}{\partial \beta} d\beta
\]

Consider a quasi-static process where \( x \) and \( \beta \) vary so slowly that the system is distributed according to the canonical distribution:

\[
d\ln(Z) = \beta dW - \overrightarrow{E} d\beta = \beta dW - d(\overrightarrow{E}\beta) + \beta d\overrightarrow{E} \Rightarrow d(\ln Z + \beta \overrightarrow{E}) = \beta(dW + d\overrightarrow{E}) \equiv \beta dQ
\]

\[
dS = \frac{dQ}{T}; S \equiv k(\ln Z + \beta \overrightarrow{E})
\]

\[
\beta = \frac{1}{kT} \Rightarrow TS = kT \ln Z + \overrightarrow{E}
\]

\[
F \equiv \overrightarrow{E} - TS = -kT \ln Z
\]

Thus \( \ln Z \) is very simply related to Helmholtz free energy
Z = \sum_{r} e^{-\beta E_r}

T \to 0 \Rightarrow \beta = \frac{1}{kT} \to \infty

\text{The only terms of appreciable magnitude are those with the lowest possible value of the energy } E_r \text{ or } \Omega_0 \text{ states corresponding to ground state:}

Z \to \Omega_0 e^{-\beta E_0}

\rightarrow \text{Third law of thermodynamics}

\implies \text{Imagine a system } A^{(0)} \text{consisting of two systems } A \text{ and } A' \text{ which are weakly interacting with each other. } A \text{ is presented by energy state } E_r \text{ and } A' \text{ by states } E'_s. \text{ A state of the combined system } A+ A' \text{ is then denoted by a pair of } r,s; \text{ since } A \text{ and } A' \text{ interact only weakly, corresponding energy of this state is simply given by:}

E_{rs}^{(0)} = E_r + E'_s; Z^{(0)} = \sum_{r,s} e^{-\beta E_{rs}^{(0)}} = \sum_{r,s} e^{-\beta (E_r + E'_s)} = e^{-\beta E_r} e^{-\beta E'_s} = (\sum_{r} e^{-\beta E_r})(\sum_{s} e^{-\beta E'_s}) = ZZ'

\Rightarrow \ln Z^{(0)} = \ln Z + \ln Z'

\text{But } \overline{E} = -\frac{\partial \ln Z}{\partial \beta} \Rightarrow \overline{E}^{(0)} = \frac{\ln Z + \beta \overline{E}}{Z} \Rightarrow S = k(\ln Z + \beta \overline{E}) \Rightarrow S^{(0)} = S + S'

\text{Therefore the “extensive” parameters of two weakly interacting systems are additive. We can also show that the two systems with different temperature will tend to have same temperature in contact.}

\boxed{\text{Canonical distribution implies all the thermodynamics relations from previous discussions}}

\text{For a canonical system and a particular state } E_r: \quad P_r = \frac{e^{-\beta E_r}}{Z} \Rightarrow \bar{E} = \sum_r E_r P_r \Rightarrow d\bar{E} = \sum_r (E_r dP_r + P_r dE_r)

\text{The work done by the system in this quasi-static process:} \quad dW = \sum_r P_r (-dE_r) = -\sum_r P_r dE_r

\text{In doing work, the energy of each state, occupied with the given } P_r, \text{ is thus simply changed by } dE_r \text{ by virtue of the change of external parameters. The heat absorbed in this process:} \quad dQ = d\bar{E} + dW \Rightarrow dQ = \sum_r E_r dP_r

\text{In absorbing heat, the energy of each state is thus unaffected, but its probability of occurrence is changed}
Approximation methods for mean values for a system with $E$ known

We saw how easy is to calculate the mean values (with partition function) for a canonical distribution e.g a system in contact with a heat reservoir or a system with known mean energy $\bar{E}$.

How an isolated system with specified $V$ and $N$ (number of particles) whose energy lies between $E$ and $E+\delta E$?

If a parameter $y$ has the value $y_r$, in state $r$, the $\bar{y}$:

$$\bar{y} = \frac{\sum_r y_r}{\Omega(E)}$$

Here all summation are subject to the condition that one sums only over those states where $E<E_r< E+\delta E$.

The calculation is hard because of the energy constraint as compared to canonical distribution where we could sum over all states without any restriction!

One way to circumvent this difficulty is to replace this restriction with a weaker condition that only the mean value $\bar{E}$ is known. The approximation is valid as:

$$\frac{\Delta E}{E} \approx \frac{1}{\frac{1}{f^2}} \quad (f: \text{number of degrees of freedom})$$

So even if the energy should be so precisely known that $\delta E/E \sim 10^{-11}$, the approximation is still good enough for a systems consisting of a mole of particles.

Calculating the dispersion however is more delicate!
Generalization: Grand canonical distribution

System A is in equilibrium with system A´ but here it can also exchange particles

\[ E + E' = E^{(0)} = \text{cte} \]
\[ N + N' = N^{(0)} = \text{cte} \]

What is the probability to find the system A in the state \( r \) with \( E_r \) and \( N_r \)?

\[ P_r(E_r, N_r) \propto \Omega'(E^{(0)} - E_r, N^{(0)} - N_r) \]

Since \( E_r << E^{(0)} \) and \( N_r << N^{(0)} \):

\[ \ln \Omega'(E^{(0)} - E_r, N^{(0)} - N_0) = \ln \Omega'(E^{(0)}, N^{(0)}) - \left[ \frac{\partial \ln \Omega}{\partial E'} \right]_0 E_r - \left[ \frac{\partial \ln \Omega}{\partial N'} \right]_0 N_r \]

Here the derivatives are evaluated for \( E' = E^{(0)} \) and \( N' = N^{(0)} \); they are therefore, constants characterizing the reservoir. Denote them by:

\[ \beta \equiv \left[ \frac{\partial \ln \Omega}{\partial E'} \right]_0; \alpha = \left[ \frac{\partial \ln \Omega}{\partial N'} \right]_0 \]

\[ \Omega'(E^{(0)} - E_r, N^{(0)} - N_0) = \Omega'(E^{(0)}, N^{(0)}) e^{-\beta E_r - \alpha N_r} \Rightarrow P_r \propto e^{-\beta E_r - \alpha N_r} \]

This is called the “grand canonical” distribution.

\[ T \equiv (k \beta)^{-1}; \mu = -kT \alpha \] Is called the “chemical potential” of the reservoir.
\[ Z = \sum_r e^{-(E_r + \mu N_r) / kT} \]

\[ \bar{E} = \frac{\sum_r E_r e^{-(E_r + \mu N_r) / kT}}{Z} ; \bar{N} = \frac{\sum_r N_r e^{-(E_r + \mu N_r) / kT}}{Z} \]

\[ Z \equiv \text{the grand partition function} \neq Z \]

A grand canonical distribution is also valid for the system with known $\bar{E}$ and $\bar{N}$ instead of $\mu$ and $T$.

Also once again it is a good approximation to use grand canonical distribution to calculate the means of $N$ and $E$ for a canonical distribution where $E$ and $N$ are fixed to some precision.