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Preliminaries

The title of the book is “Introduction to mathematical statistical physics”. I would like to explain what “mathematical” means here. Mathematical physics in general, and mathematical statistical physics in particular, emerged in its present form thirty or forty years ago as an attempt of mathematicians to understand mathematical structures that form the basis of fundamental theories in physics. Since physicists and mathematicians deal with the same subject, the difference between the physical approach and the mathematical one is, from the formal point of view, not absolute. However, such a difference exists and it is mainly of a psychological nature. Roughly speaking, physicists want to get a quick explanation of an experiment, which may be nonrigorous and not correct in details. On the other hand, mathematicians are not interested in the experimental data and they want to construct a clear and noncontradictory picture of the phenomena based on physical postulates.

Of course, mathematicians studying physics convert it to mathematics with all the accepted canons: theorems, lemmas, proofs, exact definitions and so on. In addition, opportunities appear for applying many fine and abstract mathematical theories to physics.

It should be mentioned that there is an inverse influence of these studies on mathematics. The purpose and motivations of mathematical theories are more and more penetrated by the spirit of physics. But this is a separate subject, which requires a special lecture.

These lectures are aimed at beginners and emphasis is made on explaining the main ideas, notions and facts, rather than on technical tools. The inner motivation of the lectures is to introduce the reader to problems centering around the main concept of modern mathematical statistical physics — the concept of limiting Gibbsian field. In particular, the major part of these lectures is devoted to the famous Pirogov–Sinai theory, which allows us to establish the existence of several such fields for a given system (this is treated now as phase transition).

After studying these lectures the reader should turn to more detailed texts, such as the famous book by Ruelle [1], the book by Thompson [8], the monograph by Simon [9] and others (see the bibliography). Unfortunately, in these books there is no explanation of the Pirogov–Sinai theory. The only monograph where one can find such an explanation is in the book by Sinai [4]. But it is explained there in very general and concise form, which is rather difficult for beginners.

It is useful also to look in textbooks on physics.

LECTURE 1

Typical Systems of Statistical Physics (Phase Space, Dynamics, Microcanonical Measure)

Statistical physics considers large physical systems: they consist of a large number of components and occupy a large volume in the space \mathbb{R}^3 (or the lattice \mathbb{Z}^3). Here we give some examples of such systems.

BASIC EXAMPLES

1.1. Classical gas (phase space and energy). Let $\Lambda \subset \mathbb{R}^3$ be a bounded domain. Consider a system of N identical (point) particles moving inside Λ . Each particle is characterized by its position $q_i \in \Lambda$ and velocity $v_i \in \mathbb{R}^3$, $i = 1, \dots, N$. Thus the state of our system is defined by the sequence

$$((q_1, v_1), (q_2, v_2), \dots, (q_N, v_N)) \equiv (Q, V)$$

where $q_i \in \Lambda, v_i \in \mathbb{R}^3$, $i = 1, 2, \dots, N$. Sometimes we denote this sequence by (Q, V) (Q is a collection of positions, V is a collection of velocities). A set of such sequences (we denote it by $\Omega_{\Lambda, N}$) is a Cartesian product:

$$\Omega_{\Lambda, N} = (\Lambda \times \mathbb{R}^3)^N = (\Lambda \times \mathbb{R}^3) \times (\Lambda \times \mathbb{R}^3) \dots (\Lambda \times \mathbb{R}^3) \subset (\mathbb{R}^3 \times \mathbb{R}^3)^N = \mathbb{R}^{6N}.$$

The space $\Lambda \times \mathbb{R}^3$ is the space of the states of a single particle. The set $\Omega_{\Lambda, N}$ is usually called the *phase space* of the system. The *energy* of the system, which is a function of state (Q, V) usually called the *Hamiltonian* (it is one of the basic characteristics of the system), has the form

$$H_{\Lambda, N}(Q, V) = \sum_{i=1}^N \frac{mv_i^2}{2} + \sum_{1 \leq i < j \leq N} U(q_i - q_j) + \sum_{i=1}^N V_b(q_i).$$

The first sum is the *kinetic energy* and the second and the third ones are the *potential energy*. Here m is the common mass of the particles, $U(q_i - q_j)$ is the *potential* corresponding to interaction between pairs of particles in points q_1 and q_2 , and V_b is the so-called boundary potential (the interaction of particles with the external field). Further we shall always assume that interaction between the particles $U(q_1 - q_2)$ is *short-range*. This means that the function $U(q_1 - q_2)$ rapidly decreases when the distance $|q_1 - q_2|$ between the particles increases. Often we shall even assume for simplicity that the function $U(q_1 - q_2)$ has finite range (compact support): $U(q_1 - q_2) = 0$ if $|q_1 - q_2| \geq R$ (R is a constant that is called the “*radius of interaction*”). Moreover it is usually assumed that the potential $U(q_1 - q_2)$ actually depends only on the distance $|q_1 - q_2|$ between the particles: $U(q_1 - q_2) = U(|q_1 - q_2|)$. In concrete calculations one mostly uses the so-called Lennard–Jones potential:

$$U(r) = \frac{A}{r^{12}} - \frac{B}{r^6},$$

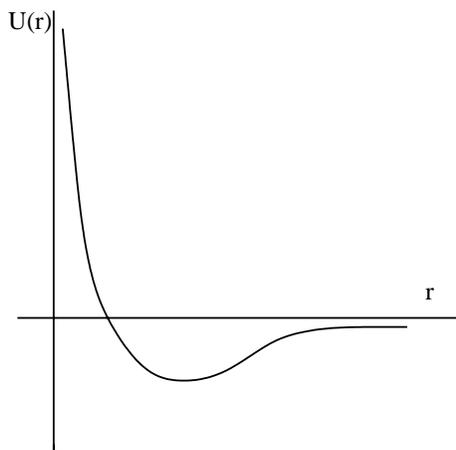


FIGURE 1.1. The typical form of the potential

in which parameters $A > 0$ and $B > 0$ depend on the model. The form of the graph of function $U(r)$ is shown on the Figure 1.1.

THE DYNAMICS (motion) of the system of particles is defined by the following system of differential equations (*equations of motion*):

$$\frac{dq_i}{dt} = v_i,$$

$$m \frac{dv_i}{dt} = \sum_{i \neq j} F(q_i - q_j) + F_b(q_i), \quad i = 1, 2, \dots, N$$

(Newton equations).

Here $\frac{dv_i}{dt}$ is the acceleration and

$$F(q_j - q_i) \stackrel{\text{def}}{=} -(\nabla U)(q_j - q_i), \quad F_b(q_i) \stackrel{\text{def}}{=} -(\nabla V_b)(q_i)$$

are the vectors with components

$$-\nabla U \stackrel{\text{def}}{=} \left\{ -\frac{\partial U}{\partial q^{(1)}}, -\frac{\partial U}{\partial q^{(2)}}, -\frac{\partial U}{\partial q^{(3)}} \right\} \quad \text{and similarly for } (-\nabla V_b)$$

($q = (q^{(1)}, q^{(2)}, q^{(3)})$ are the coordinates of the point $q \in \mathbb{R}^3$) describing the force with which the particle j acts on the particle i . I want to emphasize that usually $U(r) \rightarrow \infty$ as $r \rightarrow 0$. As we see from the equations of motion, this means that the particles repel each other if the distance between them is short.

The particles move inside Λ according to these equations. When one of the particles reaches the boundary of Λ , the equations of motion do not hold. Therefore it is necessary to add to these equations some rules of reflection of the particles from the boundary of the domain Λ . For example, we can consider the *elastic reflection* condition: the angle of incidence is equal to the angle of reflection. Formally, such a rule can be specified by the boundary potential V_b .

The equations of the motion together with the reflection rule generate a motion in the phase space $\Omega_{\Lambda, N}$ (i.e., the set of maps $\Omega_{\Lambda, N} \rightarrow \Omega_{\Lambda, N}$). Namely, each point

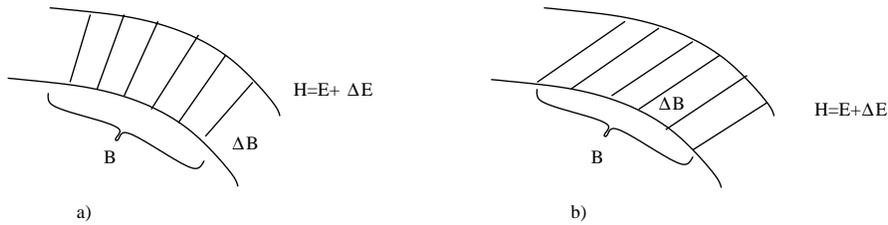


FIGURE 1.2. The two ways of definition of the microcanonical measure: a) with the help of normals; b) with the help of arbitrary bundle of parallels.

$(Q_0, V_0) \in \Omega_{\Lambda, N}$ at time t goes to the point (Q_t, V_t) along the integral curve of the equations of motion passing through the point (Q_0, V_0) at time 0.

Let us denote by S_t the map of the phase space $\Omega_{\Lambda, N}$ into itself given by this motion:

$$S_t : (Q_0, V_0) \rightarrow (Q_t, V_t).$$

The family of these mappings $\{S_t, t \in \mathbb{R}^1\}$ are called *dynamics*. It is very important that the dynamics $\{S_t, t \in \mathbb{R}^1\}$ preserve the following quantities:

a) the $6N$ -dimensional volume in $\Omega_{\Lambda, N}$,

$$\text{Vol}_{6N}(S_t A) = \text{Vol}_{6N}(A), \quad A \subseteq \Omega_{\Lambda, N}$$

(conservation of the volume);

b) the energy $H_{\Lambda, N}$,

$$H_{\Lambda, N}(S_t(Q_0, V_0)) = H_{\Lambda, N}((Q_0, V_0))$$

(conservation of the energy).

Hence each surface of constant energy (level surface of the energy)

$$\Omega_{\Lambda, N, E} = \{(Q, V) \in \Omega_{\Lambda, N} : H_{\Lambda, N}(Q, \Lambda) = E\}$$

is mapped by S_t into itself:

$$S_t \Omega_{\Lambda, N, E} = \Omega_{\Lambda, N, E}.$$

Thus we can consider the dynamics S_t on each surface $\Omega_{\Lambda, N, E}$ separately.

MICROCANONICAL MEASURE. We can define a special measure $\nu_{\Lambda, N, E}$ on the surface $\Omega_{\Lambda, N, E}$, which is also preserved by the dynamics in $\Omega_{\Lambda, N, E}$. Namely, we put

$$(1.1) \quad \nu_{\Lambda, N, E}(B) \stackrel{\text{def}}{=} \lim_{\Delta E \rightarrow 0} \frac{\text{Vol}(\Delta B)}{\Delta E}.$$

Here $B \subset \Omega_{\Lambda, N, E}$ is a subset of $\Omega_{\Lambda, N, E}$ (a domain on this surface); the domain $\Delta B \subset \Omega_{\Lambda, N}$ is formed by segments of normals drawn from the surface $\Omega_{\Lambda, N, E}$ at the points of B up to the intersection with the surface $\Omega_{\Lambda, N, E+\Delta E}$ (see Figure 1.2a).

The following general assertion holds. Let $f(x), x \in \mathbb{R}^n$, be a smooth function of $x \in \mathbb{R}^n$ having finite number of critical points (the points in which $f'(x) = 0$). Then limit (1.1) exists for any surface $f(x) = E$ and any domain B on this surface (see [11]). The measures $\nu_{\Lambda, N, E}$ are sometimes called *microcanonical measures* (in mathematical literature they are called the Gelfand–Leray measures).

REMARK. Instead of domain ΔB defined above, in (1.1) one can consider a domain which is formed by segments of any bundle of parallel lines drawn from the points in B up to the intersection with the surface $\Omega_{\Lambda,N,E+AE}$ (see Figure 1.2b).

Because of properties a) and b) (conservation of volume and of energy) and in view of the previous remark the measure $\nu_{\Lambda,N,E}$ on the surface $\Omega_{\Lambda,N,E}$ is preserved by the dynamics S_t in $\Omega_{\Lambda,N,E}$. This means that

$$\nu_{\Lambda,N,E}(S_t B) = \nu_{\Lambda,N,E}(B), \quad B \subseteq \Omega_{\Lambda,N,E}.$$

REMARKS. 1. In the general case there are sometimes other “integrals of motion”

$$I_i, \quad i = 1, \dots, k,$$

i.e., are functions on the phase space that are invariant with respect to dynamics. Examples of such functions are, for instance, the total momentum $m \sum_{i=1}^N v_i$, the angular momentum $\sum_i [q_i, v_i]$ and so on ($[\cdot, \cdot]$ is the vector product). In this case the intersections of level surfaces of all integrals of motion are invariant with respect to dynamics and we can introduce the microcanonical measure (which is also invariant with respect to dynamics) on each of these sets:

$$\Omega_{\Lambda,N,E,C_1,\dots,C_k} = \{(Q, V) : H_{\Lambda,N}(Q, V) = E, I_i(Q, V) = C_i, i = 1, \dots, k\}.$$

Below we assume for simplicity that there are no others integrals of motion except the energy.

2. There is a conjecture (the famous Boltzman Ergodic Hypothesis) that in the general case (in the absence of others integrals of motion) the microcanonical measure is the unique smooth measure on $\Omega_{\Lambda,N,E}$ that is invariant with respect to the mappings S_t . This means that any other invariant measure on $\Omega_{\Lambda,N,E}$ with a smooth density with respect to the microcanonical measure coincides with the microcanonical one up to a constant factor. This conjecture is only proved in certain particular cases. It should be mentioned that modern ergodic theory arose mainly from attempts to prove this hypothesis.

1.2. Configuration gas. These systems play an auxiliary role and appear as simplifications of the previous systems by omitting the velocity of the particles and considering their positions only. The state of such a system is a sequence (configuration)

$$Q = (q_1, \dots, q_N), \quad q_i \in \Lambda, \quad i = 1 \dots N, \quad \Lambda \in \mathbb{R}^3$$

and the corresponding phase space is a Cartesian product

$$\Lambda^N = \Lambda \times \Lambda \times \dots \times \Lambda \equiv \Omega_{\Lambda,N}^{\text{conf}} \subset \mathbb{R}^{3N}.$$

The energy $H_{\Lambda,N}(Q)$ is the potential part of the energy of the classical gas

$$H_{\Lambda,N}(Q) = \sum_{1 \leq i < j \leq N} U(q_i - q_j) + \sum_{i=1}^N V_b(q_i).$$

Of course, there are no dynamics in this case. However, it is useful to consider the surfaces of constant energy

$$\Omega_{\Lambda,N,E}^{\text{conf}} = \{Q \in \Omega_{\Lambda,N}^{\text{conf}} : H_{\Lambda,N}(Q) = E\}$$

and the microcanonical measures $\nu_{\Lambda,N,E}^{\text{conf}}$ on these surfaces, which are defined just in the same way as before.

1.3. Lattice gas. It is a simplified model of the previous system: the particles can only occupy points of the cubic lattice $\mathbb{Z}^3 \subset \mathbb{R}^3$ (points with integer coordinates). In addition it is assumed that different particles occupy different points.

Thus the states of the system are sequences

$$Q = (q_1, \dots, q_N), \quad q_i \in \Lambda, \quad i = 1, \dots, N, \quad q_i \neq q_j \text{ for } i \neq j$$

(for simplicity, we omit the boundary potential). Here $\Lambda \subset \mathbb{Z}^3$ is a finite subset of the lattice \mathbb{Z}^3 , for example a cube with side L :

$$\Lambda = \{q \in \mathbb{Z}^3, \quad 0 \leq q^{(i)} \leq L, \quad i = 1, 2, 3\},$$

($q^{(1)}, q^{(2)}, q^{(3)}$) are the coordinates of the point $q \in \mathbb{Z}^3$.

The energy $H_{\Lambda, N}(Q)$ of the state Q is defined as in the previous example:

$$H(Q) = \sum_{1 \leq i < j \leq N} U(q_i - q_j).$$

Here $U(s)$, $s \in \mathbb{Z}^3$, $s \neq 0$ is a potential defined on the lattice \mathbb{Z}^3 (except for the point $s = 0$); it rapidly decreases as s goes to infinity. As before, we shall often assume that the function $U(s)$ has compact support: $U(s) = 0$ if $|s| > R$.

1.4. Lattice spin systems. This is a large class of systems considered in statistical physics. Some of them have a real physical meaning, others are studied as suitable simplified models of more complicated systems.

We start with the simplest example of such a system.

Let $\Lambda \subset \mathbb{Z}^3$ be a finite subset of \mathbb{Z}^3 (for example Λ is a cube). Consider the set Ω_Λ of functions (configurations)

$$\sigma = \{\sigma(x), x \in \Lambda\}$$

which take two values: $\sigma(x) = +1$ or -1 . The set Ω_Λ is the phase space of our system. Physically this system describes magnetism: Λ is a piece of a crystal lattice and every site is occupied by an elementary magnet, which can be directed upwards or downwards (the magnetization or “spin” of the magnet is equal to $+1$ or -1 respectively).

The energy of the configuration $\sigma = \{\sigma(x), x \in \Lambda\}$ has the form

$$H_\Lambda(\sigma) = \sum_{x, x' \in \Lambda, x \neq x'} U(x - x') \sigma(x) \sigma(x') + h \sum_{x \in \Lambda} \sigma(x).$$

The summation is over all unordered pairs of points x, x' of Λ in the first sum and over all points $x \in \Lambda$ in the second sum. The function $U(s)$ ($s \in \mathbb{Z}^3$, $s \neq 0$) (interaction potential between spins) is the same as before. Parameter h is a magnetic field. In the simplest model, the so called *Ising* model, the potential vanishes for $|s| > 1$. This means that only neighboring spins interact.

Systems of the same kind are obtained by other choices of the set S of the values of the configuration. The phase space Ω_Λ consists as before of the functions (configurations)

$$\sigma = \{\sigma(x), x \in \Lambda\}, \quad \sigma(x) \in S.$$

EXAMPLE. A model of *planar rotators*. In this case the space S is the unit circle: the configuration takes values $\sigma(x)$, which are unit vectors lying in the same plane. The energy of the configuration $\sigma = \{\sigma(x), x \in \Lambda\}$ has the form

$$H_\Lambda(\sigma) = \sum_{x, x'} U(x - x') (\sigma(x), \sigma(x')),$$

where $(\sigma(x), \sigma(x'))$ is the scalar product of $\sigma(x)$ and $\sigma(x')$. As before, $U(s)$ is called the potential energy. This system is another model describing magnetism: the elementary magnet can take not only two values but all values on the circle.

At this point I stop listing examples of the systems considered by statistical physics.

REMARK. Although real physical systems are three-dimensional (that is, they are located in three-dimensional space \mathbb{R}^3 (or three-dimensional lattice \mathbb{Z}^3)), people often study one- or two-dimensional models as well. Their investigation helps to understand and predict many phenomena of the three-dimensional models. Therefore we shall also consider one- and two-dimensional systems.

LECTURE 2

Statistical Ensembles (Microcanonical and Canonical Ensembles, Equivalence of Ensembles)

Large systems (that is, systems with large N and Λ) exhibit a collective behavior where the details of motion of each single particle are nonessential. Therefore in studying such systems one does not resort to a detailed description of dynamics S_t in the phase space of the system, as it is done in usual mechanics when studying systems with a small number of particles. Here we follow another approach. As I already mentioned, for large systems we are not interested in the fate of a single particle. Instead, we are interested in the fraction of the particles having a particular property.

For example, we can be interested in the fraction of the particles having a fixed velocity or being in a fixed part of the space, and so on. Or we can be interested in the fraction of pairs of particles possessing some property, for example, being at a certain distance from one another. Mathematically it is convenient to convey this idea by introducing a suitable probability distribution P on the phase space Ω of the system. Then we can find the mentioned proportions as probabilities of appropriate events (that is, sets of the phase space). Further, for any physical variable that is function $F(\omega)$, $\omega \in \Omega$, of the state of physical system (in the other words, any function F defined on phase space Ω) we can find its mean value with respect to the distribution P

$$\langle F \rangle_P = \int_{\Omega} F(\omega) dP(\omega).$$

For example, we can find the mean value of the energy $\langle H \rangle_P$ or of the kinetic energy $\langle \sum \frac{mv_i^2}{2} \rangle_P$ (in the case of classical gas), or the mean value of total velocity $\langle \sum v_i \rangle_P$ and so on.

The main physical postulate of statistical physics, which connects our theoretical constructions with experimental observations is that for a large system and a large class of physical variables F the values F measured experimentally almost coincide with their mean values $\langle F \rangle_P$ with respect to a suitable probability distribution P on Ω . This postulate contains some imprecise expressions (“almost coincide”, or “some class of physical variables”) which we shall make more precise later by introducing the notion of thermodynamic limit. The question is: “What is a suitable distribution?”

In general, the so-called nonequilibrium case, when the system as a whole changes in time, the description of such a distribution and its construction is a very complicated problem and it will not concern us here. We shall only study the case of equilibrium systems. In this case the probability distributions on the phase space can have, as we shall see, one of several precise forms. First we introduce these distributions for the case of classical gas.

It is supposed that the time evolution of any probability distribution defined on the phase space of classical gas is generated by dynamics S_t in that space. This means that the distribution P_t at time $t > 0$ is obtained from initial distribution P_0 (at time 0) by the formula

$$(2.1) \quad P_t(A) = P_0(S_t^{-1}A), \quad A \subset \Omega_{\Lambda,N}.$$

Here $A \in \Omega_{\Lambda,N}$ is an arbitrary set in the phase space, and the set $S_t^{-1}A$ is transformed to A during time t due to the dynamics. Of course, *equilibrium distribution* P^{equilib} has to be invariant with respect to that evolution, that is

$$P^{\text{equilib}}(A) = P^{\text{equilib}}(S_t^{-1}A)$$

for any $A \subset \Omega_{\Lambda,N}$ and any $t > 0$. There are many probability distributions on the phase space possessing such invariance property with respect to the evolution. However, I would like to emphasize that not every measure invariant with respect to the dynamics is an equilibrium measure, but only some special ones among them. I am going to describe them.

2.1. Microcanonical distribution or microcanonical ensemble.¹ These are the simplest equilibrium distributions. They are obtained by normalizing microcanonical measures $\nu_{\Lambda,N,E}$, which were introduced before. We denote the microcanonical distributions by $P_{\Lambda,N,E}^{\text{microcanon}}$

$$P_{\Lambda,N,E}^{\text{microcanon}}(A) = \frac{\nu_{\Lambda,N,E}(A)}{\nu_{\Lambda,N,E}(\Omega_{\Lambda,N,E})}$$

where $\nu_{\Lambda,N,E}(\Omega_{\Lambda,N,E}) \equiv Q_{\Lambda,N,E}$ is a normalizing factor. Each such distribution is concentrated on its own level surface of energy

$$H_{\Lambda,N} = E.$$

Up to the factor $Q_{\Lambda,N,E}^{-1}$, the measure coincides with the microcanonical measure $\nu_{\Lambda,N,E}$ and therefore it is invariant with respect to evolution (2.1).

2.2. Gibbs canonical measures. Although the microcanonical distributions are the most natural ones, they are not very convenient for calculations and theoretical analysis. Therefore, instead of the family of the microcanonical distributions ($P_{\Lambda,N,E}^{\text{microcanon}}, E \in \mathbb{R}^1$) (Λ and N are fixed) another family of equilibrium distributions is introduced:

$$P_{\Lambda,N,\beta}^{\text{canon}}, \quad \beta > 0$$

the so-called *Gibbs canonical distributions*. (Gibbs was an American mathematician who had an essential influence on the development of statistical physics.) In contrast to the microcanonical ones, these distributions are nonsingular, i.e., they have densities with respect to the usual Lebesgue measure ($6N$ -dimensional volume) in space \mathbb{R}^{6N} . These densities have the form

$$\begin{aligned} P_{\Lambda,N,\beta}^{\text{canon}}(Q, V) &= \frac{1}{Z_{\Lambda,N,\beta}} \exp\{-\beta H_{\Lambda,N}(Q, V)\} \\ &= \frac{1}{Z_{\Lambda,N,\beta}} e^{-\beta\{\sum_i \frac{mv_i^2}{2} + \sum_{1 \leq i < j < N} U(q_i - q_j)\}}. \end{aligned}$$

¹Sometimes equilibrium distributions are called “ensembles”.

(Recall the notation $(Q, V) = ((q_1, v_1), (q_2, v_2), \dots, (q_N, v_N))$). Here $\beta > 0$ is the parameter (*inverse temperature*) and $Z_{\Lambda, N, \beta}$ is the normalizing factor,

$$Z_{\Lambda, N, \beta} = \int_{\Omega_{\Lambda, N}} e^{-\beta H_{\Lambda, N}(Q, V)} \Pi dq_i \Pi dv_i.$$

It is called the *partition function* or the *statistical sum* (statistical integral).

Since the energy $H_{\Lambda, N}$ and Lebesgue measure $\Pi dq_i \Pi dv_i$ are invariant with respect to the dynamics S_t in $\Omega_{\Lambda, N}$, the Gibbs distributions $P_{\Lambda, N, \beta}^{\text{canon}}$ are also invariant.

2.3. The equivalence of ensembles. It turns out that both families of equilibrium distributions — microcanonical and canonical ones — are equivalent in some sense. This will be discussed in more detail later, but now in order to understand how Gibbs's distribution $P_{\Lambda, N, \beta}^{\text{canon}}$ is obtained from the microcanonical one, we will consider the following problem. Consider the *ideal* gas, i.e., gas with $U = 0$, in a domain Λ . Let $\Lambda_0 \subset \Lambda$ be a fixed domain inside Λ . Let $\Omega_{\Lambda, N}^{\Lambda_0, s} \subset \Omega_{\Lambda, N}$ be a set of states $(Q, V) \in \Omega_{\Lambda, N}$ such that $|Q \cap \Lambda_0| = s$. Let us denote

$$(Q_0, V_0) = (Q, V)|_{\Lambda_0} = ((q_1^0, v_1^0), \dots, (q_s^0, v_s^0)) \subset (Q, V), \quad (q_1^0, \dots, q_s^0) = Q \cap \Lambda_0.$$

What is the probability distribution for $(Q_0, V_0) \in \Omega_{\Lambda_0, s}$ computed in the microcanonical distribution? Clearly, the density $p_{\Lambda, N}^{\Lambda_0, s}(Q_0, V_0)$ of this distribution is equal to

$$p_{\Lambda, N}^{\Lambda_0, s}(Q_0, V_0) = \frac{Q_{\Lambda - \Lambda_0, N - s, E - H_{\Lambda_0, s}(Q_0, V_0)}}{Q_{\Lambda, N, E}},$$

where

$$H_{\Lambda_0, s}(Q_0, V_0) = m \sum_{i=1}^s \frac{(v_i^0)^2}{2}$$

and

$$Q_{\Lambda, N, E} = \nu_{\Lambda, N, E}(\Omega_{\Lambda, N, E}).$$

The quantity

$$Q_{\Lambda - \Lambda_0, N - s, E - H_{\Lambda_0, s}(Q_0, V_0)}$$

has a similar meaning. To compute $\nu_{\Lambda, N, E}(\Omega_{\Lambda, N, E})$ we use the following general formula:

$$\nu_{\Lambda, N, E}(\Omega_{\Lambda, N, E}) = \frac{d}{dE} \text{Vol}_{6N} \{(Q, V) \in \Omega_{\Lambda, N} : H_{\Lambda, N}(Q, V) < E\}.$$

We have

$$\begin{aligned} & \text{Vol}_{6N} \{(Q, V) \in \Omega_{\Lambda, N} : H_{\Lambda, N}(Q, V) < E\} \\ &= \Lambda^N \text{Vol}_{3N} \left\{ \sum_{i=1}^N |v_i|^2 < \frac{2E}{m} \right\} = \Lambda^N \cdot \left(\frac{2E}{m} \right)^{\frac{3N}{2}} \cdot \omega_{3N}, \end{aligned}$$

where ω_{3N} is the $3N$ -dimensional volume of a unit ball in \mathbb{R}^{3N} :

$$\sum_{i=1}^N |v_i|^2 < 1, \quad v_i = (v_i^{(1)}, v_i^{(2)}, v_i^{(3)}).$$

It is known that (see [12]) that

$$\omega_{3N} = \frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2} + 1)},$$

where $\Gamma(\cdot)$ is the Euler gamma function. Using these formulas we finally obtain the following expression for $Q_{\Lambda,N,E}$:

$$Q_{\Lambda,N,E} = \Lambda^N \omega_{3N} \left(\frac{3N}{2}\right) \left(\frac{2E}{m}\right)^{\frac{3N}{2}-1} \left(\frac{2}{m}\right) = \frac{2\Lambda^N \pi^{\frac{3N}{2}} \left(\frac{2E}{m}\right)^{\frac{3N}{2}-1}}{m\Gamma\left(\frac{3N}{2}\right)}.$$

Correspondingly, for $Q_{\Lambda-\Lambda_0, N-s, E-H_{\Lambda_0,s}}(Q_0, V_0)$ we find

$$Q_{\Lambda-\Lambda_0, N-s, E-H_{\Lambda_0,s}}(Q_0, V_0) = \frac{2(\Lambda-\Lambda_0)^{(N-s)} \pi^{\frac{3}{2}(N-s)} \left\{ \frac{2}{m} \left(E - \frac{m}{2} \sum_{i=1}^s (v_i^0)^2 \right) \right\}^{\frac{3}{2}(N-s)-1}}{m\Gamma\left(\frac{3}{2}(N-s)\right)}.$$

Substituting these expressions in the formula for $p_{\Lambda,N}^{\Lambda_0,s}(Q_0, V_0)$ and passing to the limit as $\Lambda \nearrow \mathbb{R}^3$, $\frac{N}{|\Lambda|} \rightarrow \rho$, $\frac{E}{|\Lambda|} \rightarrow e$ (the so-called thermodynamic limit; we shall consider it in detail later), and using the Stirling formula, (see [13])

$$\Gamma(n) = n^n e^{-n} (2\pi/n)^{\frac{1}{2}} (1 + o(1)), \quad n \rightarrow \infty,$$

we get

$$\lim_{\Lambda \nearrow \mathbb{R}^3, \frac{N}{|\Lambda|} \rightarrow \rho, \frac{E}{|\Lambda|} \rightarrow e} p_{\Lambda,N}^{\Lambda_0,s}(Q_0, V_0) = \frac{1}{Z(\Lambda_0, s, \beta)} e^{-\beta \sum_{i=1}^s \frac{m(v_i^0)^2}{2}},$$

where $\beta = \frac{3}{2} \frac{\rho}{e}$. This is the Gibbs distribution for the ideal gas consisting of s particles inside Λ_0 . It turns out that similar (but more complicated) computations can be performed in the general case of a non-ideal gas. This result shows that the Gibbs distribution appears as a probability distribution for a finite subsystem of a large system with microcanonical distribution. This means, in particular, that the mean value $\langle F \rangle_{\text{microcanon}}$ of some quantity F that depends only on the part (Q_0, V_0) of the state $(Q, V) \in \Omega_{\Lambda,N}^{\Lambda_0,s}$ (that is, the state of a subsystem of the large system inside a fixed subvolume $\Lambda_0 \subset \Lambda$) calculated by microcanonical distribution for the whole system almost coincides with the mean value $\langle F \rangle_{\text{canon}}$ calculated by the canonical Gibbs distribution for the subsystem

$$(2.2) \quad \langle F \rangle_{\Lambda,N,E}^{\text{microcanon}} \approx \langle F \rangle_{\Lambda_0,s,\beta}^{\text{canon}},$$

provided that Λ, N, E are large and β is chosen in a suitable way. In this sense both families of distributions are equivalent. The sign \approx means that both terms in (2.2) differ by $o(1)$ in the limit $\Lambda \nearrow \mathbb{R}^v$, $N \rightarrow \infty$, $\frac{N}{|\Lambda|} \rightarrow \rho$, ρ is fixed (see details in Lecture 4). It is supposed that (2.2) is true also for specific values (per particle) for so-called summatory quantities: $\frac{1}{N} F(Q, V)$. Here $F(Q, V)$, for instance, is

$$F(Q, V) = \sum_{i=1}^N f_1((q_i, v_i)), \quad (Q, V) = \{(q_1, v_1) \dots, (q_N, v_N)\}$$

(a one-particle summatory function) or

$$F(Q, V) = \sum_{1 \leq i < j \leq N} f_2((q_i, v_i), (q_j, v_j))$$

(a two-particle summatory function). Functions f_1 and f_2 are defined on spaces $\mathbb{R}^3 \times \mathbb{R}^3$ or $(\mathbb{R}^3 \times \mathbb{R}^3) \times (\mathbb{R}^3 \times \mathbb{R}^3)$ correspondingly and f_2 tends to zero as $|q_i - q_j| \rightarrow \infty$. How does the correspondence between parameters E and β making

the ensemble $P_{\Lambda,N,E}^{\text{microcanon}}$ equivalent to the ensemble $P_{\Lambda,N,\beta}^{\text{canon}}$ look? Evidently, we have $\langle H_{\Lambda,N,E} \rangle_{H_{\Lambda,N,E}^{\text{microcanon}}} = E$. On the other hand,

$$\begin{aligned} \langle H_{\Lambda,N} \rangle_{\Lambda,N,\beta}^{\text{canon}} &= \frac{1}{Z_{\Lambda,N,\beta}} \int_{\Omega_{\Lambda,N}} H_{\Lambda,N}(Q,V) e^{-\beta H_{\Lambda,N}(Q,V)} dQ dV \\ &= -\frac{\partial \ln Z_{\Lambda,N,\beta}}{\partial \beta}. \end{aligned}$$

Hence, $E = -\frac{\partial \ln Z_{\Lambda,N,\beta}}{\partial \beta}$. The solution of this equation with respect to β , $\beta = \beta(E)$, gives us the needed correspondence. In the case of the ideal gas we can easily calculate $Z_{\Lambda,N,\beta}$ and obtain $E = \frac{3N}{2\beta}$. In the thermodynamic limit $\Lambda \nearrow \mathbb{R}^3$, $\frac{N}{|\Lambda|} \rightarrow \rho$, $\frac{E}{|\Lambda|} \rightarrow e$ this equality turns into the relation $\beta = \frac{3\rho}{2e}$, which we got before.

2.4. The configuration gas. The microcanonical and canonical Gibbs distribution in space $\Omega_{\Lambda,N}^{\text{conf}}$ are introduced in a similar way. In particular, the Gibbs canonical distribution is defined by the density

$$p_{\Lambda,N,\beta}(Q) = \frac{1}{Z_{\Lambda,N,\beta}^{\text{conf}}} e^{-\beta \sum_{1 \leq i < j \leq N} U(q_i - q_j)}, \quad Q = (q_1, \dots, q_N)$$

where

$$Z_{\Lambda,N,\beta}^{\text{conf}} = \int_{\Lambda^N} e^{-\beta \sum_{1 \leq i < j \leq N} U(q_i - q_j)} \prod dq_i$$

is the partition function (or statistical integral) of the configuration gas.

IMPORTANT REMARK. If we return to classical gas we notice that the velocities and positions of the particles are independent with respect to the canonical distribution $P_{\Lambda,N,\beta}^{\text{canon}}$ since its density has the form

$$p_{\Lambda,N,\beta}^{\text{canon}}(Q,V) = \frac{1}{Z_{\Lambda,N,\beta}} e^{-\beta \sum \frac{mv_i^2}{2}} e^{-\beta \sum_{1 \leq i < j \leq N} U(q_i - q_j)}.$$

The statistical integral $Z_{\Lambda,N,\beta}$ has the form

$$\begin{aligned} Z_{\Lambda,N,\beta} &= \left(\int_{(\mathbb{R}^3)^N} e^{-\beta \sum \frac{mv_i^2}{2}} \prod_{i=1}^N dv_i \right) \left(\int_{\Lambda^N} e^{-\beta \sum_{1 \leq i < j \leq N} U(q_i - q_j)} \prod_{i=1}^N dq_i \right) \\ &= \left(\frac{2\pi}{\beta m} \right)^{\frac{3N}{2}} Z_{\Lambda,N,\beta}^{\text{conf}}. \end{aligned}$$

Finally we can rewrite

$$p_{\Lambda,N,\beta}^{\text{canon}}(Q,V) = \frac{\prod_{i=1}^N \exp\{-\beta mv_i^2/2\}}{(2\pi/\beta m)^{\frac{3}{2}}} e^{-\beta H_{\Lambda,N}^{\text{conf}}(Q)} Z_{\Lambda,N,\beta}^{\text{conf}}.$$

The last formula shows that 1) velocities v_1, \dots, v_N are independent and independent of the position of particles, 2) each velocity v_i is distributed by the Gauss law (or by the Maxwell law as it is called in physics), 3) the distribution of the positions of the particles (the so-called configuration part of the Gibbs distribution) coincides with the Gibbs distribution $P_{\Lambda,N,\beta}^{\text{conf}}$ for configuration gas. As I mentioned earlier, the configuration gas is an auxiliary system. Indeed, the study of the Gibbs distributions for the classical gas is reduced to that for configuration gas because the Gaussian distribution for velocities is very simple and the main difficulties are included in the configuration part of the Gibbs distribution. Therefore we shall

only study configuration gas. If necessary, we can always return to the classical one.

LECTURE 3

Statistical Ensembles — Continuation (the System of Indistinguishable Particles and the Grand Canonical Ensemble)

3.1. The system of indistinguishable particles. In addition to the micro-canonical and small canonical distributions there is yet another family of equilibrium distributions in statistical physics, the so-called grand canonical Gibbs distributions.

I shall define them, as we have agreed, only for the configuration gas and the reader can easily extend this definition to the case of classical gas. However, first I slightly change the phase space of configuration gas and introduce the phase space for a system of indistinguishable particles.

First, we shall consider only the states

$$Q = (q_1, \dots, q_N) \in \Lambda^N = \Omega_{\Lambda, N}^{\text{conf}}$$

of configuration gas with pairwise distinct points $q_i \neq q_j$, $i \neq j$. The set of such sequences (we denote it by $(\Lambda^N)'$) differs from Λ^N (the set of all states Q) by a set of zero volume

$$\text{Vol}_{3N}(\Lambda^N \setminus (\Lambda^N)') = 0.$$

Indeed, $\Lambda^N \setminus (\Lambda^N)'$ is the set of all sequences (q_1, \dots, q_N) that have at least two coinciding points, and, therefore, this set lies in a submanifold of codimension at least three. From the probability point of view, we can neglect such a set. Now we define the phase space of a system of N *indistinguishable* particles. The state of such a system is defined by an unordered collection of positions $\{q_1, \dots, q_N\}$ or simply by an N -point subset of Λ . Thus the totality $C_{\Lambda}^{(N)}$ of such subsets $\{q_i\}$ is, by definition, the phase space $\Omega_{\Lambda, N}^{\text{indistin}}$ of a system of N indistinguishable particles:

$$\Omega_{\Lambda, N}^{\text{indistin}} \stackrel{\text{def}}{=} C_{\Lambda}^{(N)}.$$

Denote by π the canonical map

$$\pi : (\Lambda^N)' \rightarrow C_{\Lambda}^{(N)}, \quad Q = (q_1, \dots, q_N) \mapsto \{q_i\} = c,$$

where (q_1, \dots, q_N) is an ordered sequence of the pairwise distinct points and $\{q_i\}$ is the set of these points. Evidently, each element $c \in C_{\Lambda}^{(N)}$ has $N!$ preimages $\pi^{-1}c \in (\Lambda^N)'$. We introduce the $3N$ -dimensional volume (the so called Lebesgue–Poisson measure) in $C_{\Lambda}^{(N)}$ by the formula

$$\mu_{\Lambda}^{(N)}(A) \equiv \text{Vol}_{3N}(A) \stackrel{\text{def}}{=} \frac{\text{Vol}_{3N}(\pi^{-1}A)}{N!},$$

where $A \subseteq C_\Lambda^{(N)}$ and $\pi^{-1}A \subseteq (\Lambda^N)'$ is the complete preimage of A under π . In particular,

$$\mu_\Lambda^{(N)}(C_\Lambda^{(N)}) = \frac{|\Lambda|^N}{N!}.$$

Since the energy $H_{\Lambda,N}(Q)$ of the configuration gas of identical particles is a symmetric function of (q_1, \dots, q_N) , we can consider it as a function of $c = \{q_i\}$. Then we can define the small Gibbs distribution on the space $\Omega_{\Lambda,N}^{\text{indistin}}$ of indistinguishable particles by its density with respect to measures $\mu_\Lambda^{(N)}$:

$$\begin{aligned} p_{\Lambda,N,\beta}^{\text{canon(indistin)}}(c) &= \frac{1}{Z_{\Lambda,N,\beta}^{\text{indistin}}} e^{-\beta H_{\Lambda,N}(c)}, \\ Z_{\Lambda,N,\beta}^{\text{indistin}} &= \int_{C_\Lambda^{(N)}} e^{-\beta H_{\Lambda,N}(c)} d\mu_\Lambda^{(N)}(c) \\ &= \frac{1}{N!} \int_{(\Lambda^N)'} e^{-\beta H_{\Lambda,N}(Q)} \prod dq_i = \frac{1}{N!} Z_{\Lambda,N,\beta}^{\text{distin}}. \end{aligned}$$

The interpretation of a system of N identical particles as a system of indistinguishable particles is more correct, although it is not at all obligatory because for a symmetric function of $Q = (q_1, \dots, q_N)$ we have $F(Q) = F(c)$, $c = \pi Q$ and the mean values coincide:

$$\langle F \rangle_{\Lambda,N,\beta}^{\text{distin}} = \langle F \rangle_{\Lambda,N,\beta}^{\text{indistin}}.$$

Now as we pass to grand canonical distributions, this point of view — to consider a system of identical particles as a system of indistinguishable ones — is very natural and reasonable. First we consider a system consisting of an arbitrary finite number of indistinguishable particles in a domain Λ . The state of such a system is an arbitrary finite subset $c \subset \Lambda$, and the phase space of that system, which we denote by Ω_Λ , is the totality C_Λ of all such subsets,

$$\Omega_\Lambda \stackrel{\text{def}}{=} C_\Lambda.$$

Evidently,

$$C_\Lambda = C_\Lambda^{(0)} \cup C_\Lambda^{(1)} \cup \dots \cup C_\Lambda^{(N)} \dots,$$

where

$$C_\Lambda^{(0)} = \{\emptyset\}$$

is the empty subset, which describes the absence of particles in the system (vacuum).

3.2. The grand canonical Gibbs ensemble. We can introduce the measure μ_Λ on space C_Λ which coincides on each subset $C_\Lambda^{(N)}$ with the measure $\mu_\Lambda^{(N)}$ on $C_\Lambda^{(N)}$ introduced earlier. If we assume that $\mu_\Lambda(\emptyset) = 1$, we obtain, in particular, that

$$\mu_\Lambda(C_\Lambda) = 1 + |\Lambda| + \dots + \frac{|\Lambda|^N}{N!} + \dots = e^{|\Lambda|}.$$

Next we define the energy $H_\Lambda(c)$ of such a system by the formula

$$H_\Lambda(c) = H_{\Lambda,N}(c) \quad \text{if } N(c) = N > 0$$

($N(c)$ is the number of the points in c) and

$$H_\Lambda(\emptyset) = 0.$$

Finally we can define the family of *grand canonical Gibbs distributions* (ensembles) as the family of probability distributions on the phase space $\Omega_\Lambda (= C_\Lambda)$. This family is defined by the following densities with respect to the measure μ_Λ :

$$p_{\Lambda, \beta, \mu}^{\text{grandcanon}}(c) = (\Xi(\Lambda, \beta, \mu))^{-1} e^{-\beta(H_\Lambda(c) + \mu N(c))}.$$

Here $\beta > 0$ and $\mu \in R^1$ are parameters and $\Xi(\Lambda, \beta, \mu)$ is a normalizing factor (called the grand statistical sum or the grand partition function):

$$\begin{aligned} \Xi(\Lambda, \beta, \mu) &= \int_{C_\Lambda} e^{-\beta(H_\Lambda(c) + \mu N(c))} d\mu_\Lambda(c) \\ &= 1 + \sum_{N=1}^{\infty} e^{-\beta\mu N} \int_{C_\Lambda^{(N)}} e^{-\beta H_{\Lambda, N}(c)} d\mu_\Lambda^{(N)}(c) \\ &= 1 + \sum_{N=1}^{\infty} e^{-\beta\mu N} Z_{\Lambda, N, \beta}^{\text{indistin}} = 1 + \sum_{N=1}^{\infty} \frac{e^{-\beta\mu N}}{N!} Z_{\Lambda, N, \beta}^{\text{distin}}. \end{aligned}$$

We obtain the family of probability distributions $\{P_{\Lambda, \beta, \mu}^{\text{grandcanon}}; \beta; \mu\}$, which depend on two parameters: β (inverse temperature) and μ (*chemical potential*). The idea of passing from the canonical distribution to the grand canonical ensemble is the same as the idea of passing from the microcanonical distribution to the canonical distribution. In the first case the distribution with fixed value of energy $H_{\Lambda, N} = E$ is replaced by a distribution with arbitrary values of energy and the parameter E is replaced by the parameter β . In the second case the distribution with fixed values of the number of particles N is replaced by the distribution with a variable number of particles and the parameter N is replaced by the parameter μ . The grand canonical ensemble may look less natural than microcanonical or canonical ones, but it is the most convenient one for calculation and for the theoretical analysis. It turns out that the family of grand canonical distributions is equivalent to the family of canonical ones in the sense mentioned earlier: the mean values calculated with the help of these ensembles “almost coincide”:

$$\langle F \rangle_{\Lambda, \beta, \mu}^{\text{grandcanon}} \approx \langle F \rangle_{\Lambda, N, \beta}^{\text{canon}},$$

provided a certain correspondence between N and μ exists and Λ and β remain fixed. This correspondence is obtained by the formula

$$N = \langle N(c) \rangle_{\Lambda, N, \beta}^{\text{canon}} = \langle N(c) \rangle_{\Lambda, \beta, \mu}^{\text{grandcanon}} = - \frac{\partial \ln \Xi(\Lambda, \beta, \mu)}{\beta \partial \mu}.$$

The solution $\mu = \mu(N)$ of the equation

$$N = - \frac{\partial \ln \Xi(\Lambda, \beta, \mu)}{\beta \partial \mu}$$

gives us the necessary correspondence. The exact assertion about the equivalence of the grand and the canonical ensembles is valid within the thermodynamic limit and we shall return later to it in more detail. We notice that a conditional distribution of probability

$$\Pr(c \in A | N(c) = N), \quad A \subset C_\Lambda^{(N)},$$

generated by the grand Gibbs distribution on the space $C_\Lambda^{(N)}$ in the case where the number of particles is fixed and is equal to N , coincides with the canonical Gibbs

distribution on $C_\Lambda^{(N)}$. Indeed, for $A \subset C_\Lambda^{(N)}$ we have

$$\begin{aligned} \Pr(c \in A/N(c) = N) &= \frac{\Pr(c \in A/N(c) = N)}{\Pr(N(c) = N)} \\ &= \frac{(\Xi(\Lambda, \beta, \mu))^{-1} \int_A e^{-\beta(H_{\Lambda, N}(c) - \mu N)} d\mu_\Lambda^{(N)}(c)}{(\Xi(\Lambda, \beta, \mu))^{-1} \int_{C_\Lambda^{(N)}} e^{-\beta(H_\Lambda(c) + \mu N)} d\mu_\Lambda^{(N)}(c)} = \frac{\int_A e^{-\beta H_{\Lambda, N}(c)} d\mu_\Lambda^{(N)}(c)}{Z_{\Lambda, N, \beta}^{\text{indistin}}}. \end{aligned}$$

This is a probability of the event A calculated in the canonical distribution on $C_\Lambda^{(N)}$. Note finally that the grand canonical ensemble appears from the microcanonical ensemble in exactly the same way as the canonical one: the distribution of probability for a subsystem of a large system in Λ in a fixed volume $\Lambda_0 \subset \Lambda$ (with an arbitrary number of particles) in the thermodynamic limit $\Lambda \nearrow \mathbb{R}^3$, $\frac{N}{|\Lambda|} \rightarrow \rho$, $\frac{E}{|\Lambda|} \rightarrow e$, coincides with the grand canonical ensemble in Λ_0 for an appropriate choice of parameters β and μ : $\beta = \beta(e, \rho)$ and $\mu = \mu(e, \rho)$.

Thus we have three families of equilibrium distributions for classical gas: the microcanonical, the canonical and the grand canonical distributions; they are equivalent to each other for large systems.

3.3. The case of lattice gas. We can consider all three ensembles for the lattice gas. In this case the phase space Ω_Λ of a finite system (in a finite set $\Lambda \subset \mathbb{Z}^V$) is finite and the probability distribution on Ω_Λ is defined by specifying the probability of each state of the system.

We consider only the system of indistinguishable particles in the set $\Lambda \subset \mathbb{Z}^3$. The entire phase space of such a system is the totality C_Λ of all subsets $c \subseteq \Lambda$:

$$\Omega_\Lambda = C_\Lambda.$$

Microcanonical distribution with fixed values N and E is defined on the set

$$\Omega_{\Lambda, N, E} = \{c : N(c) = N, H_\Lambda(c) = E\}$$

and coincides with the uniform distribution on $\Omega_{\Lambda, N, E}$:

$$\Pr_{\Lambda, N, E}(c) = |\Omega_{\Lambda, N, E}|^{-1}$$

($|\Omega_{\Lambda, N, E}|$ is cardinality of $\Omega_{\Lambda, N, E}$). Since the energy

$$H_\Lambda(c) = \sum_{q, q' \in c} U(q - q')$$

takes discrete values, the parameter E also takes a discrete set of values. The canonical Gibbs distributions are defined on sets $\Omega_{\Lambda, N}$

$$C_\Lambda^{(N)} = \{c \in C_\Lambda : N(c) = N\}$$

by the probabilities

$$\begin{aligned} \Pr_{\Lambda, N, \beta}(c) &= Z_{\Lambda, N, \beta}^{-1} \exp\{-\beta H_\Lambda(c)\}, \quad c \in C_\Lambda^{(N)}, \\ Z_{\Lambda, N, \beta} &= \sum_{c \in C_\Lambda^{(N)}} e^{-\beta H_\Lambda(c)}. \end{aligned}$$

Finally, grand canonical ensembles are defined on the entire space C_Λ by the probabilities

$$\Pr_{\Lambda, \beta, \mu}(c) = \frac{1}{\Xi(\Lambda, \beta, \mu)} e^{-\beta H_\Lambda(c) - \mu N(c)}$$

$$\Xi(\Lambda, \beta, \mu) = \sum_{c \in C_\Lambda} e^{-\beta H_\Lambda(c) - \mu N(c)}.$$

3.4. The lattice spin systems. Let us recall that the phase space of such a system (inside $\Lambda \subset \mathbb{Z}^3$) is the set Ω_Λ of the configurations (or functions)

$$\sigma = \{\sigma(x), x \in \Lambda\}, \quad \sigma(x) = \pm 1.$$

The energy $H_\Lambda(\sigma)$ of the configuration σ is given by the formula

$$H_\Lambda(\sigma) = \sum_{\substack{x_1, x_2 \in \Lambda, \\ x_1 \neq x_2}} U(x_1 - x_2) \sigma(x_1) \sigma(x_2) + h \sum_{x \in \Lambda} \sigma(x).$$

The Gibbs distribution in this case is defined on the set Ω_Λ by the Gibbs formula

$$\Pr_{\Lambda, \beta}(\sigma) = \frac{1}{\Xi(\Lambda, \beta)} e^{-\beta H_\Lambda(\sigma)}, \quad \Xi(\Lambda, \beta) = \sum_{\sigma} e^{-\beta H_\Lambda(\sigma)}.$$

LECTURE 4

The Thermodynamic Limit and the Limit Gibbs Distribution

4.1. The thermodynamic limit. I have already mentioned several times that the size of systems considered in statistical physics is large compared to the characteristic size of a particle, and the number of particles is large. Mathematically it means that for any local physical variable F its average with respect to a finite equilibrium ensemble (the microcanonical ensemble with fixed Λ, N, E or the canonical ensemble with fixed Λ, N or finally, the grand canonical ensemble with fixed Λ) does not have a physical meaning, and only the limit value of it is meaningful. Now I shall explain this in detail.

First let us recall that a *local variable* is a function F_B on the phase space of a system — say, on the phase space of the configuration gas of indistinguishable particles — that depends on positions of the particles in a fixed domain $B \subset \mathbb{R}^3$:

$$F_B(c) = F_B(c \cap B), \quad c \in \Omega_\Lambda.$$

The notion of the thermodynamic limit includes the following.

1. $\Lambda \nearrow \mathbb{R}^3$, which means that we consider an arbitrary extending sequence of domains

$$\Lambda_1 \subset \Lambda_2 \subset \dots \subset \Lambda_N \subset \dots,$$

which fill the entire space

$$\bigcup \Lambda_n = \mathbb{R}^3.$$

2. In addition, in the case of canonical ensemble we choose a sequence of numbers of particles N_i such that

$$\frac{N_i}{|\Lambda_i|} \rightarrow \rho, \quad i \rightarrow \infty.$$

This means that we fix the limit *density* ρ of particles (with fixed β).

3. Finally, in the case of microcanonical ensemble we choose N_i and values of energy E_i in such a way that

$$\frac{E_i}{|\Lambda_i|} \rightarrow e, \quad \frac{N_i}{|\Lambda_i|} \rightarrow \rho, \quad i \rightarrow \infty.$$

This means that in addition to the limit density of particles, we fix the *specific energy per unit volume* e . In the case of a grand canonical ensemble the parameters β and μ are fixed.

Thus for any local function F_B there exist the following limits.

$$1) \lim_{\Lambda \nearrow \mathbb{R}^3, \frac{E}{|\Lambda|} \rightarrow e, \frac{N}{|\Lambda|} \rightarrow \rho} \langle F_B \rangle_{\Lambda, N, E}^{\text{microcanon}} = \langle F_B \rangle_{\infty, \rho, e}^{\text{microcanon}}, \text{ or}$$

2) in the case of a canonical ensemble

$$\lim_{\substack{\Lambda \nearrow \mathbb{R}^3, \{N \\ |\Lambda|}} \rightarrow \rho, \beta \text{ is fixed} \langle F_B \rangle_{\Lambda, N, \beta}^{\text{canon}} = \langle F_B \rangle_{\infty, \rho, \beta}^{\text{canon}},$$

3) finally, in the case of a grand canonical ensemble

$$\lim_{\Lambda \nearrow \mathbb{R}^3, \beta, \mu \text{ are fixed}} \langle F_B \rangle_{\Lambda, \beta, \mu}^{\text{grandcanon}} = \langle F_B \rangle_{\infty, \beta, \mu}^{\text{grandcanon}}.$$

These limits are called *thermodynamic* limits. Of course, there is a question of why these limits exist for any local function and any sequence of set

$$\Lambda_1 \subset \Lambda_2 \subset \dots \subset \Lambda_N \subset \dots$$

and why they do not depend on this sequence. We shall return to this question later; now we just assume that such limits exist.

Thus, I want to emphasize that statistical physics studies the properties of systems and mean values of physical quantities after the passage to the thermodynamic limit. Of course, there are problems related to the finite size of the system, for example the influence of the boundary of Λ , but the basic problems of statistical physics look more natural and even more simple after passing to the thermodynamic limit. As we shall see later, several important notions of statistical physics can be rigorously defined only in the framework of the thermodynamic limit (for example, the important notion of phase transition). Of course, one has to remember that real physical systems are finite and the thermodynamic limit means some idealized description of reality, but that can be said about any mathematical (or theoretical) method in physics.

For a long time the thermodynamic limit was understood and used too formally: the mean values of some local variables and some relations between them used to be calculated in a finite ensemble and then, in the formulas obtained, the limit passage was carried out. Only about twenty five years ago was the thermodynamic limit interpreted more obviously and meaningfully. Let us consider for instance the grand canonical ensemble and let the limits

$$\lim_{\Lambda \nearrow \mathbb{R}^3} \langle F_B \rangle_{\Lambda, \beta, \mu} = \langle F_B \rangle_{\infty, \beta, \mu}$$

exist as indicated before. One may ask whether it is possible to consider the limit value $\langle F_B \rangle_{\infty, \beta, \mu}$ as an average of F_B for some probability distribution. It turns out that this can be done, and thus we come to an important notion of the limit Gibbs distribution. However, before we introduce such a distribution we must define the space on which this distribution is given, that is, the *phase space of the infinite system*. For a case of configuration gas of indistinguishable particles in \mathbb{R}^3 we assume that the state of an infinite system is defined by a locally finite subset $c \subset \mathbb{R}^3$. Recall that a subset $c \subset \mathbb{R}^3$ is said to be *locally finite* if for any bounded domain $B \subset \mathbb{R}^3$, part of c inside B is finite:

$$|c \cap B| < \infty.$$

The totality of such subsets is denoted by C_∞ and thus the phase space Ω_∞ of an infinite system is equal to C_∞ :

$$\Omega_\infty = C_\infty.$$

4.2. Definition of limit Gibbs distributions. We fix the interaction potential between particles and the values of parameters β and μ and then for any bounded domain Λ we consider the grand canonical Gibbs distribution $P_{\Lambda,\beta,\mu}^{\text{grandcanon}}$ defined on the space $\Omega_\Lambda = C_\Lambda$ with parameters β and μ and the energy

$$H_\Lambda(c) = \sum_{q_i, q_j \in c} U(q_i - q_j).$$

The probability distribution $P_{\infty,\beta,\mu}$ defined on the space C_∞ is called the *limit Gibbs distribution* if for any local function F_B the limit

$$\lim_{\Lambda \nearrow \mathbb{R}^3} \langle F_B \rangle_{\Lambda,\beta,\mu}$$

exists and is equal to the mean value of F_B with respect to $P_{\infty,\beta,\mu}$:

$$\langle F_B \rangle_{\infty,\beta,\mu} \equiv \int F_B dP_{\infty,\beta,\mu},$$

i.e.,

$$\lim_{\Lambda \nearrow \mathbb{R}^3} \langle F_B \rangle_{\Lambda,\beta,\mu} = \langle F_B \rangle_{P_{\infty,\beta,\mu}}.$$

So far we have considered grand canonical distribution $P_{\Lambda,\beta,\mu}$ and defined the Gibbs limit distribution using the limits of the mean values of local function F_B , $B \subset \mathbb{R}^3$.

Other ensembles can be considered in a similar way. For instance, in the case of a canonical ensemble we can define the limit Gibbs distribution $P_{\infty,\rho,\beta}$ by the formulas

$$\lim_{\Lambda \nearrow \mathbb{R}^3, \frac{N}{|\Lambda|} \rightarrow \rho} \langle F_B \rangle_{P_{\Lambda,N,\beta}} = \langle F_B \rangle_{P_{\infty,\rho,\beta}}$$

and similarly for a microcanonical ensemble. Thus if we assume that such limit distributions exist, we get three families of limit distributions

$$\{P_{\infty,\beta,\mu}^{\text{grandcanon}}\}, \quad \{P_{\infty,\rho,\beta}^{\text{canon}}\}, \quad \{P_{\infty,\rho,e}^{\text{microcanon}}\}$$

on the space C_∞ .

4.3. Limiting equivalence of ensembles. According to the main hypothesis, all three families actually coincide. This means that there exists actually just one family and different ways of its parametrizations; to be more precise, there is a correspondence

$$\mu \rightarrow \rho = \rho(\mu) \quad (\text{with fixed } \beta)$$

such that

$$P_{\infty,\beta,\mu}^{\text{grandcanon}} = P_{\infty,\rho(\mu),\beta}^{\text{canon}}.$$

Then there is another correspondence

$$e \rightarrow \beta = \beta(e) \quad (\text{with fixed } \rho)$$

such that

$$P_{\infty,\rho,e}^{\text{microcanon}} = P_{\infty,\rho,\beta(e)}^{\text{canon}}.$$

Finally, there is a similar correspondence between pairs of parameters (β, μ) and (ρ, e) for which $P_{\infty,\beta,\mu}^{\text{grandcanon}}$ and $P_{\infty,\rho,e}^{\text{microcanon}}$ coincide. These assertions are called the *equivalence principle of limit equilibrium ensembles*

I want to make an important remark about this principle. Namely, it is true only in some domain of values of parameters (for instance, the parameters (β, μ)), namely, for the so-called *regular values* of parameters. These are the values of parameters for which limit Gibbs distributions exist (and the limits are unique) and

possess many good properties (ergodicity, fast decreasing correlations, and so on). At present, for a large class of systems it has been proved that pairs of parameters (β, μ) , where $\beta > 0$ is small or $\mu > 0$ is large, are regular. However, it is known that for many systems there exist *singular* values of parameters (β, μ) . For these values of the parameters there exist several limit Gibbs distributions (I shall say later what this means), and/or they lose “good” properties. This phenomenon is known as the *phase transition*. In particular the equivalence principle of ensembles can be violated for singular values of parameters (β, μ) . The study of limit Gibbs distributions for singular values of parameters (β, μ) is the most difficult problem in statistical physics.

I have described the thermodynamic limit and the limit Gibbs distributions for configuration gas. Similarly one can introduce these notions for other systems: classical gas, lattice gas and spin systems.

In the case of classical gas, the phase space of the infinite system consists of the all countable subsets of pairs

$$c = \{(q_i, v_i)\} \subset \mathbb{R}^3 \times \mathbb{R}^3$$

such that for any bounded domain $\Lambda \subset R$ number of pairs $(q_i, v_i) \in c$ with $q_i \in \Lambda$ is finite.

In the case of lattice gas, the phase space of the infinite system consists of all subsets $c \subset \mathbb{Z}^3$.

Finally, for the spin system the state of the infinite system is a configuration (function)

$$\sigma = \{\sigma(x), \quad x \in \mathbb{Z}^3\}, \quad \sigma(x) = \pm 1,$$

defined on the whole lattice \mathbb{Z}^3 . The definition of the thermodynamic limit and limit Gibbs distributions in all cases repeat that for the case of the configuration gas.