PACS numbers: 05.20.-y, 05.45.-a, 05.90.+m, 63.20.K-

Why does statistical mechanics 'work' in condensed matter?

V V Brazhkin

DOI: https://doi.org/10.3367/UFNe.2021.03.038956

1049

1050

1052

1052

1054

1055

1056

1057

Contents

- 1. Introduction
- 2. Ergodicity, mixing properties, and Gibbs distribution
- 3. Statistical mechanics in gases
- 4. Gibbs distribution in solids
- 5. Hierarchy of times in establishing the Gibbs distribution
- 6. Diffusion and ergodicity in solids
- 7. Conclusion
- References

Abstract. The reasons behind the possibility of using the Gibbs distribution in condensed matter are considered. While the basics of statistical mechanics in gases are covered in great detail in many textbooks and reviews, the reasons for using the Gibbs distribution in crystals, glasses, and liquids are rarely considered. Most textbooks still only speak of a qualitative replacement of the mechanical description with a statistical one when considering a very large number of particles. At the same time, it turns out that the Gibbs distribution is not formally applicable to a harmonic crystal of a large number of particles. However, a system of even a small number of coupled anharmonic oscillators can demonstrate all the basic features of thermodynamically equilibrium crystals and liquids. It is the nonlinearity (anharmonism) of vibrations that leads to the mixing of phase trajectories and ergodicity of condensed matter. When the system goes into a state of thermodynamic equilibrium, there are 3 characteristic time scales: the time of thermalization of the system (in fact, the time of establishment of the local Gibbs distribution in momentum space and establishment of the local temperature); the time of establishment of a uniform temperature in the system after contact with the thermostat; and, finally, the time of establishment of ergodicity in the system (in fact, the time of 'sweeping' the entire phase space, including its coordinate part). The genesis of defect formation and diffusion in crystals and glasses, as well as their ergodicity, is discussed.

Keywords: Gibbs distribution, ergodicity, local instability, nonlinear oscillations, thermalization, diffusion

V V Brazhkin

Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, Kaluzhskoe shosse 14, 108840 Troitsk, Moscow, Russian Federation E-mail: brazhkin@hppi.troitsk.ru

Received 3 August 2020, revised 11 March 2021 Uspekhi Fizicheskikh Nauk **191** (10) 1107–1116 (2021) Translated by V L Derbov

1. Introduction

The focus of statistical physics is the study of laws that govern the behavior and properties of objects consisting of a large number of particles. True, it is a priori unclear what 'large' means and how, apart from the scale of fluctuations, a system of 10²³ particles differs from a system of 10 or 100 particles and how the laws of thermodynamics can be applied to the latter. The main substantive idea of statistical physics is the possibility of using the Gibbs distribution in many-particle systems, which determines the statistical distribution of the characteristics of a relatively small part of any large closed system. The 'fulfillment' of the Gibbs distribution is equivalent to the statement that the system is in a state of thermodynamic equilibrium. At first glance, the question presented in the title of this article seems to be of little meaning. It would seem that the huge number of atoms or molecules that make up a condensed medium should automatically allow using all the laws of statistical physics. However, this is not as obvious as it seems at first glance.

Gibbs considered two systems: one completely isolated from the environment, whose energy is constant, and a system in contact with a thermostat, for which the number of particles is fixed, and the energy is constant only on average [1]. For systems of the first type, the microcanonical Gibbs distribution is valid, while for systems of the second type, it is the canonical distribution [1, 2]. Below, we will speak exactly of the canonical distribution. The canonical Gibbs distribution establishes an exponential dependence of the probabilities of the states of a many-particle system on the state energy and the inverse temperature $(\omega_n = A \exp(-E_n/T))$ [1, 2]. Moreover, the fact that the Gibbs distribution 'works' in a system, means, in fact, the possibility of introducing the temperature itself, i.e., the system is 'thermalized'. In this case, the temperature is defined as a quantity, inverse to the energy derivative of the logarithm of the number of states (entropy).

In an ideal gas, the Boltzmann and Maxwell distributions automatically follow from the Gibbs distribution. If a quasiclosed many-particle system is initially in a nonequilibrium state, then, according to the second law of thermodynamics, V V Brazhkin

its entropy will increase in time, and the system will return to the state of thermodynamic equilibrium, in which the Gibbs distribution is valid. The 'derivation' of the Gibbs distribution can be found in most classical monographs [2] and generally follows the original presentation by J Gibbs himself [1]. From a mathematical point of view, this distribution is due to the fact that the probabilities of independent events are multiplied, and the probability of the simultaneous occurrence of several events is an exponential function of their number.

The problem of a transition from time-reversible physical equations of classical and quantum mechanics to the statistical description of the system can be divided into several steps. The first global level is largely of a historical and philosophical character. Time-reversible equations are fundamentally unable to yield irreversible solutions and, therefore, an increase in entropy, system thermalization, etc. The problem of irreversibility and ergodicity and the substantiation of statistical mechanics were closely dealt with by W Thomson, J Maxwell, R Clausius, H Helmholtz, L Boltzmann, M Planck, H Poincaré, J Gibbs, A Einstein, P Ehrenfest, J von Neumann, M Born, W Pauli, L Onsager, E Hopf, G Birkhoff, N N Bogolyubov, R Kubo, L Van Hove, N S Krylov, Ya G Sinai, L D Landau, I Prigogine, and many other distinguished scientists (see [3-8] and references therein).

Many researchers, starting with Boltzmann and Einstein, believed that the irreversibility of the behavior of manyparticle systems is merely an illusion. A popular point of view implies considering the entire Universe for precise analysis, and it is impossible to state unambiguously whether the Universe is an open system or a closed one. This approach was shared by N N Bogolyubov and L D Landau. The incompleteness of knowledge, namely, the fundamental inaccuracy of coordinates and momenta due to various processes, including the interaction with vacuum fluctuations of the field, was also considered (starting with H Lewis and Born) an important factor related to this problem.

Recently, the inclusion of an observer in the measurement or investigation process has become a popular trend in this area. This approach is most vividly presented in the work of L Macone [9], according to which the second law of thermodynamics is a trivial consequence of the fact that processes with decreasing entropy cannot leave a trace in the minds of researchers. In this regard, it is also necessary to recall the activities of M B Menskii, concerned with the quantum theory of consciousness, and his partly provocative but very interesting note in the journal *Physics–Uspekhi* [10]. In a sense, this trend was anticipated by R E Peierls, who viewed the entire Universe as a gigantic experiment conducted by a god experimenter. According to Peierls, in this case, the irreversibility arises only in the experimenter's mind. A separate marginal direction that does not involve an observer in consideration is the modification of the original equations of quantum and classical mechanics to make them initially irreversible in time (see, e.g., [11]). Work on the study of the partial loss of information in black holes and other exotic objects in our Universe also stands apart.

Physics–Uspekhi has already published a number of reviews on nonequilibrium statistical mechanics. For example, G A Martynov [12] reminds us that the reasons for the irreversibility of kinetic processes are: (a) the impossibility of absolute accuracy in measuring coordinates and momenta when specifying the initial data; and (b) the instability of the

dynamics of systems. In fact, the importance of the incompleteness of knowledge about coordinates and momenta for the problem under consideration was noted by G Lewis in 1930. The same point of view in a pragmatic perspective is presented in the course of theoretical physics by L D Landau [2], where the quasi-closed part of a large system (thermostat) is initially considered, and the thermostat can weakly affect the subsystem, leading to small uncertainties in the momenta and particle coordinates, which rapidly increase with time. Following this tradition, we will not consider the root cause of small uncertainties or fluctuations either, but will discuss the features of the system dynamics, more precisely, the reasons for dynamic instability.

Note that most of the points that will be discussed here are, of course, fairly well known. Moreover, in a number of modern textbooks on statistical physics (see, e.g., [13]), considerable attention is paid to the issues of ergodicity and the mixing of phase trajectories. There are also modern monographs, in which problems of nonequilibrium statistical mechanics are considered in some detail and at a higher level of mathematical rigor [8]. Several reviews in *Physics–Uspekhi* (e.g., [14]) and monographs [15, 16] are devoted to the relationship between nonlinear dynamics and statistical mechanics.

At the same time, most of the monographs mentioned have been released, unfortunately, in a small print run. Many scientists (as well as students) still have the idea that a necessary condition for the fulfillment of the laws of statistical mechanics is the 'thermodynamic limit' - a macroscopically large (10²³) number of particles. However, a large number of particles by itself does not lead to the possibility of a statistical description (see, e.g., the so-called Toda chain [17]). Moreover, ergodicity and 'correct' statistical behavior of a system can be observed for systems with a very small number of particles and degrees of freedom (N > 2) [13, 15]. In a number of monographs and reviews, including those in Physics-Uspekhi (see, e.g., [14, 15]), the relation between the theory of nonlinear oscillations and the foundations of statistical mechanics has already been noted, but no emphasis was placed on these issues. The purpose of this paper is to remind readers of the reasons for the applicability of the laws of statistical mechanics for condensed matter. In statistical physics and equilibrium thermodynamics of macroscopic systems, the time dependence is absent. However, when considering system thermalization and the appearance of ergodicity, we have to introduce the dynamics of particles and the corresponding times into consideration. In this article, we analyze the corresponding equilibration times. It is interesting that considering the dynamics of particles on the most general grounds allows drawing nontrivial conclusions about diffusion in solids.

2. Ergodicity, mixing properties, and Gibbs distribution

The issues raised in this section relate first and foremost to the field of mathematics or mathematical physics, so I apologize to the readers that the consideration is not always appropriately rigorous.

The ergodicity of particle motion is one of the best-known and most important properties of a statistical system. The ergodicity means that, in the limit of long-term observation, the time during which the system is in an element of the phase space is proportional to the phase volume of this element. For



Figure 1. Illustration of difference between ergodic quasiperiodic motion (a) and motion with mixing (b).

an ergodic system, the time average of any function of state equals the statistical average over the microcanonical distribution and depends only on energy. It is the ergodicity that allows introducing the notion of probability for an individual dynamic trajectory.

For a long time, ergodicity was considered a necessary and sufficient condition for the applicability of the Gibbs distribution. However, it was later found that a condition stronger than ergodicity, namely, the mixability of motion or mixing of phase trajectories (or simply mixing), is required for a statistical description [6, 13, 15]. The notion of mixing (or mixability) was introduced by Gibbs, and a serious basis for this notion was provided by E E Hopf and N S Krylov; however, its importance was fully understood only in the second half of the 20th century. It was also known for a long time that the motion of a system may be quasiperiodic, even in the presence of ergodicity [15]. The motion in the phase space in this case is reminiscent of the winding of a thread on a spool or the scanning of a beam over an oscilloscope screen, which, of course, does not correspond to the intuitive view of random processes (Fig. 1). A physically clear analogy is that the flow of trajectories in this case is laminar. A fundamentally different picture is observed in the case of mixing. With time, an initially small spherical region of the phase space rapidly spreads over the entire phase space, preserving its volume due to the Liouville theorem. The shape of the region's boundary becomes more and more complex, and its penetration into distant parts of the phase space occurs due to the appearance of multiple long and thin sprouts from the initially compact domain (Fig. 2). Formally, the mixing condition has long been known in physics as a condition for decoupling temporal correlations (precisely because of the huge number of intertwined 'sprouts'). Note that the mixing condition automatically implies the ergodicity of the system, while the reverse is not true [6, 15].

It was quite quickly discovered that the mixing property must be associated with the dynamic instability of the system [6]. As mentioned above, an initially small compact domain in the phase space spreads over the entire space, which means a rapid propagation of phase trajectories, as well as their entanglement (since the phase space is bounded). In fact, the mixing leads to a loss of information. The flow of trajectories in this case is turbulent. This type of motion is called a local instability. It is the local instability that gives rise to the mixing, which, in turn, provides a sufficient condition for the possibility of using the Gibbs distribution and system thermalization.

The mixing makes it possible to introduce the notion of 'statistically independent events', such as the appearance of a phase trajectory in various parts of the phase space. It is



Figure 2. Illustration of 'spreading' of a 'phase liquid' drop in the phase space.

important that the mixing is also possible in systems with a very small number of particles (N > 2) [15, 16]. If a system is not initially in the equilibrium state, then, in the case of ergodicity, the equilibrium values of macroscopic quantities are achieved only on average in time [8], while in the case of mixing they asymptotically tend to their equilibrium values in the limit of large times.

Note that the time independence of entropy in systems whose dynamics are described by equations reversible in time was already known to Gibbs [18], and 100 years later this fact was multiply 'rediscovered'. A way out of this predicament was also proposed by Gibbs. According to his proposal, 'finegrained mathematical' entropy should be replaced with 'coarse-grained physical' entropy, when the phase space is coarsely divided into regions of finite phase volume. The coarsening is accompanied by the loss of information about individual trajectories in the phase space exactly because of the mixing mechanism. Surely, the reversibility is also lost in this case, and the coarse-grained physical entropy can increase. In this sense, the definition of entropy as a measure of information loss is quite convenient and constructive.

Note that in computer modeling (e.g., within the method of molecular dynamics) the ergodicity and mixability of many-particle systems are also ensured by similar coarsening procedures, namely, rounding the numbers to a finite number of digits (although the 'computer' and 'natural' coarsening are, of course, not equivalent).

At a certain stage of scientific progress, it seemed that the situation would become clearer with the transition from a classical to a quantum mechanical description. In quantum mechanics, there is a natural mechanism for coarsening, namely, the minimal volume of a cell in the phase space cannot be less than $(2\pi\hbar)^{3N}$, where \hbar is the Planck constant, and N is the number of particles. At the same time, the reversibility of quantum mechanical equations also leaves no chance of losing information without an additional coarsening procedure of measurement or observation in the quantum system. In addition, as correctly mentioned in modern monographs [13], the magnitude of physical entropy variation cannot depend on the coarsening scale, in particular, cannot be determined by the value of the Planck constant.

From the above considerations, it follows that the generally accepted idea of phase space 'sweeping' as a condition for the Gibbs distribution applicability is not quite true. In the quantum mechanical description, such sweeping can occur without loss of information about the wave functions of the particles. Generally, the procedure of phase space coarsening, although useful for understanding the physics of the processes, cannot be introduced unambiguously. Moreover, it was recently shown that the 'coarse-

grained' entropy might not be approximating the 'finegrained' one, even if the scale of graining tends to zero [8].

Within the framework of the present brief paper, we will not discuss new terms or concepts that continually appear in this field, such as 'K-entropy' and 'weak mixing', which are more mathematical than physical. Readers can familiarize themselves with both of them from classical [15] and more modern [8] reviews and monographs.

To summarize, it is possible to say that for the 'correct Gibbs' behavior of a system, a mechanism of information loss is necessary, and local instability during the mixing process is exactly what provides such a mechanism in the presence of arbitrarily small external perturbations or small uncertainty in the initial coordinates and momenta of the particles.

3. Statistical mechanics in gases

The two simplest and best-studied types of particle motion dynamics, rectilinear uniform motion and harmonic vibration, arise as solutions of simple linear equations. These are exactly the types of dynamics which are commonly used in simplified descriptions of many-particle systems. The first type corresponds to an ideal gas, and the second, to a harmonic crystal. The liquid state is the most complex from the point of view of particle motion dynamics, because, even in a maximally simplified approach, the dynamics of a liquid do not reduce to these two simplest cases.

An ideal gas, i.e., one in which the interaction of particles can be ignored, is the simplest model system of many particles. It is the gas that is considered the basic model system for statistical mechanics in most papers and monographs, starting with the classical work by Boltzmann [6, 8, 12]. In classical textbooks on statistical physics [2], the concrete reason for local instability leading to ergodicity and mixing in a gas is not considered. It is only assumed that even an arbitrarily small interaction between subsystems in some time will lead to the possibility of a statistical description. In this regard, as before, it is stated that a very large number of particles is necessary for the occurrence of thermalization. At the same time, in the case of an ideal gas, the smallest subsystem that can be considered in the limit is one particle, and the Gibbs distribution can be applied directly to it. This is how the Boltzmann and Maxwell distributions for an ideal gas are derived [2].

Note that the absence of interaction between particles in an ideal gas means only the possibility of ignoring this interaction most of the time, when the molecules or atoms of the gas move rectilinearly and uniformly. At the same time, collisions between particles or with the subsystem boundary are of key importance, although the time of these collisions is negligibly small. These are exactly collisions that lead to the 'thermalization' of the gas. In an ideal gas without collisions, the 'Gibbs' distribution does not work at all, i.e., in this system no thermodynamic equilibrium is reached.

Numerous present-day monographs and reviews direct attention to the issue of collisions of particles [8, 12]. Exactly a system with exchange by impacts possesses the property of phase trajectory mixing. As a hypothesis, this statement was made already by Boltzmann, while in a more distinct form it was formulated by N S Krylov [6]. The first rigorous result was obtained in 1963 by Ya G Sinai [19]: a system of two balls in a rectangle possesses the mixing property (the Sinai scattering billiard). The reason for local instability in the Sinai billiard is the convex shape of the balls, or walls in the case of the motion of a single ball. Due to collisions, the



Figure 3. Illustration of growing uncertainty of the momentum vector upon scattering from a convex surface (billiards).

uncertainty in the momentum direction of a particle exponentially grows with an increase in the number of collision events, which leads to 'sweeping' the entire phase space in the presence of an arbitrarily small perturbation from other subsystems (Fig. 3). Note that several models, including Hadamard's billiard, describing the motion of a point particle on surfaces with negative curvature preceded the Sinai billiard. Hadamard's billiard is probably the earliest (1898) example of studying deterministic chaos. Later, Sinai's results were generalized to a larger number of balls and parallelepipeds of different dimensions [20]. Note that, with certain assumptions related to the initial conditions, even a collisionless gas in a polyhedron with plane walls will be an ergodic system.

We would like to note that the real problem of scattering of atoms or molecules in collisions is, of course, not quite equivalent to the scattering of balls [12]. However, the conclusion about the exponential increase with time (or with the increasing number of collision events) of the uncertainty in the particle momentum direction remains valid. The idea of the exponential growth of small perturbations of particle coordinates and momenta during collisions became generally accepted only in the last decade and found no reflection in classical textbooks on statistical physics [2].

Thus, the reason for the mixing of phase trajectories in gases and the applicability of the Gibbs distribution is the scattering of particles during collision processes, since, in the course of multiple collisions, the uncertainties of coordinates and momenta accumulate exponentially (with time or with increasing number of collisions) and a loss of information occurs.

4. Gibbs distribution in solids

A rarified gas is considered a model system in an overwhelming majority of papers and monographs devoted to the problems of ergodicity and mixing in statistical mechanics. At the same time, the genesis of the Gibbs distribution in condensed media (solids, liquids) is rarely considered. In most classical textbooks (e.g., [2]), a crystal at low temperatures is considered an ensemble of independent harmonic oscillators. Then, all expressions related to a single vibrational degree of freedom in a diatomic molecule of a gas are used [2]. However, it is obvious that the possibility of applying the Gibbs distribution in crystals does not follow directly from the ergodicity and mixability of diatomic molecules in a gas.

The issue of ergodicity of crystals is, generally speaking, ambiguous. In contrast to particles in gases and liquids, the particles in a crystal at low temperatures vibrate with small amplitudes and in the process of these vibrations sweep only a small part of the phase space rather than cover the entire phase space. Moreover, a crystal state with a definite structure corresponds to a deep energy minimum in the configuration phase space, separated by high energy barriers from other configurations of particles (for example, other crystalline phases dynamically stable under the given conditions). As a result, during the time of the experiment, no changes in the configuration of the average position of particles occurs, and the system turns out to be 'locked' in the state of a stable or metastable crystal (see [21] on the applicability of statistical physics and thermodynamics to metastable states of crystals and glasses). N N Bogolyubov proposed using the term 'conditionally ergodic systems' in application to crystals [5].

The behavior of a harmonic crystal is rigorously described by a combination of normal vibrational modes. If only one mode is excited, there is no mechanism to excite other modes, and such a system formally has zero entropy. Moreover, even if we assume a small uncertainty of the initial coordinates and momenta in the system of harmonic oscillators, these uncertainties will remain small with time, since, in a harmonic system, local instabilities are absent, and there is no mechanism for uncertainty accumulation and information loss. Therefore, a set of coupled harmonic oscillators is not a thermodynamically equilibrium system.

Much less attention is paid in the literature to the thermalization of a system of oscillators than to the thermalization of gases. Worth mentioning is the rigorous result obtained by N N Bogolyubov on the thermalization of a single oscillator brought into contact with a thermalized thermostat of a large number of oscillators [5]. In recent years, a number of rigorous results in this field were obtained by V V Kozlov [8]. Various cases of sympathetic pendula (a system of identical harmonic oscillators connected by springs) were considered. Such systems are, of course, not ergodic; moreover, they are integrable [8]. At the same time, the energies of coupled oscillators equalize with time on average, which can be interpreted as the equalization of 'temperatures' of the subsystems.

The next obvious step in explaining thermalization in a system of oscillators is the introduction of nonlinearity (anharmonicity) for coupling. Indeed, the integrability and the possibility of a complete description of the dynamics in time are rather an exclusion for nonlinear systems. We recall that a system with N degrees of freedom is called integrable if it has N independent integrals of motion. There are only a few classes of exactly solvable systems of nonlinear equations, including the abovementioned Toda chain of an infinite number of particles. An overwhelming majority of nonlinear systems are nonintegrable. However, nonlinearity in a system does not automatically lead to stochastization and thermalization.

One of the first attempts to study thermalization was the modeling of a chain of 64 particles connected with springs with small nonlinearity (the famous work by Fermi, Pasta, and Ulam (FPU)) [22]. The problem was established by E Fermi, who was interested exactly in the relation between the nonlinearity of interparticle interaction and the con-

densed medium ergodicity. One mode or a few modes were excited in the simulation. In spite of the expectations, the energy in the FPU chain did not distribute uniformly over the vibration modes (only a few spectrally adjacent modes were excited), and the system itself regularly 'almost' returned to its initial state. Formally, there is nothing surprising in such a conditionally periodic character of system motion, because, according to the Poincaré recurrence theorem, the energies of individual particles oscillate and, of course, do not tend to definite values when time unlimitedly increases.

The paper by Fermi, Pasta, and Ulam strongly influenced the physics of integrable nonlinear systems and solitons. Analyses of excitations in a chain of particles with nonlinear interaction has shown the formation of vibrational resonances in the spectrum. Later, it was found that a criterion of thermalization of such a system is the overlap of all neighboring resonances (the Chirikov criterion [15]). The Fermi–Pasta–Ulam paradox is removed when exciting highenergy modes or increasing the nonlinearity of interaction. In this case, the conditionally periodic character of the motion vanishes and the chain is thermalized [15].

In the general case, a nonlinear dynamic system with several degrees of freedom is nonintegrable. The dynamics of such a system have a complex and frequently chaotic character. Nevertheless, as we saw with the example of the FPU chain [22], in some cases, a certain regularity is preserved in the motion of particles. Such systems are described by the Kolmogorov–Arnold–Moser (KAM) theory (the theory is presented in a series of papers; a simplified interpretation 'for physicists' is presented in monographs [15, 16]). The KAM theory considers systems close to integrable and provides a description of quasiperiodic solutions at small nonlinearity. Thus, the KAM theory shows that quasiperiodic solutions constitute the majority of all dynamic solutions (the role of chaotic solutions is minor).

The KAM theory and the FPU paradox are rare examples of the existence of conditionally periodic solutions in nonlinear systems. In the general case, as mentioned above, nonlinear systems are nonintegrable. The anharmonicity of the oscillators leads to the nonlinearity of the corresponding equations, and the nonlinear problem can be solved only for some kinds of anharmonicity and only for a small number (2–4) of coupled oscillators [16]. However, even in such a small number of oscillators, the basic features of the behavior of any system of nonlinear oscillators manifest themselves. Let us enumerate these features [15, 16].

(1) In an anharmonic oscillator, the frequency of oscillations depends on the amplitude. Systems with 'soft' nonlinearity, in which the frequency decreases with an increase in the amplitude, and those with 'hard' nonlinearity, in which the frequency grows, are distinguished.

(2) For a few coupled anharmonic oscillators, the motion becomes quasiperiodic, i.e., there is a distribution of oscillation periods instead of establishing a definite frequency in a harmonic system. Moreover, the mean period of oscillations in a system of nonlinear oscillators depends on the oscillation amplitude. The oscillations cannot be separated into independent normal modes.

(3) In a system of coupled harmonic oscillators, an alternating transfer of energy from one oscillator to another (beats) occurs. On average, the uniform energy distribution is preserved in time. For coupled anharmonic oscillators, beats also occur, but, besides that, the energy aperiodically localizes at certain oscillators (uniform energy distribution is absent).

(4) Starting with a certain energy (oscillation amplitude), for a few coupled anharmonic oscillators, bifurcations occur, i.e., the instability of quasiperiodic oscillations and the appearance of new solutions (new types of particle motion). If the particles involved in a bifurcation are in an external field of interaction with other particles, the bifurcation leads to a change in the mean equilibrium position of the oscillating particles.

(5) Upon a further increase in energy, the motion of particles in the system of nonlinear oscillators becomes completely stochastic and the features of quasiperiodic motion disappear.

Thus, for the appearance of statistical properties in a system, it is not at all necessary to have a large number of degrees of freedom. These properties can arise in a system of three particles only [15]. The hopping of particles that occurs in solids (glasses and crystals) with an increase in temperature can be associated with bifurcations of solutions for a system of nonlinear coupled oscillators. To summarize, we can ascertain that a system of even a small number (2-4) of coupled nonlinear oscillators demonstrates all the basic types of the motion dynamics of matter particles [14–16]. Of course, the small number of particles immediately requires considering high-power fluctuations, which are absent in the thermodynamic limit. All thermodynamic quantities will experience fluctuations, inversely proportional to the square root of the number of particles. The role of fluctuations and mesoscopic effects in small systems are considered in many modern monographs (see, e.g., [23]).

Quite a few papers and reviews, including those published in *Physics–Uspekhi*, are devoted to stochastic instability in various nonlinear and oscillatory systems [14, 24, 25]. However, in application to the basic issues of condensed media ergodicity, these aspects of nonlinear dynamics are not really considered. In the presence of anharmonicity of interaction, in the process of vibration, the particles in a solid do not return to the same points of the phase space. Like Peano curves, the centers of gravity of the particles in the process of motion densely cover quasispherical regions. Arbitrarily small uncertainties of the initial coordinates and momenta make the system of nonlinear oscillators 'sweep' a certain volume in the phase space and have a nonzero entropy.

We recall that a system of any number of harmonic oscillators without a nonlinearity cannot be thermalized and formally has zero entropy at any amplitude of oscillations (if only some vibration modes are excited, there is no mechanism for energy transfer to other modes). The Gibbs distribution in the system of oscillators arises because of anharmonicity and weak interaction with a thermostat. The local instability leading to the mixing of phase trajectories in condensed media is related to the overlap of neighboring resonances in the spectra of nonlinear oscillations (and the formation of the so-called stochastic layer as a seed for instability [15]) and to bifurcations [16]. Considering nonlinear oscillations in a quantum mechanical system leads to a number of additional complications, but it does not change the general picture [15].

As a rule, excitations in condensed media are described by introducing quanta of normal vibrations — phonons. The anharmonicity of vibrations corresponds to the interaction ('collision') of phonons with their scattering (multiphonon processes). Thus, the statistical description of a gas becomes possible due to the collisions of the particles, while the statistical description of condensed media is due to the 'collisions' of quasiparticles — phonons. In contrast to the number of particles, the number of phonons can change in the process of collisions (the creation of a few phonons from one phonon, merging of several phonons into one, etc.). In liquids, the reasons for mixing are both these mechanisms, the collisions of particles and multiphonon processes.

Note that, in a system of harmonic oscillators, the coordinate and momentum distributions of particles are calculated exactly. The momentum of any particle is limited and unambiguously related to the energy of the corresponding mode. At the same time, in a thermalized vibrational system, the momentum distribution follows from the Gibbs distribution. The probabilities of the values of coordinates and momenta of oscillators are given by the Bloch formula [2], and in the classical limit are reduced to the Maxwell distribution. As already mentioned above, the description of a thermalized crystal in classical monographs on statistical physics relies on the already solved problem of vibrations of a diatomic molecule in a thermalized gas of such molecules [2]. In fact, the crystal thermalization in this approach is 'hardwired' in the collisions of diatomic molecules of the gas. As we have seen, actually, the thermalization of solids is provided by the nonlinear interaction of oscillators, i.e., 'collisions' and scattering of phonons.

Anharmonic condensed media with short-range interparticle coupling, such as a crystal or liquid of nearly hard spheres, demonstrate the possibility of a continuous transition from the 'collision' of phonons to the collision of particles. For most usual condensed media, this change in the description (from the scattering of phonons to the collision of particles) occurs in the supercritical fluid state near the so-called Frenkel line [26].

5. Hierarchy of times in establishing the Gibbs distribution

When a macroscopic system is brought into contact with a thermostat, or it is supplied with energy in any other way (e.g., by internal heating due to the absorption of radiation), a hierarchy of times of equilibrium state establishment arises. Both for collisions of particles and for multiphonon processes, the uncertainty of coordinates and momenta increases exponentially with the growing number of events. Such a strong dependence leads to complete mixing after a few ten events. Indeed, it is possible to estimate the necessary number of particle collisions of phonon scattering processes based on the initial uncertainty of the coordinates and momenta of the particles or on the weak impact on the environment. The relative accuracy of determining the coordinates and momenta in the measurements, as a rule, does not exceed 10^{-10} . An uncertainty of the same scale is induced by the interaction with a thermostat. In the process of exponential growth of uncertainties of coordinates and momenta, the loss of information will occur during 20-25 collisions.

It is curious that a 'strong' estimate can be made based on the 'granularity' of space-time. The coordinate cannot be measured with an error less than the Planck length $\approx 10^{-35}$ m. This granularity, of course, cannot be considered the original cause of nondeterminism. At the same time, note that the ratio of the Planck length to the characteristic interparticle distance (10^{-9} m) amounts to 10^{-26} . Even such a small uncertainty will lead to the complete loss of information in the case of exponential error growth during about 60 scattering events. Similarly, in computer modeling, the error due to rounding to 8 decimal places leads to a loss of information about the initial coordinates and momenta during 20 collisions of each particle. Therefore, for an estimate, it is possible to assume that in any case the local thermalization is achieved during a few ten particle collisions or phonon scattering events.

In gases under normal pressure, the characteristic time between collisions equals a few ten picoseconds. Therefore, the time of local thermalization of gases amounts to a few hundred picoseconds. Note that, when considering the established equilibrium in gases, N N Bogolyubov distinguished two time scales, a fast one (collisionless 'synchronization' of correlation functions) and a slow one (the time to 'sweep' the phase space, including its coordinate part) [5]. The short time actually corresponds to one collision event, and the long one, to a few thousand collisions.

The time of the condensed matter thermalization can be estimated from the rate of multiphonon processes by analogy with the consideration of the 'free path length' of phonons in the analysis of heat conduction in dielectrics [27, 28]. At temperatures of 100-1000 K, the characteristic 'lifetime' of phonons in crystals is from a few picoseconds to a few nanoseconds. The time of condensed medium thermalization is, respectively, a few ten nanoseconds. When decreasing the temperature, the free path length of phonons and their lifetime increase due to both the effective reduction in the anharmonicity effect with a decrease in amplitude and the decrease in the number of short-wave high-energy phonons [27, 28]. At ultralow temperatures, the thermalization time can increase to a few microseconds. In contrast to the velocity of gas particles, the velocity of quasiparticles (phonons) is almost unchanged with temperature (it is merely the speed of sound). An increase in thermalization time with a decrease in temperature for condensed media actually occurs because of the fact that the gas of phonons becomes effectively more rarefied (from the point of view of phonon interaction). In liquids and dense supercritical fluids, the lifetimes of phonontype excitations and the time intervals between the collisions of particles amount to a few picoseconds. Correspondingly, the thermalization times in these media will be the smallest, a few ten picoseconds. Thus, the thermalization of macroscopic systems occurs at times from a few ten picoseconds (for dense fluids) to a few microseconds (for pure crystals at low temperatures).

What do these thermalization times mean? In fact, it is the time of establishment of the local Gibbs distribution in the momentum space (and, respectively, the equilibrium temperature) in regions with a characteristic size of 10–100 nm. If, for example, in a computer simulation we create a system of particles with nearly equal energy per particle, the equilibrium temperature will eventually be established just in a time equal to that of thermalization. In experiments, the thermalization time can be directly observed if an amount of energy is imparted to a macroscopic system of particles almost uniformly over the volume, e.g., by absorbing a pulse of radiation.

In the absence of a uniform supply or extraction of energy over the volume, the temperature of the system will become established after contacting a thermostat. When the system is brought into contact with a thermostat, the equilibrium temperature in the system will be established through the motion of the thermalized front. The time for the equilibrium temperature to become established in the entire sample, naturally, depends on its dimensions. A front itself 10– 100 nm thick (exactly the region in which particles or phonons have interacted several dozen times) with the new equilibrium temperature will be formed during the thermalization time, and the velocity of its movement into the sample depth is limited by the thermal diffusivity of the system. In turn, the thermal diffusivity is determined by the phenomena of phonon and electron transfer (in solids) or transfer of particles (in gases and supercritical fluids). For samples with a size of 1–10 mm, this time can vary from a few tenths of a second for pure crystals with high heat conduction to a few ten seconds for fluids.

Let us proceed to a discussion of the third time scale, the time to establish complete ergodicity in the system. In fact, this is the time of 'sweeping' of the entire available phase space. In the absence of convection, this time is determined by the slowest diffusion processes. In gases, the time of sweeping of the coordinate part of the phase space can be estimated from the conditional 'size' ('area') of the particles (atoms, molecules), the volume per particle, and the mean velocity of particles (in fact, it is the 'slow' diffusion Bogolyubov time [5]). For gases under normal conditions, the time to sweep the entire coordinate space is a few nanoseconds, i.e., it is close to the thermalization time. For rarefied gases, the time to achieve complete ergodicity can substantially increase, up to fractions of a microsecond. For nonviscous liquids and dense supercritical fluids, the time to sweep the coordinate part of the phase space is also close to the thermalization time and amounts to a few ten picoseconds. Quite different is the situation for diffusion processes and the time to achieve 'complete' ergodicity in solids.

6. Diffusion and ergodicity in solids

As mentioned in Section 4, the issue of ergodicity in crystals is not quite unambiguous. In addition, in crystals there are thermodynamically equilibrium defects—vacancies (for some crystals with a body-centered cubic (bcc) lattice interstitial atoms). Vacancies are exactly what provides the self-diffusion processes in a crystal, slightly increasing its entropy. The vacancies themselves or vacancy–interstitial atom pairs arise because of rare fluctuations and hops of particles (bifurcations in the system of nonlinear oscillators).

It should be noted that the mechanism of formation of thermodynamically equilibrium vacancies itself is rarely discussed. As mentioned above, in a thermalized solid, the momentum and energy distribution of particles is Maxwellian. The beats and energy redistribution between anharmonic oscillators are complex and irregular in time. However, obviously, in a system with a macroscopically large number of oscillators at an arbitrarily small mean energy per oscillator, there is always a nonzero probability of accumulating the energy in an individual oscillator, sufficient for a bifurcation of the solution—a hop of a movable particle. The physical mechanism for this is the local transfer of energy to one of the neighboring oscillators in the process of nonlinear oscillations.

The energy of formation of a vacancy–interstitial atom pair exceeds the value of $k_B T_m$ by 30–50 times, where k_B is the Boltzmann constant, T_m is the melting temperature [27–29]. As a result, the equilibrium concentration of vacancies in crystals at temperatures close to T_m is established during $10^{10}-10^{15}$ oscillations, i.e., in $10^{-3}-10^2$ s. In most crystals, the vacancy mechanism of diffusion is implemented: an atom moves to the neighboring vacancy, creating a new one. The corresponding energies of the process activation exceed the value of $k_B T_m$ by 20–40 times [27–29]. In most crystals, the self-diffusion coefficients at temperatures close to that of melting correspond (on average) to a noticeable displacement of atoms (by a few lattice constants) at times of $10^{-4} - 10^{-1}$ s [27-29]. The contribution of equilibrium vacancies to the entropy implies a dynamic picture with the possibility of vacancy motion over the entire volume. That is, all atoms of the crystal should have the potential to participate in the diffusion. Therefore, the thermalization of the crystal caused by the nonlinearity of vibrations automatically leads to the existence of a noticeable number of particles that provide diffusive hops of atoms in the lattice and establishment of the equilibrium concentration of defects (mainly vacancies), as well as the establishment of conditionally ergodic state of the crystal.1

At temperatures close to the melting one, the conditional ergodicity of a crystal occurs after a rather long time (up to 10^2 s). In this sense, the thermalization, i.e., the establishment of a local equilibrium temperature, is only a sufficient base for ergodicity, but the time of sweeping the coordinate part of the phase space can substantially exceed the thermalization time. At low temperatures, the time of formation of the equilibrium number of vacancies in crystals and their diffusion over noticeable distances becomes astronomically large. However, this is not essential: in a crystal, due to rigorous symmetry, the main part of the phase space remains unachievable for the crystal particles. As a result, the hops of atoms in a crystal do not lead to a substantial increase in entropy — only the contribution of the entropy of vacancies is added. At low temperatures, both the equilibrium concentration of vacancies and their contribution to the entropy are small, and the crystal can still be considered a conditionally ergodic system, even if at experimental times the processes of vacancy formation and diffusion did not occur.

The issue of thermalization and ergodicity of glasses is even more complicated. As a rule, glasses are considered nonergodic systems. This is because, at temperatures substantially less than the vitrification temperature, no relaxation processes (hops of all particles) have time to occur in experimental times. The time of ergodicity establishment (sweeping the phase space) at the vitrification temperature is 10–100 s (in fact, based on this relaxation time, the vitrification temperature itself is determined). On astronomical time scales, glasses are quite ergodic systems (if no crystallization occurs during such times). Glasses, as well as overcooled liquids, are metastable systems, and the thermodynamics can be applied to them only with reservations [21].

In the context of the present paper, it is important for us only that, due to the anharmonicity in glasses, as in crystals, the local thermalization of the vibrational system occurs over a few microseconds. After bringing a glass into contact with a thermostat, it is possible to say that, in a few seconds, in the entire sample of glass, an equilibrium temperature will be established. As in crystals, in glasses, the diffusive hops of particles and defects are observed. However, in contrast to the hops in crystals, the hops of movable particles in glasses occur through all possible regions of space (since a glass is a topologically disordered system). Therefore, from the point of view of entropy at infinite times, the glass at nonzero



Figure 4. Temperature dependence of entropy *S*. $T_{\rm m}$ is the melting temperature, $T_{\rm K}$ is the Kauzmann virtual temperature, $T_{\rm g}$ is the vitrification temperature, corresponding to the kink in the temperature dependence of the entropy at small experimental times. At astronomically large times, the overcooled liquid at $T < T_{\rm g}$ is ergodic with the appropriate increment of entropy (indicated by the arrow).

temperature is a liquid (in the process of motion, the particles sweep the entire coordinate part of the phase space). That is, while the incomplete ergodicity of crystals at low temperatures can be, in fact, ignored, for glasses this is not so. The relaxation processes in glasses at temperatures below that of vitrification lead to substantial changes in their entropy (Fig. 4). As a result, glasses at low temperatures are completely thermalized systems with 'working' local Gibbs distribution in the momentum space and equilibrium temperature. However, at experimental times, the ergodicity in glasses, as a rule, is not achieved. On the scale of astronomically large times, glasses can be considered to be merely overcooled liquids—they are both thermalized and ergodic, including in the coordinate space.

Therefore, thermalization of macroscopic systems and the establishment of the local equilibrium temperature occur on a time scale from a few ten picoseconds to a few microseconds as a result of multiple collisions of particles and multiphonon processes. The Gibbs distribution provides the ergodicity of the system; the time to reach complete ergodicity in gases and in liquids is comparable with the time of their local thermalization, while in solids it is substantially larger. Crystals can always be considered conditionally ergodic systems, since the contribution to thermodynamics from rare hops of particles can be ignored at any values of time. At the same time, glasses at usual experimental times are thermalized, but nonergodic, systems. The contribution to thermodynamic properties and ergodicity from diffusive hops in glasses can be ignored at short times, but must be taken into account at astronomically large times, when glasses become ergodic systems, substantially increasing their entropy.

7. Conclusion

Although the importance of the Gibbs distribution for describing different systems was understood more than a century ago, the physics of the processes underlying it remain interesting and largely not properly understood. At a small uncertainty of momenta and coordinates of particles (taken 'from heaven'), the mixing of phase trajectories is a necessary and sufficient condition for the existence of the Gibbs

¹ According to the Bloch formula, taking into account the quantum nature of vibrations becomes substantial at temperatures much lower than the Debye temperature, when the number of vacancies and self-diffusion coefficient are negligibly small.

distribution and system thermalization. For gases, the reason of such mixing is the collisions of the particles, for solids, the scattering of quasiparticles (phonons), and for liquids, both types of processes.

Multiphonon processes lead not only to thermalization of solids but also to the creation of equilibrium defects and the possibility of diffusive hops of particles, related to the bifurcational solutions for nonlinear oscillations. In glasses, these diffusion processes under an increase in temperature lead to a transition to a liquid state. In crystals, the selfdiffusion of particles leads to conditional ergodicity, and in glasses at superlong times, to complete ergodicity.

Acknowledgments

The author is grateful to V N Ryzhov, A K Murtazaev, M V Sadovskii, and N V Surovtsev for the useful discussions and to I V Danilov for help with manuscript preparation. The study was financially supported by the Russian Scientific Foundation (19-12-00111).

References

- Gibbs J W The Collected Works Vol. 1 (New Haven, CT: Yale Univ. Press, 1948); Gibbs J W Termodinamika. Statisticheskaya mekhanika (Moscow: Nauka, 1982) in Russian
- Landau L D, Lifshitz E M Statistical Physics Vol. 1 (Oxford: Pergamon Press, 1980); Translation from Russian: Statisticheskaya Fizika (Moscow: Nauka, 1976)
- Uhlenbeck G E, Ford G W Lectures in Statistical Mechanics (Providence, RI: American Mathematical Society, 1963); Translation into Russian: Lektsii po Statisticheskoi Mekhanike (Moscow: Mir, 1965)
- Zubarev D N Nonequilibrium Statistical Thermodynamics (New York: Consultants Bureau, 1974); Translated from Russian: Neravnovesnaya Statisticheskaya Termodinamika (Moscow: Nauka, 1971)
- Bogolyubov N N Izbrannye Trudy po Statisticheskoi Fizike (Selected Works on Statistical Physics) (Moscow: Izd. MGU, 1979)
- Krylov N S Works on Substantiation of Statistical Physics (Princeton, NJ: Princeton Univ. Press, 1979); Translated from Russian: Raboty po Obosnovaniyu Statisticheskoi Fiziki (Moscow–Leningrad: Izd. Akad. Nauk SSSR, 1950)
- 7. Sinai Ya G Russ. Math. Surv. 25 (2) 137 (1970); Usp. Mat. Nauk 25 (2) 141 (1970)
- Kozlov V V Ansambli Gibbsa i Neravnovesnaya Statisticheskaya Mekhanika (Gibbs Ensembles and Nonequilibrium Statistical Mechanics) (Moscow–Izhevsk: RKhD, Inst. Komp'yut. Issled., 2008)
- 9. Maccone L Phys. Rev. Lett. 103 080401 (2009)
- 10. Menskii M B Phys. Usp. 48 389 (2005); Usp. Fiz. Nauk 175 413 (2005)
- 11. Volovich I V Found. Phys. 41 516 (2011)
- 12. Martynov G A Phys. Usp. **39** 1045 (1996); Usp. Fiz. Nauk **166** 1105 (1996)
- Sadovskii M V Statistical Physics 2nd ed. (Berlin: De Gruyter, 2019); Translated from Russian: Lektsii po Statisticheskoi Fizike (Moscow–Izhevsk: Inst. Komp'yut. Issled., 2003)
- Zaslavskii G M, Chirikov B V Sov. Phys. Usp. 14 549 (1972); Usp. Fiz. Nauk 105 3 (1971)
- Zaslavsky G M Chaos in Dynamic Systems (New York: Harwood Acad. Publ., 1985); Translated from Russian: Stokhastichnost' Dinamicheskikh Sistem (Moscow: Nauka, 1984)
- Kosevich A M, Kovalev A S Vvedenie v Nelineinuyu Fizicheskuyu Mekhaniku (Introduction to Nonlinear Physical Mechanics) (Kiev: Naukova Dumka, 1989)
- Manakov S V Sov. Phys. JETP 40 269 (1975); Zh. Eksp. Teor. Fiz. 67 543 (1974)
- Gibbs J W Elementary Principles in Statistical Mechanics, Developed with Especial Reference to the Rational Foundations of Thermodynamics (New York: C. Scribner's Sons, 1902); Translated into Russian: Osnovnye Printsipy Statisticheskoi Mekhaniki, Izlagaemye

so Spetsial'nym Primeneniem k Ratsional'nomu Obosnovaniyu Termodinamiki (Moscow-Izhevsk: RKhD, 2002)

- Sinai Ya G Sov. Math. Dokl. 4 1818 (1963); Dokl. Akad. Nauk SSSR 153 1261 (1963)
- Arnold V I, Avez A Problèmes Ergodiques de la Mécanique Classique (Paris: Gauthier-Villars, 1967); Translated into English: Ergodic Problems of Classical Mechanics (New York: W.A. Benjamin, 1968); Translated into Russian: Ergodicheskie Problemy Klassicheskoi Mekhaniki (Izhevsk: RKhD, 1999)
- 21. Brazhkin V V Phys. Usp. 49 719 (2006); Usp. Fiz. Nauk 176 745 (2006)
- Fermi E, Pasta J R, Ulam S "Studies of nonlinear problems", Los Alamos Report LA-1940 (Los Alamos, NM: Los Alamos Natl. Lab., 1955); Fermi E, Pasta J, Ulam S *The Collected Papers of Enrico Fermi* Vol. 2 (Chicago, IL: The Univ. of Chicago Press, 1965) p. 978; Translated into Russian: Fermi E, Pasta J, Ulam S "Issledovanie Nelineinykh Zadach", Fermi E *Nauchnye Trudy* Vol. 2 (Moscow: Nauka 1972) p. 647
- Imry Y Introduction to Mesoscopic Physics 2nd ed. (Oxford: Oxford Univ. Press, 2002); Translated into Russian: Vvedenie v Mezoskopicheskuyu Fiziku (Moscow: Fizmatlit, 2002)
- Zaslavskii G M Sov. Phys. Usp. 22 788 (1979); Usp. Fiz. Nauk 129 211 (1979)
- 25. Zaslavskii G M Usp. Fiz. Nauk 131 302 (1980)
- Brazhkin V V Phys. Usp. 60 954 (2017); Usp. Fiz. Nauk 187 1028 (2017)
- 27. Kittel Ch Introduction to Solid State Physics (New York: Wiley, 1971); Translated into Russian: Vvedenie v Fiziku Tverdogo Tela (Moscow: Nauka, 1978)
- Ashcroft N W, Mermin N D Solid State Physics (New York: Holt, Rinehart and Winston, 1976); Translated into Russian: Fizika Tverdogo Tela (Moscow: Mir, 1979)
- Damask A C, Dienes G J Point Defects in Metals (New York: Gordon and Breach, 1963); Translated into Russian: Tochechnye Defekty v Metallakh (Moscow: Mir, 1966)