Summary

The short introduction to thermodynamics is given in minimalist approach. Basic knowledge of classical physics is preassumed for the reader of this manuscript. First lecture covers statistical physics with reference to technical sciences.

Keywords and phrases: thermodynamical potentials, grand canonical, canonical and microcanonical ensembles, statistical physics

1. Motivation behind Statistical Physics

In 1cm$^3$ of material as piece of wood we have as much as $10^{23}$ atoms. Modeling of each atom behavior on microscopic level or atom mutual interactions brings enormous complications and is beyond current computation capability. Despite this fact we can predict quite many properties of the given material. It turns out that in the case of thermal equilibrium or in the non-equilibrium case that is not far from thermal equilibrium we can have only few parameters that characterize the system and thus microscopic degrees of freedom can be omitted. In such way thermodynamics laws can be formulated (or more precisely microscopic degrees of freedom become unimportant). We can correlate thermodynamic variables as pressure, temperature, volume or mass density for given classes of materials. Among those variables we have extensive variables (as mass or volume) and intensive variables as pressure or temperature that does not depend on the scale. Thermodynamics usually do not
pay attention to one microscopic configuration of the world but takes into account processes that occur with big frequency and usually are responsible from transferring the system from one microscopic configuration into another one. Because of law of big numbers we arrive to the equivalence of occurrence of given events and their probability. At certain point one can recognize that statistical ensemble is the basic tool used in statistical physics. On another hand statistical ensemble is the tool that is associated to one particle and to many particles in description of quantum mechanics. Therefore certain analogies occur between statistical physics and quantum mechanics. Since the classical picture of the world is more intuitive we start the survey on the statistical physics using the classical physics. Later we can apply the concepts of statistical physics to quantum physics. Indeed second quantization known in advanced quantum mechanics needs to formulated always with reference to statistical physics and great canonical ensemble known from statistical physics course. What is more the concept of programmable matter allows us to generate the new type of systems going beyond known laws of physics [in first appearance since laws of physics are always conserved]. We can apply the concepts of statistical physics to the robotic agents and movement of cars (or other agents) in the city (or in other environments), to sociology, economics or to telecommunication systems. Very last three examples brings certain amount of complications since we can never fully justify when two or more social agents becomes indistinguishable or distinguishable. In such case we are often force to make radical assumptions. For systems of finite size (but still not of infinite size as in thermodynamical limit) it is possible to use both the statistical laws and the description with microscopic degrees of freedom. The prize to be paid for such assumption is the limited accuracy of statistical picture that is not fully corresponding to rigorous statistical limit that is reserved only for homogenous systems of infinite size and when number of particles goes to infinity. Nevertheless the thermometer of small size made of glass and with mercury inside can measure the temperature of our body in finite time of 5 minutes. Even the glass in window is the state of matter that is not in thermodynamic stability. The glasses in windows older than 100 years usually are thicker in lower part since glass can flow very slowly under gravitation force. Despite the fact that thermodynamical limit is not fullfilled in orthodox way as it is the case of mercury thermometer of finite size the use of concepts of thermodynamics for finite size systems and in measurement of given property of thermodynamical system done in finite time is quite effective and practical.

1.1. Ideal gas and the equation of state

First idealistic and didactic case is the model of ideal gas made of hard impenetrable and very stiff spheres of finite radius that collides in elastic way. Let us consider the particle of finite mass and radius in 2 (3) dimensional box of \((L \times L \times L)\). If we reduce
situation to 1 dimension it gives situation as depicted in Fig.1. In such case we can also use virial theorem.

Fig. 1. Case of particle confined in 1 dimension (left) and 2 or 3 dimensional case of particles confined in big tank. Relation with of macroscopic and microscopic variables is visualized [4].

Nevertheless just by using Newtonian physics we obtain the relation between pressure and volume given by the change of particle momentum. We assume that collisions are perfect elastic and that are lasting infinitely short time. The change of momentum with time is \( \frac{dp_x}{d\tau} = \frac{2p_x}{2T} = \langle F_x \rangle = \langle p \rangle S \), where \( F_x \) is average force acting on each wall confining particle and having surface \( S \). At the same time \( \frac{2L}{2T} = v_x \) what brings \( \frac{L}{v_x} = T \) and consequently gives \( \frac{mv_x^2}{L} = S \langle p \rangle \) so \( \langle p \rangle V = 2E_k \). Now it is necessary to assume that \( E_k = \gamma T \) that means kinetic energy parameterized in linear way by temperature \( T \). Thus we arrive to the well-know case of equation of state for ideal gas \( pV = nRT \), where \( n \) is average density of mols per volume of ideal gas and \( R \) is constant (known as ideal, or universal, gas constant, equal to the product of the Boltzmann constant and the Avogadro constant). Similar reasoning can be conducted in 2 and 3 dimensional case and will lead to the same equation of state. The presented model of ideal gas is important since it shows the connection between pressure, volume and kinetic energy. It gives first definition of temperature and develops our intuition about entropy. It will be also helpful in formulation laws of thermodynamics that needs to be confirmed by more complicated models.

In general the following equation of the state is fulfilled

\[ pf(V) = nRT. \] (1)

One of particular cases of mentioned equation is van der Waals equation.

\[ (p + aN^2/V^2)(V - Nb) = nRT \] (2)

This equation brings the correction to contribution to particle pressure since it assumes 2 body particle-particle interaction conveyed at certain distance and represented by term \( \frac{a}{V^2} \). At the same time this equation assumes that the gas can be squeezed into some minimum residual volume \( b \). Quite obviously if we have \( N \) balls with certain radius it is the case. It is quite important that ideal gas model does
not predict any phase transition while van der Waals model is able to describe phase transition. Van der Waals equation is also able to predict existence of tricritical point in water when there is coexistence of all 3 phases: solid, liquid and gas.

2. Laws of thermodynamics

Now we need to formulate or to postulate 4 laws of thermodynamics. There are many excellent books on this topic as [1], [3]. It shall be underlined that those laws can be achieved only in thermodynamical limit when number of particles under consideration \( n \to +\infty \) and volume of system goes to infinity with constant kept density of particles \( n \to \frac{N}{V} \to +\infty = \text{constant} \). In practical way it means that we need to deal with infinite uniform physical systems that are never existing in nature since systems perceived by us are of finite size and usually non-uniform (only in certain small volume can be regarded as uniform). Also observation time needed for assessment average value of thermodynamical quantities shall be infinite but in case of experiment is large and finite. This means that in practical cases the thermodynamics laws are very useful approximation of reality.

**O: Zero law of thermodynamics** states that if \( A \) system is in thermal equilibrium with \( B \) system and if \( B \) system is in thermal equilibrium with \( C \) system that \( A \) is in thermal equilibrium with \( C \) system.

Example can be verified experimentally. If I use thermometer with mercury and place it to the body for sufficient long time it will achieve thermal equilibrium with our body. In normal state of our body (that is average case) the thermometer should measure 36.6 C degrees. If we pass given thermometer to another person and he/she measures the temperature of his/her body and gets 36.6 degree C than we can say that two bodies are in the thermal equilibrium. We shall notice that in order to achieve thermal equilibrium between two physical systems (finite or infinite) we need to wait infinite long time, which is not the case of real experiments.

Another issue that was not touched is the fact that system in given thermodynamical equilibrium might be subjected to some local excitation. Usually excitations decay with some characteristic time \( \tau \). However if the excitation is not small it might bring the whole system to new phase as by pushing the system into phase transition. In this context it is interesting to point on the case of matter subjected to extremly energetic gamma radiation. If one photon coming from space has extremly high energy as 1 Joule and hits the solid state that is in equilibrium state it will generate the whole moving cloud of highly energetic particles. Only after certain time the whole system thermalize and will approach equilibrium. However before thermalization the
system cannot be described by thermodynamics that avoids microscopic degrees of freedom (and assumes that all microscopic degrees of freedom can be approximated by few thermodynamic parameters) and one needs to account all particle-particle interactions.

Only basing on imagination and suggestions coming from model of ideal gas we can postulate zero, first and second law of thermodynamics. However the reality exhibits much complex behaviour than ideal gas. We need to assume that more detailed quantum description of matter will bring the corrections to model of ideal gas. From classical and quantum description of the world we can obtain 3rd law of thermodynamics.

**I: First law of thermodynamics** states that work performed over given physical system is equivalent to the transfer of heat and change of internal energy of the given physical system. This law of thermodynamics is depicted in Fig.2. This can expressed by equation $dW = dU + dQ$ which means of given work $dW$ is used (partitioned) into change of internal energy of the system $dU$ and into heat energy $dQ$.

This law can also be stated that energy can be converted from one form into another form but never disappears.

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Fig. 2. Work and heat equivalence in 2 cases [4]: (Left) conversion of kinetic energy into heat in water, (Right) conversion of heat energy into kinetic energy. Depicted situation is known as James Joule’s famous experiment that demonstrated the mechanical equivalence of heat energy and work.

**II: Second law of thermodynamics** states that entropy of open system always increases with long time.

Entropy is a measure of uncertainty or lack of information. Let us consider the
case of brick moving on some rough surface with occurrence of friction perpendicular
to the Earth gravitational field. Since we never fully know the exact texture of surface
the exact mechanism of heat generation cannot be modeled for given system. One
moving brick is slowing down and its energy kinetic energy movement in one direction
is transferred to many energetic channels. Such situation is very common in nature.
We use to say that the entropy is increasing. Formally the whole system is still
deterministic. Nevertheless at some point we are loosing the ability to model its exact
state due to lack of full information on the system and due to finite computational
resources. In such way we are pushed into statistical way of thinking.

Another similar example can be the situation with kinetic energy of macroscopic
ball moving in space. It can be always changed into heat energy of many vibrating
particles from which given ball is made of. While moving macroscopic ball has certain
dynamical state, which is correlated with certain information allowing deterministic
prediction of ball position and velocity, many vibrating particles in the ball does
not transfer explicit information that can be perceived on macroscopic level. If such
ball (as the bullet coming from gun) hits its solid target most of its kinetic energy
is converted into heat. Thus entropy is a measure of the amount of energy which is
unavailable to do work. Entropy change $dS$ is defined as $dS = \frac{dQ}{T}$.

The principle of entropy increase is illustrated on the example of diffusion of ink
in water and charged billiard balls moving on billiard table in Fig.17. - Fig.22 and
participating in perfect elastic collisions (that last infinitely short time and there is
no transfer of charge between balls). They participate in elastic collisions. The phys-
ical system under evolution with time is occupying (passing via) all available states
(possibilities).

It shall be notes that the entropy might fluctuate but for sufficiently long time
will always increase. The entropy fluctuations are prominent for small systems that
are very far from assumptions coming from thermodynamical limit.

Second law of thermodynamics also states that it is not possible to build the en-
gine efficient in 100 percent that transfers heat energy (as coming from combustion
of some fuel type as oil) into mechanical work and that such engine has efficiency
always smaller than 100 percent. Such conclusion can be extracted from right side
of Fig.2.

Heat flow from hotter body to colder body is due to principle of increasing entropy.
It shall be mentioned that in nanosystems it is not always the case since thermody-
namic limit is not fullfilled.
It is worth mentioning that increasing entropy points direction of time arrow. All irreversible process are characterized by entropy increase. Diffusion process is very characteristic and illustrating principle of entropy increase. In this context Brownian movement is also example of the case when entropy is increasing.

**III: Third law of thermodynamics (sometimes known as zero law or Nernst law)** states that for temperature of physical system going to zero we have entropy of system going to zero. Basically it means that density of states (number of possible configurations) is decreasing when system approaches zero temperature. The dramatic effect is that in case of all physical systems specific heat is proportional to temperature for sufficiently low temperatures $T \to 0$.

The entropy is the measure of volume of possible states occupied by the system. In certain cases entropy can be understood as lack of ordering. For low temperatures tends to be zero (Nernst law). Thus ferromagnetic (antiferromagnetic) materials tends to have all spins directed in one direction in low temperatures in parallel (or in antiparallel fashion) and entropy is going to 0. On another hand in high temperature situation spins can have arbitrary direction and thus it can be translated as lack of ordering. This lack of ordering is due to the fact that spins have much bigger phase space.

With increase of temperature we have more and more possible states in which particles might be and thus volume of occupied states is bigger. Thus we are dealing with increasing entropy.

Another fundamental quantity is temperature. In case of hard spheres it parameterizes their average kinetic energy in proportional way. Thus we have $E_k = \frac{1}{2}mv_k^2 = ak_bT$, where $a$ is some constant. However it needs to be defined in more precise way in relation to other thermodynamic variables.

Before moving to more detailed description it is necessary to mention 3 basic cases that needs to be analyzed and that have name of ensembles: microcanonical, canonical and grand canonical ensemble. In first case the good number is energy $E$, in second case the good number is free Helmoholtz energy $F$ and in third case the good number is grand canonical potential $\Omega$.

In insulated physical system we have energy conservation as it is the case of satellite moving on given orbit in gravitational field of Earth (with absence of other sources of fields). In case of satellite is convenient to describe the system with use of Hamiltonian (that is the sum of kinetic and potential energy) approach so position of $i$-th particle $q_i(t)$ and its momentum $p_i(t)$ with components $s = x, y, z$ are governed by equations $\left( \frac{dp_{i,s}}{dt} = - \frac{dH}{dq_{i,s}}, \frac{dq_{i,s}}{dt} = + \frac{dH}{dq_{i,s}} \right)$. Hamiltonian is preserved in case of
insulated physical system. The good example is pendulum depicted in Fig.3. In mentioned example we have full determinism of behavior of system with time. At the same time we have all the information about the system.

![Fig. 3. Pendulum and its phase space [19].](image)

It shall be underlined that in general the whole universe can be described by one Hamiltonian. However this Hamiltonian is unknown since we do not know all position and velocities of particles at given time and we have limited computation possibilities. At the same time there are still new laws of physics that need to be discovered or reformulated.

We have to accept the fact that we do not know the positions of all particles and their energy. However they still transport energy and momentum. The equivalence of heat to work (that can be understood as change of kinetic energy) was the base for first thermodynamic principle.

In such case kinetic energy can be converted into heat and some heat can be converted into kinetic energy while some energy can be stored as internal energy.

On another hand temperature is measure of average kinetic energy of vibrating particles.

The main principle governing the thermodynamical ensembles is principle of maximum entropy.

If we set conglomeration of balls concentrated in one region on the billboard table and evolve in time after long evolution they will be dislocated in more kind of uniform way. Thus the entropy of the system will be maximized after long evolution time.

Now we need to formalize all concepts and physical quantities as (pressure \(p\), temperature \(T\), entropy \(S\)) and bring reference to certain physical cases.

Let us start from concept of entropy. We will define it as the measure of states that can be achieved by the system.
2.1. Characterization of microcanonical ensemble (NVE)

Such ensemble is basically isolated physical system that has no interaction with external world. The system is confined in space with certain fixed volume $V = \text{constant}$, fixed average energy $E$ and fixed number of particles $N = \text{constant}$. Thus we deal with NVE ensemble. All particles are subjected to equations of motions expressed as

$$\frac{d}{dt}p = +\frac{dH(q,p)}{dq}$$

(3)

and

$$\frac{d}{dt}q = -\frac{dH(q,p)}{dp}.$$  

(4)

We have two conjugate variables as $q$ and $p$ that determines of phase space. (In case of classical harmonic oscillator $q = x$ and $p = m\frac{dx}{dt} = mv$ and $H(q,p) = \frac{p^2}{2m} + k\frac{q^2}{2}$.)

The scheme of system in microcanonical ensemble is given by collection of particles confined in isolated container what is depicted in Fig.4.

![Fig. 4. Physical situation corresponding to microcanonical ensemble as N particles confined in box of volume V with impenetrable and isolative walls [9].](image)

We can make some analogies with our solar system or with atom described in classical way (when we omit the emission of electromagnetic waves due to acceleration of charged particles and when electrons and nucleus are impenetrable balls of certain radius). Basing on this analogy we can state that certain orbits have higher frequency of appearance than others.

However in most general case we are dealing with $N$ body Hamiltonian for specified big number of particles $N_t$. In such case the evolution of the system depends only on the initial parameters of all positions of particles and their velocities. Still total Hamiltonian of system is time independent. The Poincar recurrence theorem states (as given by Wikipedia) that certain confined (as bounded particles) systems will, after a sufficiently long but finite time, return to a state very close to the initial state. The result applies to isolated mechanical systems subject to some constraints, e.g., all particles must be bound to a finite volume. The example of usage of Poincare recurrence theorem is depicted in Fig.5.
2.2. Liouville theorem

Let us assume that given measure observable \( f(q,p) \) depends explicitly on position and momentum of all particles in the system. Due to the evolution of all position and momenta in time we have non-explicit dependence of \( f \) on time. We can write

\[
\frac{df}{dt} = \frac{df}{dq} \frac{dq}{dt} + \frac{df}{dp} \frac{dp}{dt} = [\dot{q} \frac{d}{dq} - \dot{p} \frac{d}{dp}]f = [\frac{dH}{dp} \frac{d}{dq} - \frac{dH}{dq} \frac{d}{dp}]f = -i\hat{L}f. \tag{5}
\]

It shall be noticed that the solution can be written in operator form as \( f(t) = e^{-i\hat{L}(t-t_0)} f(t_0) \). Liouville approach is valid both in classical and in quantum picture.

In this context it is usefull to introduce Poisson bracket of two variables \( A(p,q) \) and \( B(p,q) \) defined as \( \{ A, B \} = (\frac{d}{dq}A \frac{d}{dq}B - \frac{d}{dq}B \frac{d}{dq}A) \). Indeed Poissonian will be the precursor of commutator of two obserables \( A \) and \( B \) (\( [A, B] = AB - BA \)) so heavily used in quantum mechanics. The equation of motion for observable \( f \) is

\[
\frac{df}{dt} = \{ f, H \}. \tag{6}
\]

It shall be underlined that aveaged measured value of \( f \) observable is given as

\[
\langle f \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(p,q)\rho(p,q)dpdq. \tag{7}
\]

Similar relation occurs in quantum mechanics. There are certain analogies between quantum physics and statistical physics.
Act of observation is usually performed in time scale that is infinitely long in comparison in time scale characteristic for microscopic processes.

\[ <f> = \lim_{T \to +\infty} \int_0^T f(t) dt. \] (8)

Here we will assume that \( f(p, q) \) distribution is constant. Such assumption is only partially true in case of \( N \) number of interacting particles in given volume as it is depicted in Fig.4, where one can have mixture of balls positively and negatively charged and impenetrable.

\[ f(p, q) = \begin{cases} \frac{1}{\Gamma(N, V, E)}, & \text{if } E < H(p, q) < E + \Delta \\ 0, & \text{otherwise.} \end{cases} \]

Here volume of phase space \( \Gamma(N, V, E) \) is defined as

\[ \Gamma(N, V, E) = \int d\mathbf{p} d\mathbf{r} \rho(H(p, r)) d\mathbf{p} d\mathbf{r} = \text{const} \int_{E<H(p,q)<E+\Delta} d\mathbf{p} d\mathbf{r}. \] (9)

We can state that the energies up to certain energy and momentum are occupied since particles are in bound state.

In given context we can define entropy as measure of volume of available phase space

\[ S(N, E, V) = k_b \ln(\Gamma(N, V, E)). \] (10)

It shall be noticed that only some occupied subspace is available to us that is described with thickness \( \Delta \).

Much bigger space \( \Phi(N, V, E) = \int_{H(p,q)<E} d\mathbf{p} d\mathbf{q} \). It implies relation between two spaces \( \Phi(N, V, E) \) and \( \Gamma(N, V, E) \) as \( \Gamma(N, E, V) = \frac{d\phi(N,E,V)}{dE} \Delta \). Later we can make analogy of \( \Gamma \) with space of available states at Fermi surface in solid state physics. Most states below Fermi level are not available that is the case of \( \Phi \) space. Therefore somehow more interesting is \( \Gamma \) space that is surface of \( \Phi \) space with thickness \( \Delta \).

In case of two statistically independent systems given by spaces \( \Gamma_1 \) and \( \Gamma_2 \) we have \( \Gamma = \Gamma_1 \Gamma_2 \). In such case the entropy is additive \( S = k_b \ln(\Gamma) = k_b \ln(\Gamma_1 \Gamma_2) = k_b \ln(\Gamma_1) + k_b \ln(\Gamma_2) = S_1 + S_2 \). In other case the entropy is not additive.

Now we can ask the question about the relation between temperature, energy and entropy. One of postulated relation can be \( \frac{dU}{T} = dS \) and it will be analogical to ideal gas where we replaced \( dQ \) with \( dE \) and change of internal energy \( dU \) is equivalent to \( dE \) that is the case of microcanonical ensemble.

It is first Maxwell relation that can be written for microcanonical ensemble. Let us make small hole in insulative wall. In such case the particles can leave the system
and work on them \( dW = -pdV = dU \). This brings another Maxwell relation.

Writing \( dU = dE \) is justified since we have no heat flow in case of microcanonical ensemble. We can also write \( \frac{dE}{T} = \Gamma \) and introduced Density of States \( D(E) = \frac{d\Gamma}{dE} \).

Density of states \((D(E))\) is always finite. When \( T \to 0 \quad \Gamma(T) \to \text{constant} \). It means that for low temperatures \( \Gamma(\Delta) \propto T \). It is because of \( \Delta \propto T \).

Fig. 6. Volume of phase space in microcanonical ensemble [3].

### 2.3. Considerations in relation to Liouville theorem

Instead of talking about \( q_i \) and \( p_i \) as independent variables we shall categorize them as members of phase space. In case of \( N \) particles we have \( 6N \) phase space components \( u = (q_{1,x}, q_{1,y}, q_{1,z}, ..., q_{N,x}, q_{N,y}, q_{N,z}, p_{1,x}, p_{1,y}, p_{1,z}, ..., p_{N,x}, p_{N,y}, p_{N,z}) \). We can introduce the 6th dimensional speed in our phase space. In such case we define 6N dimensional velocity in our phase space given as

\[
\frac{du}{dt} = \left( \frac{dq_{1,x}}{dt}, \frac{dq_{1,y}}{dt}, \frac{dq_{1,z}}{dt}, ..., \frac{dq_{N,x}}{dt}, \frac{dq_{N,y}}{dt}, \frac{dq_{N,z}}{dt}, \frac{dp_{1,x}}{dt}, ..., \frac{dp_{N,z}}{dt} \right)
\]

In given context it is quite natural to think about 6\( N \) dimensional current flowing in our phase space \( \Gamma \). Let us introduce density of probability of occupation of given area of space \( \rho(q_{1,x}, q_{1,y}, q_{1,z}, ..., q_{N,x}, q_{N,y}, q_{N,z}, p_{1,x}, p_{1,y}, p_{1,z}, ..., p_{N,x}, p_{N,y}, p_{N,z}) \).

Here \( \rho \) plays the same role as density of electric charge. It is normalized over the whole \( \Gamma \) space what is expressed by the condition \( \int \rho d\mathbf{q} d\mathbf{p} = 1 \) (or some constant in general case). Here \( d\mathbf{q} = dq_{1,x} dq_{1,y} dq_{1,z} dq_{2,x} dq_{2,y} dq_{2,z} ... dq_{N,x} dq_{N,y} dq_{N,z} \) and consequently \( d\mathbf{p} = dp_{1,x} dp_{1,y} dp_{1,z} dp_{2,x} dp_{2,y} dp_{2,z} ... dp_{N,x} dp_{N,y} dp_{N,z} \). Thus we can introduce mass current \( \mathbf{j} = \rho(du/dt) \) in our phase space. Explicitly it is given as

\[
\mathbf{j} = \rho \left( \frac{dq_{1,x}}{dt}, \frac{dq_{1,y}}{dt}, \frac{dq_{1,z}}{dt}, ..., \frac{dq_{N,x}}{dt}, \frac{dq_{N,y}}{dt}, \frac{dq_{N,z}}{dt}, \frac{dp_{1,x}}{dt}, ..., \frac{dp_{N,z}}{dt}, F_{1,x}, F_{1,y}, F_{1,z}, ..., F_{N,x}, F_{N,y}, F_{N,z} \right).
\]

The conservation of electric charge brings relation between electric current density
and change of current at given position in space expressed in relation
\[
\frac{dp(x,y,z)}{dt} + div_3(j(x,y,z)) = 0.
\]
Here divergence in 3 dimensional space is defined as
\[
div_3(j(x,y,z)) = \frac{d}{dx} j_x(x,y,z) + \frac{d}{dy} j_y(x,y,z) + \frac{d}{dz} j_z(x,y,z).
\]
Mathematically it can be explained by the divergence theorem (more commonly known especially in older literature as Gauss’s theorem (e.g., Arfken 1985) and also known as the Gauss-Ostrogradsky theorem). Now we can extend the definition of current to \( \Gamma \) space. In such case we obtain
\[
div_{\Gamma} \mathbf{j} = \frac{d}{dq_{1,x}} (\dot{q}_x(1)\rho) + \frac{d}{dq_{1,y}} (\dot{q}_y(1)\rho) + \frac{d}{dq_{1,z}} (\dot{q}_z(1)\rho) + \frac{d}{dq_{2,x}} (\dot{q}_x(2)\rho) + \frac{d}{dq_{2,y}} (\dot{q}_y(2)\rho) + \frac{d}{dq_{2,z}} (\dot{q}_z(2)\rho) + \ldots + \frac{d}{dq_{N,x}} (\dot{q}_x(N)\rho) + \frac{d}{dq_{N,y}} (\dot{q}_y(N)\rho) + \frac{d}{dq_{N,z}} (\dot{q}_z(N)\rho) + \frac{d}{dp_{1,x}} (\dot{p}_x(1)\rho) + \frac{d}{dp_{1,y}} (\dot{p}_y(1)\rho) + \ldots + \frac{d}{dp_{N,x}} (\dot{p}_x(N)\rho) + \frac{d}{dp_{N,y}} (\dot{p}_y(N)\rho) + \frac{d}{dp_{N,z}} (\dot{p}_z(N)\rho) = -\frac{d}{dt}\rho(q_1(1), q_2(1), q_3(1), q_4(1), q_5(1), \ldots, q_x(1), q_y(1), q_z(1), \dot{q}_x(1), \dot{q}_y(1), \dot{q}_z(1), \ldots, q_x(N), q_y(N), q_z(N)).
\]

We are considering the stationary case when probability distribution does not depend on the time so \( \frac{d}{dt}(\rho) = 0 \). For simplicity let us limit considerations to 1 dimension. We consider terms as \( L_x = \frac{d}{dq_{1,x}} (\dot{q}_x(1)\rho) + \ldots + \frac{d}{dq_{N,x}} (\dot{q}_x(N)\rho) + \frac{d}{dp_{1,x}} (\dot{p}_x(1)\rho) + \ldots + \frac{d}{dp_{N,x}} (\dot{p}_x(N)\rho) \). If \( \rho \) is uniform and is not depending on \( q(i)_x, q(i)_y, q(i)_z \) and on \( p(i)_x, p(i)_y, p(i)_z \) we have
\[
L_x = \rho \frac{d}{dq_{1,x}} (\dot{q}_x(1)\rho) + \ldots + \frac{d}{dq_{N,x}} (\dot{q}_x(N)\rho) + \frac{d}{dp_{1,x}} (\dot{p}_x(1)\rho) + \ldots + \frac{d}{dp_{N,x}} (\dot{p}_x(N)\rho).
\]

Coming back to Hamilton equations we notice that for \( i \)-th particle occurs relations
\[
\frac{dq(i)}{dq(i)} = -\frac{dp_i}{dp_x(i)} = \frac{d^2H}{dq(i)dp_x(i)}.
\]
The same properties occur for \( y \) and \( z \) coordinates so
\[
\frac{dq(i)}{dq(i)} = -\frac{dp_y(i)}{dp_y(i)} = \frac{d^2H}{dq_y(i)dp_y(i)}.
\]

The uniformity of \( \rho \) (that is lack of its dependence on position of particles and their momenta) implies the stationary condition that \( \rho \) is time independent. Mathematicians like to have ideal cases as constant uniform \( \rho \). However this is no case of any physical system!! In particular we have granular matter and point-like electric charges etc. However looking on the system from certain perspective we can attempt such assumptions.

### 2.4. Characterization of canonical ensemble (TVN)

Such ensemble is basically physical system 1 that can exchange heat but no particles (\( N_i = \text{constants} \)) with external world 2 as it is depicted in Fig.7. The good example is plastic closed bottle embedded in the steady lake.
Fig. 7. Physical situation corresponding to canonical ensemble where $T$, $V$, $N$ numbers determine the state of the small system embedded in large system with possible heat flow, and work done on small system and fixed number of particles $N_1 = constant_1$ and $N_2 = constant_2$ in both systems. The good realistic example is plastic bottle placed in the lake [9].

Fig. 8. (Left): Experimental confirmation of diffusion of ink in water. (Right): Evolution of system from states concentrated in one geometrical place of billiard table into equiprobable states.

In certain approximation we can write

$$H(q_1, p_1, q_2, p_2) = H_1(q_1, p_1) + H_2(q_2, p_2) + V(q_1, p_1, q_2, p_2) =$$
$$\approx H_1(q_1, p_1) + H_2(q_2, p_2). \quad (13)$$

The exchange of heat with external world makes the energy the quantity that is not preserved. The ensemble is known as TVN ensemble and is depicted in Fig. 7. In such case $E_2 > E_1$ (energy of given system embedded in reservoir is smaller than the energy of reservoir), mass of given system is much smaller than the mass of reservoir ($N_2 > N_1$) and $N_1 = constans$, $N_2 = constans$. Obviously sum of energy of given system $E_1$ and reservoir $E_2$ that is $E_1 + E_2$ is preserved. However it does not imply preservation of $E_1$ energy. Basing on first thermodynamical principle we have the relation $dW = dU - dQ$. Since $T=constans$ we have $dQ=TdS$ and this implies $dW = dU - dTS$. Therefore one needs introduce new quantity that is Helmholtz free energy $F = U - TS$ so $dF = dU - TdS$. There $dF$ plays role of work $dW$. Therefore role of energy was taken by free energy $F$. Indeed it is seen in Maxwell relations as when we compare canonical to micro-canonical ensemble. In particular we have $P = -\frac{dF}{dV} \mid T, V = constant$, $S = -\frac{dF}{dT} \mid N, V = constant$, $\mu = -\frac{dF}{dN} \mid T, V = constant$ in canonical ensemble, while we have $P = -\frac{dU}{dV} \mid E, T = constant$, $S = -\frac{dU}{dT} \mid V, N = constant$. 
\[ \mu = -\frac{dU}{dN} |_{E,V=\text{constant}} \] in microcanonical ensemble. In this context we shall mention that pressure is thermodynamical force coming from Maxwell relations. Instead of pressure we might have electrostatic field if we are dealing with another physical system, etc.

Partition function (for canonical ensemble) is defined as \[ Z = \sum_{n} e^{-\frac{E_n}{k_bT}}, \] where we sum over all energies \( E_n \) occuring in the system. More general definiton of partion function for TVN esemble can be pointed

\begin{equation}
Z(T,V,N) = \frac{1}{h^{3N}N!} \int \exp(-\beta H(q,p))dqdp,
\end{equation}

where \( H \) is Hamiltonian of the system, \( \beta = \frac{1}{kT} \) and \( N! \) is because of indistinguishibility of particles. Here \( h \) is Planck constant. Partition function has certain class of properties that can be exploited in statistical analysic of physical systems. If we are dealing with 2 non-interacting physical systems with Hamiltonians \( H_1 \) and \( H_2 \) and number of particles \( N_1 \) and \( N_2 \) we obtain the following partion function

\begin{equation}
Z(T,V,N) = Z_1 Z_2.
\end{equation}

We can also obtain average value of energy \( < H > \) by differentiation of partion function in way as given below:

\begin{equation}
<H> = -\frac{d}{d\beta} \frac{Z(T,V,N)}{Z} = -\frac{d}{d\beta} \log(Z(T,V,N)).
\end{equation}

Acting in the same fashion as before we can obtain \( < H^2 > = \frac{d^2}{d\beta^2} Z(T,V,N) \) so variation \( < \Delta H > = < H^2 > - (< H >)^2 \) \begin{equation}
\frac{d^2}{d\beta^2} \frac{Z(T,V,N)}{Z} - \left( \frac{d}{d\beta} \frac{Z}{Z} \right)^2.
\end{equation}

In such way we can compute any cummulant of any order of variable \( H \). Later we will see that \( e^{-\frac{F}{k_bT}} = Z \) In very real sense \( F \) can be treated as effective Hamiltonian. In the canonical ensemble, the system acquire a temperature by having a thermal contact with a thermostat (heat bath) with temperature \( T \). Thus the system is no longer isolated any more. Its total energy, i.e., Hamiltonian is no longer conserved. In other words, we should expect some fluctuation of total energy in the canonical ensemble. The non-zero variance of \( H \) is its measure of fluctuations strenght.

The mathematical comparison between microcanonical and canonical ensemble is give in Fig.9. Since energy is unique and established for microcanonical ensemble we can write volume of microstates as \( \Gamma(N,V,E) = \int dpdq\delta(E_1 - E)dE_1. \)
Physical system that can be described by canonical ensemble is electric wire lying on the table in the room of certain temperature. The number of atoms in wire are preserved. Therefore canonical ensemble shall give hint in determination of noise present in electric cable.

### 2.5. Properties of grand canonical ensemble (T, V, \( \mu \))

Such ensemble is basically physical system that can exchange particles and energy with with external world. However it is in thermal equilibrium with outside reservoir and is depicted in Fig.10. The good example is ice swimming in the lake.

\[
H(N = N_1 + N_2) = H_1(q_1, p_1, N_1) + H_2(q_2, p_2, N_2) - \mu(N_1 - N_2)
\]

\( \mu \) is the heat needed to melt the ice in very slow way so its volume can be preserved. During the whole process \( \mu \) is set to constant.

\[
\mu = \text{heat needed to melt the ice in very slow way}
\]

\[
\mu(\text{N}_1 - \text{N}_2)
\]

Fig. 10. Physical situation corresponding to grand canonical ensemble where \( \mu, V, T \) numbers determine the state of the small system embedded in large system with possible heat flow, and work done on small system and can be exchange of particles \( N_1 \neq \text{constant} \) while \( N_1 + N_2 = \text{constant} \) in both systems. The good realistic example is piece of ice swimming in the lake[9].

Since in canonical ensemble the effective allowed mechanical work was \( dF = dU -TdS \) then in grand canonical ensemble would be \( d\phi = dU - TdS - \mu dN \). Therefore we need to introduce new quantity \( \phi = U - TS - \mu N \). There is no change of volume of smaller system embedded in bigger system. Total energy change of embedded system can be achieved only when \( \mu \) and \( T \) are kept constant and when \( dU, dS \) and

<table>
<thead>
<tr>
<th>Phase space integration</th>
<th>Microcanonical ensemble</th>
<th>Canonical ensemble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase space integration</td>
<td>( \Gamma ) = ( \int d^3N \delta(E - H) )</td>
<td>( Z(T) = \int \frac{d^3N e^{-H(q,p)}}{h^3N!} )</td>
</tr>
<tr>
<td>Thermodynamic potential</td>
<td>( S(E,V,N) = k_B \ln\left( \frac{\Gamma(E)}{h^{3N}N!} \right) )</td>
<td>( F(T,V,N) = -k_B T \ln Z(T) )</td>
</tr>
</tbody>
</table>
dN are non-zero. Therefore such ensemble has the name \((\mu, V, T)\) ensemble. The new quantity has the name of grand thermodynamical potential \(\phi\). In given context we can also define another thermodynamical ensemble \(G = U - TS + pV - \mu N\) It has also the name of Gibbs free energy G and the whole ensemble has the name of Gibbs ensemble.

It is often useful to consider canonical ensembles given as depicted in Fig.11. In this context both from mathematical motivation or from physical motivation we can also postulate another thermodynamic potential as enthalpy \(H = U + pV\). The family of introduced thermodynamical potentials is specified in Fig.12. They are interlinked by Legendre transformations.

Fig. 11. Different ensembles as occurring in different biasing thermodynamical conditions [Wikipedia].

<table>
<thead>
<tr>
<th>function</th>
<th>form</th>
<th>nat. variables</th>
<th>name</th>
</tr>
</thead>
<tbody>
<tr>
<td>(U)</td>
<td>(U - TS)</td>
<td>(S, V, N)</td>
<td>energy</td>
</tr>
<tr>
<td>(F)</td>
<td>(U - TS)</td>
<td>(T, V, N)</td>
<td>free energy (Helmholtz)</td>
</tr>
<tr>
<td>(H)</td>
<td>(U + pV)</td>
<td>(S, p, N)</td>
<td>enthalpy</td>
</tr>
<tr>
<td>(G)</td>
<td>(U - TS + pV)</td>
<td>(T, p, N)</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>(\Phi)</td>
<td>(U - TS - \mu N)</td>
<td>(T, V, \mu)</td>
<td>Grand potential</td>
</tr>
</tbody>
</table>

Fig. 12. Different possibilities for definition of thermodynamical potentials. One shall relate it with conjugate thermodynamical variables 15.

The summary on thermodynamical potentials and Maxwell relations is given in 16. In this context we can point thermodynamical forces that are different in different physical systems. For example we can have pressure \(p\) in one system or intensity of electric field in another system.
Fig. 13. Simple ways to relate thermodynamical potentials with thermodynamical variables [3].

<table>
<thead>
<tr>
<th>Potential</th>
<th>Classical mechanics</th>
<th>Thermodynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Independent variables</td>
<td>$V(x, y, z)$</td>
<td>$U(S, V, N)$</td>
</tr>
<tr>
<td>Dependent variables obtained</td>
<td>$x, y, z$</td>
<td>$S, V, N$</td>
</tr>
<tr>
<td>differentiating</td>
<td>$F = -\frac{\partial V}{\partial x}$, ...</td>
<td>Maxwell relations: $P = -\left(\frac{\partial U}{\partial V}\right)_S$, ...</td>
</tr>
</tbody>
</table>

Fig. 14. Analogies between classical mechanics and thermodynamics [9].

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Entropy</td>
</tr>
<tr>
<td>Chemical potential</td>
<td>Particle number</td>
</tr>
</tbody>
</table>

Fig. 15. Conjugate variables in thermodynamics. Left variables do not depend on the system size (intensive variables), while right variables scale with system size (extensive variables). In such way for homogenous system we have $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$, where $\lambda$ is positive and non-zero. More involved reasoning can be found in [2].
<table>
<thead>
<tr>
<th>Potential</th>
<th>Natural independent variables</th>
<th>Conjugated dependent variables</th>
<th>Maxwell relations and others</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INTERNAL ENERGY</strong></td>
<td>$U$</td>
<td>$T = \left(\frac{\partial U}{\partial S}\right)_{VN}$</td>
<td>$\left(\frac{\partial T}{\partial V}\right)<em>{S} = -\left(\frac{\partial P}{\partial S}\right)</em>{V}$</td>
</tr>
<tr>
<td></td>
<td>$S, V, N$</td>
<td>$P = -\left(\frac{\partial U}{\partial V}\right)_{SN}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\mu = \left(\frac{\partial U}{\partial N}\right)_{SN}$</td>
<td></td>
</tr>
<tr>
<td><strong>ENTROPY</strong></td>
<td>$S$</td>
<td>$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{VN}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$U, V, N$</td>
<td>$P = \left(\frac{\partial S}{\partial V}\right)_{UN}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{UN}$</td>
<td></td>
</tr>
<tr>
<td><strong>FREE ENERGY</strong></td>
<td>$F = U - TS$</td>
<td>$S = -\left(\frac{\partial F}{\partial T}\right)_{VN}$</td>
<td>$\left(\frac{\partial S}{\partial V}\right)<em>{T} = \left(\frac{\partial P}{\partial T}\right)</em>{V}$</td>
</tr>
<tr>
<td></td>
<td>$T, V, N$</td>
<td>$P = -\left(\frac{\partial F}{\partial V}\right)_{TN}$</td>
<td>$U = -T^{2}\frac{\partial}{\partial T}\left(\frac{F}{T}\right)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\mu = \left(\frac{\partial F}{\partial N}\right)_{TN}$</td>
<td></td>
</tr>
<tr>
<td><strong>ENTHALPY</strong></td>
<td>$H = U + PV$</td>
<td>$T = \left(\frac{\partial H}{\partial S}\right)_{PN}$</td>
<td>$\left(\frac{\partial T}{\partial P}\right)<em>{S} = \left(\frac{\partial V}{\partial S}\right)</em>{P}$</td>
</tr>
<tr>
<td></td>
<td>$S, P, N$</td>
<td>$V = \left(\frac{\partial H}{\partial P}\right)_{SN}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\mu = \left(\frac{\partial H}{\partial N}\right)_{SN}$</td>
<td></td>
</tr>
<tr>
<td><strong>GIBBS ENTHALPY</strong></td>
<td>$G = H - TS = N\mu$</td>
<td>$S = -\left(\frac{\partial G}{\partial T}\right)_{PN}$</td>
<td>$\left(\frac{\partial S}{\partial P}\right)<em>{T} = -\left(\frac{\partial V}{\partial T}\right)</em>{P}$</td>
</tr>
<tr>
<td></td>
<td>$T, P, N$</td>
<td>$V = \left(\frac{\partial G}{\partial P}\right)_{TN}$</td>
<td>$H = -T^{2}\frac{\partial}{\partial T}\left(\frac{G}{T}\right)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\mu = \left(\frac{\partial G}{\partial N}\right)_{TN}$</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 16. Summary of thermodynamical potentials and Maxwell relations for different statistical ensembles [9].
Partition function is simply given as 
\[ Z = \sum_n e^{-\frac{E_n}{k_b T}} \], where we have the sum is over all energies \( E_n \) occurring in the system. More exact definition of partition function of grand canonical ensemble (TVN ensemble) will include use of integrals
\[ Z(T, V, \mu) = \sum_{k=0}^{+\infty} \frac{1}{k^3 N!} \int \exp(-\beta H(q, p) - \mu k) dq dp, \]
where \( H \) is Hamiltonian of the system and \( \beta = \frac{1}{kT} \). Here we can recognize that
\[ Z(T, V, \mu) = \sum_{k=0}^{+\infty} \frac{1}{k^3 N!} \int \exp(-\beta H(q, p) - \mu k) dq dp = \]
\[ = \sum_{n=0}^{\infty} Z(T, V, N)e^{n\left(\frac{\mu}{k_b T}\right)} = \sum_{n=0}^{\infty} Z(T, V, N)e^{nz}. \]
Thus we have zeta transform [z transformation known in digital signal processing] present in definition of grand canonical partition function. Term \( z = e^{\frac{\mu}{k_b T}} \) is denoted as the fugacity. Partition function for grand canonical ensemble has analogical properties as in case of canonical ensemble. For example \( \langle H \rangle = -\frac{d}{d\beta} \frac{Z(T, V, \mu)}{Z(T, V, \mu)} \) and in similar way we can compute higher cumulants of \( H \) variable. It shall be underlined that \( Z \) has its importance in Quantum Field Theory and it is the generator of Green functions. In particular we have
\[ Z[J] = \int D\phi \exp\left(\frac{i}{\hbar} \left[S[\phi] + \int d^4 x J(x) \phi \right]\right), \]
where \( S \) is action and and n-point Green function will be obtained by functional differentiation
The generating functional \( Z[J] \) can be used to calculate the above path integrals using an auxiliary function \( J \) (called current in this context). Finally we can obtain n-body Green function.
\[ G(x_1, \ldots, x_n) = (-i\hbar)^n \frac{1}{Z[J]} \frac{\delta^n Z}{\delta J(x_1) \ldots \delta J(x_n)} \bigg|_{J \to 0}. \]

More details can be found in Peskin and Schroeders book - An introduction To Quantum Field Theory.

3. Universal model of reality as combined statistical approach with microscopic corrections

We never know how many layers of organization occurs in matter that is described by laws of physics. We also know that matter organize itself in certain order. In particular the concepts as temperature or pressure are useful and their use does not impose the necessity to know all microscopic details of matter state. This order can be perceived and described by statistical physics that is able to omit most or all microscopic degrees of freedom. However there are certain situations when we cannot use thermodynamics. In such case we have to cover most aspects of the system by thermodynamics and some aspects by microscopic theory.
At first let us move to the cases that can be both described by thermodynamics and by microscopic theory as it is the case of Figures 17-22.

Fig. 17. Initial step $t_0$ and two sets of charged billiard balls with plus and minus charged in each set. The whole system is confined in rectangular box.

Fig. 18. During next time step $t_1$ electrostatic repulsive and attractive force among balls drives the evolution of the system.

Fig. 19. During next time step $t_2$ two oppositely charged sets of balls start to have contact.

Fig. 20. During following step $t_3$ two sets of balls starts to mix.

Fig. 21. During step $t_4$ the mixture of both type of balls continues.
3.1. Pictures of entropy growth

Suppose at the beginning that we have \( N \) dielectric balls with \( +q \) and \( N \) negatively charged balls with \( -q \) charge. All balls have the same mass and radius \( r \). If \( N \) positively charged balls are placed in one confined region and if \( N \) negatively charged balls are placed in another confined region they will tend to move by means of electrostatic forces. They will note exchange charge as it is our assumption. After sufficiently long time all balls will be intermixed and their entropy will increase. Described process is schematically depicted in following steps schematically depicted in Fig.17-Fig.22.

Finally stage will be situation as in \( NaCl \) crystal where \( Na^+ \) ions are situated in proximity to \( Cl^- \) ions. After long time the entropy will maximize and stay at certain value. It might fluctuate. Finally stage will be robust against disturbing factors.

3.2. Derivation of Boltzmann distribution from principle of maximum entropy growth

We describe the reasoning given in [3]. Any 1, 2 or 3 dimensional system can be separated into \( k \) geometrically separable cells with virtual walls. In such way \( N \) particles are distributed, so in the \( i \)-th cell we have \( n_i \) particles. There is \( \sum_{i=1}^{N!} \sum_{N_i!} \) of such possibilities. At the same time \( N = n_1 + .. + n_k \) is one of constrains. What is more in each container we have \( g_i \) number of energy levels. For simplicity we will assume that those energy levels have discrete levels separated by certain energy difference \( \Delta E \) so energy in given cell can have value from 0 to \( (g_i - 1)\Delta E \). This brings \( g_i^{n_i} \) possibilities in one cell.

Thus the total number of states \( \Lambda \) is given as \( W \) and can be expressed as

\[
W(N_1, N_2, ..., N_n) = \frac{N!}{\sum_{i=1}^{n} N_i!} \sum_{i=1}^{n} g_i^{N_i}.
\] (21)

Thus we have constrains as

\[
f_1(N_1, ..., N_n) = \sum_{i=1}^{n} N_i = constant_1
\] (22)
and

\[ f_2 = U(N_1, ..., N_n) = \sum_i E_i N_i = \text{constant} \]  \hspace{1cm} (23)

(Second constrain is coming from the assumption that all atoms in one cell have the same energy \( E_i \) what is possible when we conduct the whole same reasoning but accepting only atoms of almost same energies (whose energy is lying in the same narrow volume of energies) into one \( i \)-th cell). We can say that reasoning is conducted in Fourier space of positions.

We can evaluate number of states by use of Stirling formula and we obtain

\[ \ln(W) = \ln(N!) + \sum_{i=1}^{n} N_i \ln(g_i) - \sum_{i=1}^{n} \ln(N_i!). \]  \hspace{1cm} (24)

We use simplification for large \( x \) as \( \ln(x!) \approx x \ln(x) - x \).

This brings consequences

\[ \ln(W) = N \ln(N) - N + \sum_{i=1}^{n} N_i \ln(g_i) - \sum_{i=1}^{n} N_i \ln(N_i) + \sum_{i=1}^{n} N_i. \]  \hspace{1cm} (25)

In order to maximize, we need to make use of Lagrange multipliers and Constrains 1 and 2.

\[ \frac{d}{dN_j} \ln(W) + \alpha \frac{df_1}{dN_j} - \beta \frac{df_2}{dN_j} = 0. \]  \hspace{1cm} (26)

After calculations we obtain \( \beta = 1/(k_BT) \) as Legendre multiplier. Finally it turns out that \( n_i = g_i \exp(-\beta E_i) \exp(-\alpha) \) what points that from maximum entropy principle we obtain Boltzmann distribution.
Somehow similar reasoning can be conducted for derivation of Fermi and Bose-Einstein distribution. However we need to take into account the fact that bosons are symmetric under particle exchange while fermions are antisymmetric. The detailed reasoning can be found in [12].

3.3. Connection between entropy and probability

Let us assume that we are dealing with NVT ensemble.

Suppose a huge number of systems, $N$, are in thermal contact. $n1$ of which are in microstate 1, $n2$ in microstate 2, etc. The number of ways $W$ to make this...
arrangement is

\[ W = \sum_k \frac{N!}{n_1! n_2! \ldots n_k!} . \] (27)

The entropy of the entire ensemble of systems is \( S = k_b \ln(W) \).

We can use Stirling formula \( \ln(N!) \approx N \ln(N) N \) for large \( N \). Thus we obtain

\[
\log(W) = \sum_k [\log(N!) - \log(n_1! n_2! \ldots n_k!)] = \\
(N \log(N) - N) - \left( \sum_{i=1}^k \log(n_i) n_i - n_i \right) = \\
= \left( \sum_{i=1}^k n_i \log(N) - \sum_{i=1}^k \log(n_i) n_i \right) = \sum_{i=1}^k (n_i \log(N) - \log(n_i) n_i) = \\
- \sum_{i=1}^k n_i \log(n_i/N) = - \sum_{i=1}^k N \frac{n_i}{N} \log(n_i/N) = N \sum_i p_i \log(p_i). \] (28)

The obtained result is commonly known as Shannon entropy.

### 3.4. Link of statistical physics with other branches of science and fields of technology

The methodology used in statistical physics can be used in economy\cite{18} or in robotics with cognitive preprogrammed properties \cite{14}. In addition to physical forces on robotic agent might act social forces. In such case the concept of Shannon entropy can be used. Such systems will follow the principle of maximum entropy growth. More general assemblies of agents playing in different games can be modeled with use of presented methodology \cite{15}. Very particular class of agents are Braitenberg vehicles that has 2 wheels, 2 sensors and social force applied in regard to stimulation coming from light source as it is depicted in Fig.25. The way of application of social force depends on the connections between sensors and motor system. In principle they can react in complicated way since neural network can process signal passing from sensor to motor system.
Fig. 25. Scheme of Braitenberg vehicles moving in field of stimuli [14].

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INŻYNIERYJNE ASPEKTY FIZYKI STATYSTYCZNEJ I TEORII PRZEJŚĆ FAZOWYCH, CZĘŚĆ I

STREZCZENIE

Artykuł jest krótkim wprowadzeniem do fizyki statystycznej i teorii przejść fazowych. Zakładana jest wiedza czytelnika z zakresu podstaw mechaniki. Artykuł nakreśla zastosowanie metodologii fizyki statystycznej w rozmaitych gałęziach techniki.

SŁOWA KLUCZOWE: fizyka statystyczna, wielki zespół kanoniczny, zespół kanoniczny, zespół mikrokanoniczny, przejścia fazowe