

Thermodynamics and Statistical Physics

A. THERMODYNAMICS

1. Definitions. Important results

TD studies **systems**, i.e. *finite parts of the Universe*. A system is separated from the outside by a surface, actual or just thought. *Examples.*

Types of enclosures:

- *adiabatic walls*: not permeable to heat transfer
- *diathermal walls*: permeable to heat transfer
- *fixed walls*: constant volume
- *porous membrane*: fixed volume, variable no. of particles

An isolated system does not exchange with the exterior neither heat, nor work or particles.

It has fixed, adiabatic, non-permeable walls

The system is described by *state parameters*. They could be :

- *external*, depending only on external bodies (systems), e.g. volume, fields (electric, magnetic, gravitational)
- *internal*, depending not only on external systems (pressure, temperature)

Another classification:

- *intensive*, not depending on the mass (or volume, or no. of particles); ex. temperature, pressure
- *extensive*, depending on the mass (or volume, or no. of particles); ex. internal energy, entropy.

Equilibrium states

State parameters are perfectly defined only in *equilibrium states*, states when the parameters are constant and there are no stationary fluxes.

Modification of state parameters, hence of the state is called *process*. If the process is slow enough so as to assume that in each moment the system is in a stationary state the process is *quasistatic*. Otherwise it is *non-static*. We study only quasistatic processes: isotherm, isochor, isobar, adiabatic.

Comparison between TD and Statistical Physics (SP).....

2. TD principles

2.1. General principle

An isolated system always attains equilibrium. The state changes only by varying external parameters. Bigger the system, longer the time to attain equilibrium.

2.2 Zeroth law of TD

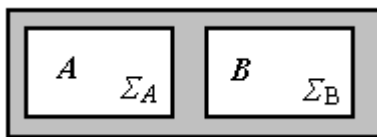
(It introduces *temperature* as a state parameter)

Related to the sensations of cold and hot. Temperature and heat.

Essential characteristic: its tendency to equalization, due to a net flow of energy called heat flow.

The equilibrium relation

Two systems A and B isolated from the outside and from each other:



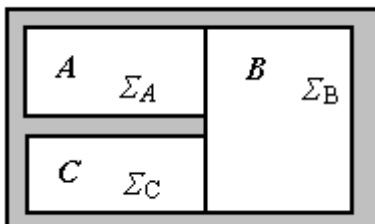
They are in equilibrium states Σ_A and Σ_B .

Eliminate the adiabatic wall between them.

If their states remain the same, we say that *the two systems were in equilibrium*, more precisely *their states are in equilibrium*.

We write $\Sigma_A \text{ E } \Sigma_B$.

Suppose now the situation below



$\Sigma_A \text{ E } \Sigma_B$ and $\Sigma_B \text{ E } \Sigma_C$.

There is overwhelming experimental proof that $\Sigma_A \text{ E } \Sigma_B$. **The equilibrium relation is transitive.** It is also idempotent, $\Sigma_A \text{ E } \Sigma_A$ and reflexive, $\Sigma_A \text{ E } \Sigma_A$. Hence the "E" relation is an *equivalence relation*.

It splits all the equilibrium states in *classes of equivalent states*. Two different classes have no common elements. All the equilibrium states of all the systems which are in equilibrium are characterized by a common parameter, *the temperature*. They "have" the same temperature. Denote the external parameters by a_i and the internal ones by A_i . The (equilibrium) states are completely described by the external parameters and the temperature T . The relations are called the *thermal equations of states*:

$$A_i = A_i(a_1, a_2, \dots, a_n, T) \quad (1)$$

Example: perfect gaz $p = RT/V$, $a=V$, $a=-p$ (see later)

The transitivity of the equilibrium relation allows to measure temperatures with a thermometer.

2.3. The first principle of Thermodynamics

This is the principle of the conservation of energy for macroscopic bodies.

Consider first an isolated system. Following the general principle of TD one can change its state only by changing the external parameters, i.e. by doing work on it. Experiments show that to change the system state from a specific equilibrium state Σ_1 to another definite equilibrium state Σ_2 the same amount of work is necessary, irrespective of the mechanism used to perform this work, or of the transitional state through the system passes. We define a function of state U , such that the work done on the system is equal to the change of this quantity:

$$W = \Delta U \quad (2)$$

Suppose now we consider changes of state for a non-isolated system. When the system performs the process $\Sigma_1 \rightarrow \Sigma_2$, but the work done is now different of the variation of the energy ΔU . We define *heat* the difference

$$Q = \Delta U - W \quad (3)$$

The internal energy U is associated with the internal degrees of freedom. It consists of the kinetic energy of atoms (and molecules) and the potential energy of the interaction between them. It is an extensive function of state and can be written as a function of the external parameters and the temperature:

$$U = U(a_1, a_2, \dots, a_n, T) \quad (4)$$

Work and heat flow are different forms of energy transfer. *They are not state functions*, they depend on the process.

Work is the energy transfer by the modification of the the macroscopic degrees of freedom, i.e. the external parameters ($p\Delta V$).

Heat flow is the energy transfer between microcopic degrees of freedom, i.e. without the modification of the external parameters.

The first law introduces the internal energy U as a function of state. For infinitesimal changes

$$dU = \delta Q + \delta W \quad (5)$$

Reversible processes: processes for which direction could be changed by an infinitesimal change in the applied conditions. They are cuasistatic and has no hysteresis. For reversible processes work is well definedby the properties of the system.

Example. the isothermal compression of an ideal gas: $\delta W = -pdV$, which for compression is positive. In a finite change $W = - \int_{V_1}^{V_2} pdV = RT \int_{V_1}^{V_2} dV / V = RT \ln \frac{V_1}{V_2}$.

For irreversible processes, usually $\delta W_{\text{irrev}} \geq -pdV$.

For cycles:

$$\oint dU = 0 \quad \oint \delta Q \neq 0 \quad \oint \delta W \neq 0 \quad (6)$$

For simple systems (only one external parameter, usually the volume)

$$\delta Q = dU + pdV \quad (7)$$

and in general

$$\delta Q = dU - \sum_{i=1}^n A_i da_i \quad (7')$$

Heat capacities

By definition

$$C = \frac{\delta Q}{dT} \quad (8)$$

Since δQ depends on the process, so does C . For an ideal gas:

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (9)$$

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p \quad (10)$$

The second law

The first law states energy balance, the second law deals with the direction of processes. Remember the general principle: left to itself, an isolated system initially not in equilibrium always advances towards an equilibrium state, although a change in the opposite direction would equally conserve energy.

Real processes are all irreversible. Examples: *heat, by itself, will never pass from a colder to a hotter body* (2nd law due to Clausius); *a process whose only effect would be the complete conversion of heat into work cannot occur* (Kelvin).

These are negative sentences and is difficult to build a theory starting with them. The quantity which points to the direction in which processes occur is *the entropy* introduced by Clausius in 1854. In 1870 Boltzmann discovered a *relation between the macroscopic entropy and the microscopic properties of a system*. This is the famous **Boltzmann relation** which will be demonstrated later. It allows a convenient passage from the microscopic (molecular) pov to the macroscopic (phenomenological, TD) pov.

The TD approach

In the relation of the 1st law (5) the only perfect (total) differential is dU . Elementary work δW and heat δQ are not perfect total differentials, i.e. they are not the differential of some function of the TD variables (external parameters and temperature). But it can be shown that using *an integrant factor, namely $1/T$* , we find a perfect diferential as below:

$$\boxed{\frac{\delta Q}{T} = dS} \quad (11)$$

This is *not* a mathematical result, but a physical result from experiments expressed in a mathematical form. The new form of the 2nd law is: *elementary heat admits an integrating factor*. This factor could be chosen to be the inverse of the absolute temperature.

The new function of state S is the (absolute) entropy. It is a function of state, as the internal energy, the pressure or the volume, depending on the external parameters a_i and the temperature T , $S = S(a_1, a_2, \dots, a_n, T)$. It is an extensive function of state. Therefore the 1st law for simple systems and for reversible changes (5) is written

$$\boxed{dU = TdS - pdV} \quad (12)$$

This gives the differential of U as a function of S and V , $U = U(S, V)$. U appears as a *characteristic function* (see later).

We can write the formal expansion $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$ and by identification with (12) one gets

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -p \quad (13)$$

The Schwartz lemma gives a first "Maxwell relation"

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (14)$$

Relation (12) is the 1st law only for reversible processes. Then

$$\delta W_{rev} = -pdV \quad \delta Q_{rev} = TdS \quad (15)$$

For irreversible changes we have the inequalities:

$$\delta W_{\text{irrev}} \geq -pdV \quad (\text{see above Eq. (6)}) \quad (16)$$

and then

$$\delta Q_{\text{irrev}} \leq TdS \Rightarrow dS \geq \frac{\delta Q_{\text{irrev}}}{T} \quad (17)$$

In Eqs. (16, 17) equality appears only for reversible processes.

The relation between the caloric and the thermal equations of state

Let's work with simple systems for which $U = U(V, T)$ and $p = p(V, T)$. Begin with 1st law for reversible changes (12): $dU = TdS - pdV$. We find successively

$$dS = \frac{dU + pdV}{T} = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] dV. \text{ Use Schwarz lemma to find}$$

$$\left(\frac{\partial U}{\partial V} \right)_T + p = T \left(\frac{\partial p}{\partial T} \right)_V \quad (18)$$

Example 1. Ideal gas. $p = \frac{RT}{V}$, $T \left(\frac{\partial p}{\partial T} \right)_V = \frac{RT}{V} = p$ and from (18)

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

This is *Joule's law for ideal gases*: internal energy of a perfect gas does not depend on the volume for isothermal processes. Therefore

$$dU_{\text{id}} = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = \left(\frac{\partial U}{\partial T} \right)_V dT = C_V dT$$

For usual temperatures C_V does not depend on T and integrating

$$\boxed{U_{\text{id}}(T, V) = C_V T + \text{const}} \quad (19)$$

Example 2. Van der Waals gas. $\left(p + \frac{a}{V^2} \right) (V - b) = RT$, $p(V, T) = \frac{RT}{V - b} - \frac{a}{V^2}$.

$$T \left(\frac{\partial p}{\partial T} \right)_V = \frac{RT}{V - b} = p + \frac{a}{V^2} \Rightarrow \left(\frac{\partial U}{\partial V} \right)_T = \frac{a}{V^2} \text{ for Van der Waals gas.}$$

The internal energy will be $U = C_V T - \frac{a}{V} + \text{const}$.

Example 3. Entropy of ideal gases and of Van der Waals gases.

$$dS = \frac{dU + pdV}{T}$$

$$\text{Ideal gases: } dS = C_V \frac{dT}{T} + R \frac{dV}{V}, \quad \boxed{S = C_V \ln T + R \ln V + S_0} \quad (20)$$

$$\text{Van der Waals gases: } S = C_V \ln T + R \ln(V - b) + S_0 \quad (20')$$

Thermodynamic potentials (characteristic functions)

A characteristic function is a function of state allows to find at once all other TD properties. They are also used to obtain equilibrium conditions. We consider only simple systems, with the particular case of the ideal gas.

Internal energy $U(S, V)$. Eqs (12-14) define this function. For irreversible processes Eq. (12) is $dU_{irrev} \leq TdS - pdV$, hence for a system at constant S and V (adiabat-isochor conditions) the internal energy U has a minimum at equilibrium (because $\Delta U \leq 0$)

$$\text{Free energy} \quad F(T, V) = U - TS \quad (21)$$

$$dF = -SdT - pdV \quad (22)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad p = -\left(\frac{\partial F}{\partial V}\right)_T \quad (23)$$

$$\text{Maxwell} \quad \left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V \quad (24)$$

Minimum of free energy at equilibrium, for isotherm-isobar processes

$$\text{Enthalpy} \quad H(S, p) = U + pV \quad (25)$$

$$dH = TdS + Vdp \quad (26)$$

$$T = \left(\frac{\partial H}{\partial S} \right)_p \quad V = \left(\frac{\partial H}{\partial p} \right)_S \quad (27)$$

$$\text{Maxwell} \quad \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p \quad (28)$$

Minimum of enthalpy at equilibrium for adiabatic-isobar processes

$$\text{Free enthalpy} \quad G(p, T) = U + pV - TS \quad (29)$$

$$dG = -SdT + Vdp \quad (30)$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_p \quad V = \left(\frac{\partial G}{\partial p} \right)_T \quad (31)$$

$$\text{Maxwell} \quad \left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \quad (32)$$

Free enthalpy minimum at equilibrium for isotherm-isobar processes

The third law

TD can not find constants as S_0 from Eq. (20). The 3rd law gives a value for the entropy of a system as the absolute temperature drops to zero. The explanation is given by statistical arguments. The content of the third TD principle is

$$\lim S = 0 \quad \text{for } T \rightarrow 0 \text{ K} \quad (33)$$

Consequences:

- the heat capacity of a system vanishes at $T=0$ K

- the thermal expansion coefficient at constant pressure vanishes at $T=0$ K. The thermal expansion coefficient at constant pressure is defined by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (34)$$

To show this begin with the Maxwell relation $\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$. The LHS tends to zero as $T \rightarrow 0$ K, hence $\alpha \rightarrow 0$ too.

B. STATISTICAL PHYSICS

Introduction. Micro and macrostates. Statistical weight. Principles

Macrostate (TD state): state of a system described by TD functions of state: U, T, p, V, F, H, G , etc. For a simple system the description by two parameters is satisfactory. For more complex systems the no. of TD parameters is small.

Microstate (molecular state): state of a system described by coordinates and momenta of all the particles inside. The no. of parameters is huge, $6 \cdot 10^{23}$ for a mole.

Ensemble (virtual ensemble): the family of microstates compatible with a macrostate.

Statistical weight: denoted by Ω , is the number of microstates from an ensemble. It is huge (10^{100}) for equilibrium states and very large (10^{100}) for states close to equilibrium.

Principles of SF.

1. The statistical weight has a maximum for equilibrium states.

2. Without any additional knowledge, we assume that each microstate from an ensemble has *a priori* the same probability.

3. TD quantities are obtained as average over ensembles of the corresponding microscopic quantities. Time average equals ensemble average.

The Boltzmann relation

It is the relation between the entropy S - a TD macroscopic quantity - and the statistical weight Ω . Imagine a system divided in two subsystems. The entropy is additive, as is the heat. The entropy is a measure of the disorder of the systems. Boltzmann assumes that the entropy depends on the statistical weight, $S=S(\Omega)$. For the two sub-systems and the whole system we write:

$$S_1(\Omega_1) + S_2(\Omega_2) = S(\Omega_1 \cdot \Omega_2)$$

We derive with respect to Ω_1 and Ω_2 and find:

$$\frac{dS_1}{d\Omega_1} = \frac{dS(\Omega_1\Omega_2)}{d(\Omega_1\Omega_2)}\Omega_2 \quad \times \Omega_1$$

$$\frac{dS_2}{d\Omega_2} = \frac{dS(\Omega_1\Omega_2)}{d(\Omega_1\Omega_2)}\Omega_1 \quad \times \Omega_2$$

$$\Omega_1 \frac{dS_1}{d\Omega_1} = \Omega_2 \frac{dS_2}{d\Omega_2} = \Omega_1\Omega_2 \frac{dS(\Omega_1\Omega_2)}{d(\Omega_1\Omega_2)} = k \equiv k_B \approx 1.38 \cdot 10^{-23} \text{ J/K}$$

$S = k \ln \Omega$
(35)

The Boltzmann distribution

Distributions

In statistical physics a distribution is a certain arrangement of particles on available states (the mathematical meaning in probabilities is a little different). Simple examples from everyday life:

Particles are N=2 different coins; states are two pockets.

The possible arrangements are:



This is the distribution of coins in the 2 pockets.

The probability that the two coins would be in the same pocket is 2/4=0.5, because there are two “good” states (the far left and the far right) from 4 possible.

Particles are N=2 *indistinguishable* microparticles which may be in two different states: Such particles are e.g. photons, or certain pairs of electrons.



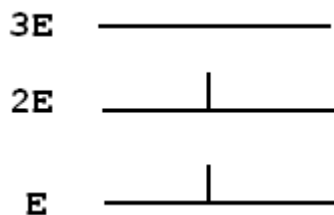
The probability that the two coins would be in the same pocket is $2/3=0.67$, so it's bigger than before. This type of *indistinguishable* microparticles is called bosons. They like to be together. Indeed, the probability that the two coins would be in the same pocket is $2/3=0.67$, because there are two "good" states (the far left and the far right) from 3 possible.

Particles are $N=2$ *indistinguishable* microparticles which may be in two different states, but this time we may have at most one particle in a state:

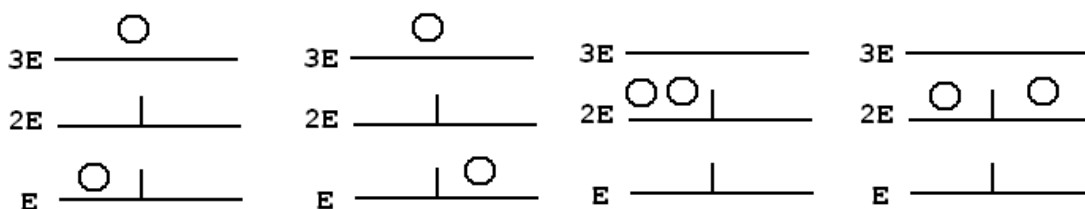


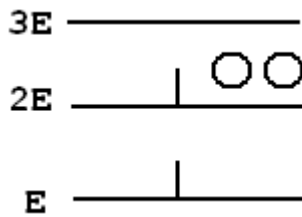
There is just one possible state. This type of *indistinguishable* microparticles is called fermions. They don't like to be together. Such particles are e.g. electrons.

In the above examples we didn't care about physics, but in physics we are interested in distributions with certain limiting conditions (constraints): constant temperature, constant energy, etc. Assume we want to find all the possible states of $N=2$ particles which may have three different states with energies E , $2E$ or $3E$; state with energy E has two sub-states (one says its degeneracy $g=2$ and state with energy $2E$ has the same double degeneracy). The sketch of the possible states is given below (without particles)



We want the possible states with the total energy $U=4E$. They are shown below for bosons:





We may say the system has one macrosate with energy $U=4E$ and 5 compatible microstates, so the statistical weight is $\Omega=5$. These 5 microstates may be classified in two families (they are known as complexities, but we shall not use this name): the first two and the other three. What is the criterion?

The probability that the two particles would have the same energy is $3/5=0.6$.

Exercices. 1. Draw the possible states for the same problem if the particles are fermions.

2. Draw the possible states for the same problem if the particles are classical.

3. Draw the possible states for the same problem if the total energy is $U=5E$.

Stirling approximation

We'll need to compute an approximation of $\ln(n!)$, when $n \gg 1$. What follows is but a rough justification of the result. Write:

$$\ln(n!) = \ln(n \cdot (n-1) \cdot (n-2) \dots 3 \cdot 2 \cdot 1) = \ln n + \ln(n-1) + \dots \ln 3 + \ln 2 + \ln 1$$

As $n \gg 1$ the difference between two adjacent arguments is much smaller than the arguments themselves for many terms. This difference is equal to 1. As it is small, we may (horrible mathematical thing) go from sum to integral putting $dx = 1$:

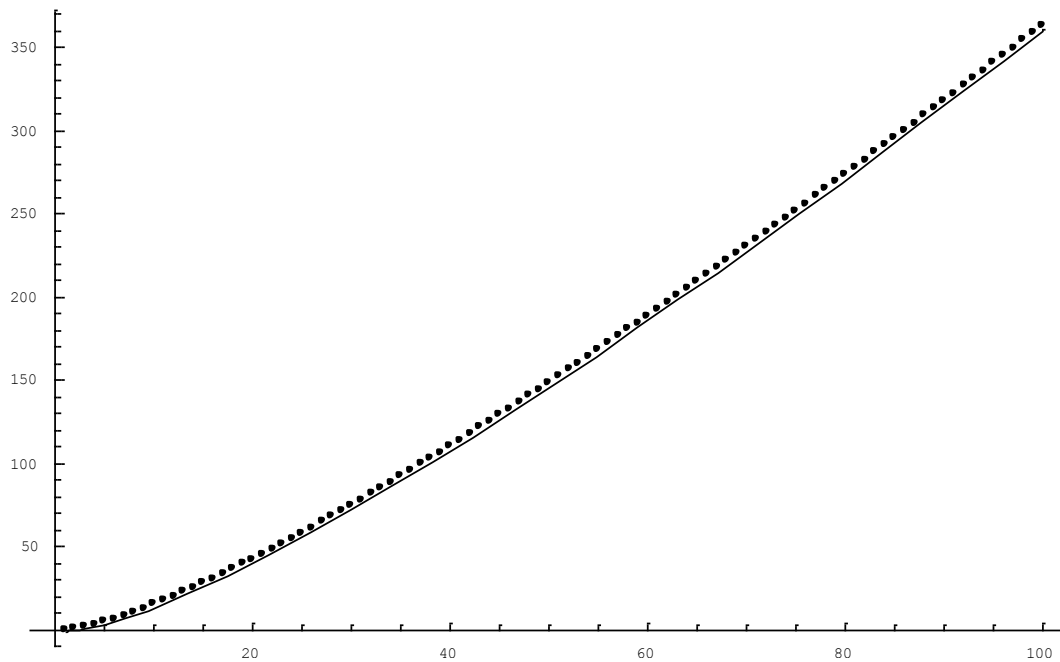
$$\ln(n!) = \ln(n) + \ln(n-1) + \dots \ln 3 + \ln 2 + \ln 1 \cong$$

$$\int_1^n \ln(x) dx = [x \ln(x) - x]_1^n \cong n \ln n - n + 1 \cong n \ln n - n$$

This is the Stirling approximation:

$$\text{Log}(n!) \cong n \text{Log} n - n \quad \text{for } n \gg 1 \quad (36)$$

The following graph shows calculated points $\text{Log}(n!)$ and the Stirling approximation for $1 < x < 100$.



The general problem is: find the equilibrium distribution of N identical particles on states with energies $\varepsilon_1, \varepsilon_2, \varepsilon_3, \dots, \varepsilon_s$, states having degeneracies $g_1, g_2, g_3, \dots, g_s$. The total energy

$$U = \sum_{i=1}^s n_i \varepsilon_i \text{ is constant, as well as the total number of particles } N = \sum_{i=1}^s n_i .$$

We have to find the number of particles on each state, that is the numbers n_1, n_2, \dots, n_s . *The equilibrium distribution is the most disordered one. That means it is the most probable distribution, the distribution with the biggest statistical weight.*

Assumptions:

the temperature is constant, as is the energy (strictly speaking the two conditions are different, but the difference is very small)

the particles are independent, in the sense that we may put any number of particles in any state, if the two conditions

$$N = \sum_{i=1}^s n_i \tag{37}$$

$$U = \sum_{i=1}^s n_i \varepsilon_i \quad (38)$$

are satisfied.

■■■ Not for exam till ■■■ Appendix

Let's compute the statistical weight Ω for a certain distribution of particles among the s states, i.e. the number of ways we obtain certain values of n_i s. It's clear that we obtain the same distribution if we permute the particles. The number of such equivalent distributions is $N!$. But here we add in all the cases where particles in one cell are permuted and that doesn't give new states. So we have to divide by $n_1!n_2!n_3!\dots n_s!$ to get the number of different ways to get a certain family of values n_1, n_2, \dots, n_s :

$$\frac{N!}{n_1!n_2!\dots n_s!}$$

To get the probability of such a distribution we have to multiply this number by the *a priori* probability to have one of these distributions.

The probability that one particle is in the first state is g_1 ; the probability to have n_1 particles in this state is $g_1^{n_1}$

The probability that one particle is in the second state is g_2 ; the probability to have n_2 particles in this state is $g_2^{n_2}$

.....

The probability that one particle is in the s 's state is g_s ; the probability to have n_s particles in this state is $g_s^{n_s}$

The probability to have n_1 particles in the first state, n_2 in the second, ..., n_s in the s 's is the product of the individual probabilities, i.e. $g_1^{n_1} g_2^{n_2} \dots g_s^{n_s}$. The statistical weight is eventually:

$$\Omega = \frac{N!}{n_1!n_2!\dots n_s!} g_1^{n_1} g_2^{n_2} \dots g_s^{n_s} \quad (3A)$$

We want the maximum of this number. It's easier to compute the maximum of its logarithm:

$$\ln\Omega = \ln\left(\frac{N!}{n_1!n_2!\dots n_s!} g_1^{n_1} g_2^{n_2} \dots g_s^{n_s}\right) = N(\ln N - 1) - \sum_{i=1}^s n_i(\ln n_i - 1) + \sum_{i=1}^s n_i(\ln g_i)$$

To find the maximum we compute the derivative and make it zero:

$$d\ln\Omega = \sum_{i=1}^s \left(\ln \frac{g_i}{n_i} - 1\right) dn_i = 0 \quad (4A)$$

Differentiation of the two conditions (1) and (2) gives two new conditions:

$$\sum_{i=1}^s dn_i = 0 \quad (5A)$$

$$\sum_{i=1}^s \varepsilon_i dn_i = 0 \quad (6A)$$

Multiply (5A) by λ and (6A) by $-\beta$ (Lagrange) and add all together to find the conditions:

$$\sum_{i=1}^s \left(\ln \frac{g_i}{n_i} - 1 + \lambda - \beta \varepsilon_i\right) dn_i = 0 \quad (7A)$$

Here all the variations are independent so each bracket is zero and we get:

$$\boxed{n_i = A g_i \exp[-\beta \varepsilon_i]} \quad (8A)$$

which is the Boltzmann distribution. One can demonstrate that $\beta = 1/k_B T$. Note the exponential behavior.

The constant A is obtained from the normalization condition

$$\sum_{i=1}^s n_i = N \quad \text{or} \quad \sum_{i=1}^s \frac{n_i}{N} = \sum_{i=1}^s P_i = 1 \quad (9A)$$

where P_i is the probability to have n_i particles with energy ε_i . Using (8A) we find:

$$\frac{1}{N} \sum_{i=1}^s A g_i \exp[-\beta \varepsilon_i] = 1 \quad \text{hence} \quad A = \frac{N}{\sum_{i=1}^s A g_i \exp[-\beta \varepsilon_i]} \quad (10A)$$

Remark 1. We have assumed energy has a discrete spectrum, it does not vary continuously. This is a quantum picture, used because it is easier to think of numbers instead of continuous varying functions. Anyway, each measurement apparatus has a lower value it can measure, the so-called resolution. We can't measure energy values with accuracy superior than the resolution. So we may assume we measure the energy in discrete portions.



Results:

Boltzmann distribution $n_i = A g_i \exp[-\beta \varepsilon_i]$ (39)

where

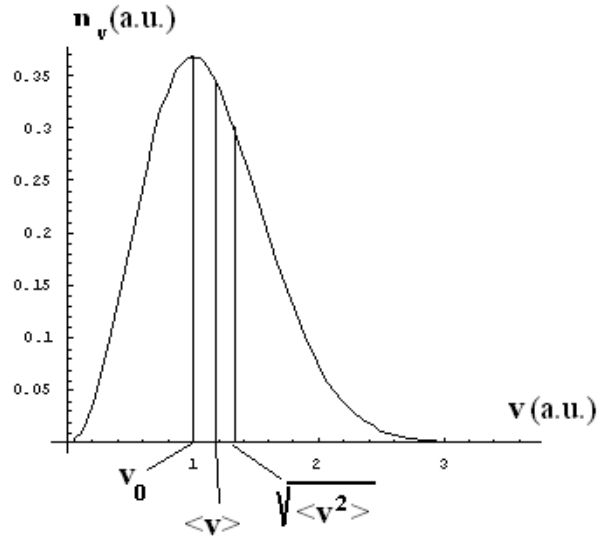
$$\beta = 1/kT \quad (40)$$

Maxwell distribution

Particular situation: we are interested only in the kinetic energy of the molecules.

$$n_v = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp \left[-\frac{mv^2}{2kT} \right] \quad (41)$$

This is the Maxwell velocities distribution. The number of molecules with velocities between v and $v+dv$ is $dn_v = n_v dv$.



$$v_0 = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M_{mol}}}, \quad \langle v \rangle = \sqrt{\frac{8kT}{\pi n}} = \sqrt{\frac{8RT}{\pi M_{mol}}}, \quad \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M_{mol}}} \quad (42)$$

Quantum distributions

Particles with integer spins, $s=0, 1, 2, 3, \dots$. They are called *bosons* and obey the Bose-Einstein statistics. The statistical weight for bosons is given by:

$$\Omega_{BE} = \prod \frac{(g_i + n_i - 1)!}{(g_i - 1)! n_i!} \quad (43)$$

At equilibrium the average number of particles with energy ε_i is given by:

$$\langle n_i \rangle_{B-E} = \frac{g_i}{\exp\left[\frac{\varepsilon_i - \mu_{B-E}}{k_B T}\right] - 1} \quad (44)$$

Particles with half-integer spins, $s=1/2, 3/2, 5/2, \dots$. They are called *fermions* and obey the Fermi-Dirac statistics. The statistical weight for fermions is given by:

$$\Omega_{FD} = \prod \frac{n_i!}{g_i!(g_i - n_i)!} \quad (45)$$

At equilibrium the average number of particles with energy ε_i is given by:

$$\langle n_i \rangle_{F-D} = \frac{g_i}{\exp\left[\frac{\varepsilon_i - \mu_F}{k_B T}\right] + 1} \quad (46)$$