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Stochastic Theory of the Classical Molecular Dynamics Method

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Abstract—The work is devoted to fundamental aspects of the classical molecular dynamics method, which was developed half a century ago as a means of solving computational problems in statistical physics and has now become one of the most important numerical methods in the theory of condensed state. At the same time, the molecular dynamics method based on solving the equations of motion for a multiparticle system proved to be directly related to the basic concepts of classical statistical physics, in particular, to the problem of the occurrence of irreversibility. This paper analyzes the dynamic and stochastic properties of molecular dynamics systems connected with the local instability of trajectories and the errors of the numerical integration. The probabilistic nature of classical statistics is discussed. We propose a concept explaining the finite dynamic memory time and the emergence of irreversibility in real systems.

Keywords: molecular dynamics, instability of trajectories, numerical integration errors, statistical laws, irreversibility

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INTRODUCTION

In 1957, a paper was published by B.J. Alder and T.E. Wainwright [1], who used newly emerging computers to integrate classical equations of motion for a system of hard spheres. This material was presented in greater detail in [2]. The results were obtained both for the equation of state and for the correlation functions. The considered systems varied from several tens to several hundreds of particles. The works were immediately noticed by I.Z. Fisher [3, 4].

The approach proposed in [1, 2], was named the molecular dynamics method (MDM), as originally molecules rather than atoms were understood by hard spheres. As early as in [5, 6], particle systems with more realistic Born–Mayer, Debye, and Lennard–Jones potentials were considered. Further, systems of interacting atoms were mostly considered. The interatomic interaction potentials became increasingly sophisticated for describing more and more diverse physical objects. The term atomistic simulation emerged and gained increasing popularity but it also fails to embrace all the MDM applications because it has to cover, among other objects included in consideration, electrolytes and nondegenerate electron-ion plasma. The combination "molecular dynamics method" has appeared very stable and remains the only term for this method, although the word "molecules" now refers not only and not so much to a molecule as such but as a rule to atoms, ions, and even electrons.

MDM is applied to sufficiently dense and nonideal systems when it is no longer possible to introduce the concept of the mean free path and theories based on the expansion in the small parameter lose their meaning. At the same time, it is desirable to continue MD calculations until the parameters of the studied system enable comparing with the results obtained for rarefied systems. This makes it possible to cover the entire range of practical importance.

MDM has now become one of the most important methods in the theory of condensed matter. The interaction of particles with each other is described by different pair and multiparticle potentials. Thermodynamic and transport properties were examined (equations of state, diffusion, viscosity, thermal conductivity, etc.), structure, time correlation functions, and some relaxation processes for a wide variety of systems, including simple liquid metals, semiconductors, dielectrics, covalent systems, collisional and dusty plasma colloids, glasses, polymers, biopolymers, and liquid crystals. Different aggregate states have been described. Along with homogeneous systems, phase equilibria and the decay of metastable states were modeled, as well as clusters, nanocrystals, processes on the surface, shock waves and solitons, the

dynamics of radiation damage in crystals, fracture of materials, cracking, and various biomolecular systems.

The progress in computer facilities enabled researchers to consider an increasing number of particles. Calculations have already been performed for 300 billions [7] and a trillion [8] particles. The realism of the models is due to the choice of the multiparticle interaction potentials derived from quantum-mechanical calculations. A huge number of publications on this topic over the years has generated many surveys and monographs. We would like to mention, for instance, [9–24].

Attempts have been made to construct a quantum MDM [25] for the description of chemical reactions, equilibrium and nonequilibrium systems with degenerate electrons, and some other problems. Despite the progress in this direction, it has not yet been possible to create quantum MDM as versatile as the classical MDM. In this review, we restrict ourselves to the classical MDM, focusing on the consistent exposition of the theoretical foundations of the method.The undeniable practical efficiency of the classical MDM and the simplicity of its underlying assumptions seems to leave no room for doubt as to its theoretical validity. In this connection, MDM is generally regarded as a purely computational method, and many researchers employing it usually do not give a second thought to what is actually calculated by MDM, being satisfied with the agreement with the experimental data provided by MDM and its predictive power.

However, some theoretical physicists have long realized that MDM, despite its numerical character and utilitarian focus, concerns the foundations of classical statistical physics and, in turn, requires a theory for its logical justification. MDM raises very serious questions.

In the first place, the total energy in the MD calculation fluctuates. The law of energy conservation only holds on the average, in contrast to the equations of classical mechanics. This fact was noted at the initial stage of the MDM development but it had not been properly recognized and was treated as a minor error.

In the second place, Henri Poincaré showed long ago that classical dynamical systems of many particles were systems with strong local instability [26]. These concepts were introduced in physics by N.S. Krylov [27] in book [28]. In connection with MDM, this circumstance was pointed out by E.E. Shnol' [29]. These issues were considered in [11, 30–32]. The authors of [33] referred to Ya. Sinai (the book [28] had not yet been translated at the time), who analyzed the results to clarify the exponential divergence of the trajectories of particles in the Lennard–Jones system.

The local instability means that different particle trajectories calculated for the same set of initial conditions, but, for example, with a different step of numerical integration, by no means correspond to a single Newtonian dynamic trajectory and exponentially diverge from it, as well as from each other. And the method devised for the solution of the Cauchy problem but leading to a bunch of exponentially diverging trajectories is unacceptable for solving differential equations from the viewpoint of the theory of numerical methods.

Despite the huge difference in scale, MDM problems are similar to the restriction on the limit of the predictability of weather forecasting [34–36]. The limit of the predictability of particle trajectories was calculated in [30] for the Lennard–Jones system.

Starting from [33], several authors paid attention to the increased number of numerical errors due to the instability of the equations of motion [10, 29, 37–41]. A constraint was proposed [38, 39] requiring MD trajectory to be close to the exact solution of Newton equations over the entire length used for statistical averaging. Since it was impossible to satisfy this requirement, E. Shnol' [29] pointed out that MDM was not entirely valid, and R.F. Fox [38] even doubted MDM's reasonableness. Work [38] stimulated the precision calculations [39]. However, instead of one long MD trajectory, a set of short sections of the same total sum length was used for averaging. Each short section was calculated with sufficient accuracy, but the initial conditions for them were selected from the canonical ensemble using the Monte Carlo method. Therefore, work [39] was unrelated to the problem for which it was intended, which was noted as early as in [42].

In the third place, how can irreversibility arise in the method based on the solution of the reversible Newton equations? It certainly emerges, as MDM perfectly describes irreversible processes. As early as in 1967, members of I. Prigogine's group calculated the evolution of the H-function for a system of 100 hard discs [43] and its recovery for time-reversible trajectories. It was found that the recovery only took place for short trajectories in the range of 1–2 relaxation times; the question of exponential instability was not discussed. In the attempt to figure out the cause of the irreversibility, Prigogine returned to this work in 1989 [44], drawing also to later numerical experiments [45, 46] on the emergence of correlations in a system of hard disks as a result of collisions. Prigogine refutes persistent unsuccessful attempts to prove the

second law of thermodynamics, the kinetic Boltzmann equation, and other irreversible laws relying solely on reversible Newton equations.

This discussion began over a hundred years ago starting from the arguments against L. Boltzmann voiced by E. Zermelo and J. Loschmidt (see, for instance, [26, 47, 48]. R. Feynman agreed with Boltzmann's arguments in his discussion with Zermelo and Loschmidt and formulated them in the following way: "Things are irreversible only in the sense that going one way is likely, but going the other way, although it is possible but according to the laws of physics, would not happen in a million years" [49, p.119]. Boltzmann's and Feynman's viewpoint is shared by N. Bogolyubov, B.V. Chirikov, Sinai [48, 50, 51], J.L. Lebowitz [52], and W.G. Hoover [15]. Reasons are offered recalling the colossal number of atoms and molecules making up macroscopic bodies, the practical impossibility of the complete mechanical description of such bodies, the nonlinearity of dynamical systems [53] and others [54, 55]. A.M. Yevseev [56] tried to work out a "purely mechanical theory of thermodynamics" by means of MDM.

Krylov [28] and K.R. Popper [47] did not share the views of Boltzmann and his supporters. Boltzmann's concept, by virtue of Poincare's recurrence theorem, admits the existence of the world with a decreasing entropy, and, therefore, should be rejected [47]. Objections to Boltzmann were also raised by J. von Neumann [57], L. D. Landau [58], Prigogine [44, 59, 60], and B. B. Kadomtsev [61] assuming that only quantum mechanics could be used to justify irreversibility. This viewpoint was most clearly articulated by Landau [58] who pointed out that nonequivalence of the both time directions in quantum mechanics "*is manifested in connection with the central process of interaction of the the quantum mechanical object with the system for quantum mechanics, obeying with a significant degree of accuracy the classical mechanics*" (see also [62] §47). Note that Landau's view echoes a brief remark made by Neumann as early as 1929 [63, footnote on p. 337]. However, in the same work, Neumann remarked that it was still unclear whether the irreversibility of the measurement process had anything to do with the irreversibility of what was actually taking place. It was noted in [64–67] that in the equations of motion of any classical molecular system there should necessarily exist some additional terms of the quantum nature. These terms are small but finite, have a stochastic nature, and trigger Lyapunov's instability.

The round-table discussion "Microscopic origins of macroscopic irreversibility" was held at the 20th International Conference on Statistical Physics (Paris, 1998). Two opposing points of view in front of two thousand scientists were defended by Lebowitz and Prigogine. A dry and brief description of their emotional speeches is given in [52, 59]. In his verbal report, Lebowitz very extensively expounded MD's results [68] as an important argument in favor of his point of view. In [52] only a few lines were devoted to this work, but Lebowitz still fails to see that the conclusions of [68] are erroneous, which will be pointed out in paragraph 2.5.

Actually, MDM ran counter to some established ideas of classical statistical physics, which are set out, for example, in [49, 58]. The discussion of these fundamental issues was launched in [11, 30, 42, 69]. They were developed in [31, 32] and in this paper. We consider the place of MDM in the system of basic concepts of statistical physics and physical kinetics and where it complements these concepts in terms of the choice of number of particles, the probabilistic character of the results of classical statistics, etc.

The original intent of the MDM is set out in Section 1, where the immediately manifested difficulties are also indicated. In Section 2 we analyze the set of particle trajectories that are actually calculated in MDM, i.e., the object whose properties are actually investigated by this method. In paragraphs 2.1–2.4 the exponential divergence of particle trajectories is treated, concepts of K-entropy and the dynamic memory time are introduced as applied to MDM problems, the connection of these notions with the total energy fluctuations is explained, and the fundamental restriction of the memory time is shown due to the finiteness of the number length in a computer. Paragraphs 2.5 and 2.6 are devoted to the conclusions from this analysis, i.e., the dynamic and stochastic properties of the set of particle trajectories calculated by MDM and the non-Hamiltonian character of these trajectories. MDM problems are compared to the problem of dynamic chaos [48, 50, 51, 70, 71, 72]. In Section 3, we attempt to reformulate some of the postulates of classical statistical physics relying on the MDM results; we also briefly point out some physical analogs of numerical integration errors. In the conclusion, in particular, practical requirements for MD simulation are listed following from the performed analysis of the MDM fundamentals.

1. ORIGINAL IDEA OF MDM

1.1. Initial Equations

The dynamics of N interacting atoms is described by the system of equations

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i(\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{1}$$

or

$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i(\mathbf{r}_1,\ldots,\mathbf{r}_N), \quad \frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i, \tag{2}$$

where m_i, $\mathbf{r}_i$, and $\mathbf{v}_i$ are the mass, coordinate, and velocity of the ith particle ($i = 1,..,N$) and $\mathbf{F}_i$ is the force acting on it, which is defined as

$$\mathbf{F}_i(\mathbf{r}_1,\ldots,\mathbf{r}_N) = -\frac{\partial U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}{\partial \mathbf{r}_i}. \tag{3}$$

The function U determines the physical properties of the system under study. The MD and Monte Carlo methods stimulated a sharp increase in interest in the development of investigations in the U type. At the first stage, the simplest systems were examined such as, for instance, solid argon, using the existing pair potentials at that time, i.e., Lennard–Jones and Buckingham. Their parameters were selected so that they were consistent with the experimental data about the properties of the considered substances. The transition to the exact pair potentials derived from the beam experiments revealed the need to take account of multiparticle interatomic interactions. In the general case

$$U(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \sum_{i<j}^{N} u_2(\mathbf{r}_i,\mathbf{r}_j) + \sum_{i<j<k}^{N} u_3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k) + \ldots . \tag{4}$$

For modeling inert gases, it proved sufficient only to consider the contribution of triple interactions. The description of the properties of semiconductors and metals becomes much more accurate when multiparticle (up to several dozens) components are taken into account (see, for instance, [73–77]). Initially function U was found empirically from the condition requiring that the set of the model characteristics was consistent with the experimental data [78–82]. At the same time, some properties of substances can, generally speaking, be described with the same accuracy not by one but by a whole family of potentials [83]. At present the study of interatomic interaction has passed to the area of *ab initio* approaches. The dynamics of a polyatomic system in the nonrelativistic approximation is described by the Schrödinger equation with the Hamiltonian function of the form

$$H = \sum_i \frac{\mathbf{P}_i}{2M_i} + \sum_\alpha \frac{\mathbf{p}_\alpha}{2m} + \frac{1}{2}\sum_{ij}\frac{Z_i Z_j e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{\alpha\beta}\frac{e^2}{|\mathbf{r}_\alpha^{el} - \mathbf{r}_\beta^{el}|} - \frac{1}{2}\sum_{i\alpha}\frac{Z_i e^2}{|\mathbf{r}_i - \mathbf{r}_\alpha^{el}|}, \tag{5}$$

containing terms corresponding to the kinetic energy of the nuclei and electrons and the Coulomb energy of their interaction. The fact that electrons are much lighter than nuclei allows us to separate the movement of ions and electrons and consider the stationary problem for an electron subsystem in the adiabatic (Born–Oppenheimer) approximation. In this case, the wave function can be represented as $\psi(\{\mathbf{r}_i\},\{\mathbf{r}_\alpha^{el}\}) = \Psi(\{\mathbf{r}_i\})\Phi(\{\mathbf{r}_i\},\{\mathbf{r}_\alpha^{el}\})$, where $\Psi(\{\mathbf{r}_i\})$ describes the motion of the nuclei and $\Phi(\{\mathbf{r}_i\},\{\mathbf{r}_\alpha^{el}\})$ depends parametrically on the coordinates of the nuclei $\{\mathbf{r}_i\}$ and describes the electron subsystem. Here the problem is split into two equations

$$\hat{H}_{el}\Phi(\{\mathbf{r}_i\},\{\mathbf{r}_\alpha^{el}\})) = U(\{\mathbf{r}_i\})\Phi(\{\mathbf{r}_i\},\{\mathbf{r}_\alpha^{el}\}) \text{ and } \hat{H}_i\Psi(\{\mathbf{r}_i\}) = E\Psi(\{\mathbf{r}_i\}),$$

where

$$H_{el} = \sum_\alpha \frac{\mathbf{p}_\alpha}{2m} + \frac{1}{2}\sum_{ij}\frac{Z_i Z_j e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{\alpha\beta}\frac{e^2}{|\mathbf{r}_\alpha^{el} - \mathbf{r}_\beta^{el}|} - \frac{1}{2}\sum_{i\alpha}\frac{Z_i e^2}{|\mathbf{r}_i - \mathbf{r}_\alpha^{el}|}, \tag{6}$$

$$H_i = \sum_i \frac{\mathbf{P}_i}{2M_i} + U(\{\mathbf{r}_i\}). \tag{7}$$

The solution of the Schrödinger equation for the electron subsystem at fixed positions of the nuclei determines the eigenvalues $U(\{\mathbf{r}_i\})$, which are parametrically dependent on the nuclear coordinates. Thus, function U is the potential of the interatomic interaction in the ground state of the electron subsystem. However, the solutions of quantum mechanical equations for an electron subsystem are only possible for

systems with a small number of atoms (up to several hundred). In such a way, the form of U can be obtained. By the use of multiparticle potentials of U of this type, investigations into the realistic models of metals with the number of atoms of up to hundreds of millions within the classical MD frame became possible (see, for instance, [84]). The transition to a fully classical description of polyatomic system corresponds to the assumption of the smallness of the de Broglie wavelength of atoms compared to the characteristic interparticle distance in the system that takes place, provided the temperatures are not too low for most of the chemical elements except the lightest ones.

1.2. Numerical Schemes

The most popular schemes are those in which the approximation error of the second derivative $d^2\mathbf{r}_i/dt^2$ is subject to the first-order difference scheme

$$\frac{\mathbf{r}_i(t+\Delta t)-2\mathbf{r}_i(t)+\mathbf{r}_i(t-\Delta t)}{\Delta t^2}=\frac{\mathbf{F}_i(t)}{m_i}, \tag{8}$$

where Δt is the numerical integration step. The simplest of such schemes is the implicit Euler scheme of the first order of accuracy with respect to the coordinates and velocities

$$\mathbf{v}_i(t+\Delta t)=\mathbf{v}_i(t)+\frac{\mathbf{F}_i(t)}{m_i}\Delta t,\quad \mathbf{r}_i(t+\Delta t)=\mathbf{r}_i(t)+\mathbf{v}_i(t+\Delta t)\Delta t. \tag{9}$$

The velocity Verlet scheme (of the second order of accuracy) is widely used:

$$\begin{gathered}\mathbf{v}_i\left(t+\frac{\Delta t}{2}\right)=\mathbf{v}_i(t)+\frac{\mathbf{F}_i(t)}{m_i}\frac{\Delta t}{2},\quad \mathbf{r}_i(t+\Delta t)=\mathbf{r}_i(t)+\mathbf{v}_i\left(t+\frac{\Delta t}{2}\right)\Delta t,\\ \mathbf{v}_i(t+\Delta t)=\mathbf{v}_i\left(t+\frac{\Delta t}{2}\right)+\frac{\mathbf{F}_i(t+\Delta t)}{m_i}\frac{\Delta t}{2}.\end{gathered} \tag{10}$$

The optimality of schemes like (8)–(10) with respect to the accuracy/performance ratio was explained in [85, 86], where the efficiency of schemes of different orders of accuracy was investigated as applied to MD problems. The idea can be illustrated by the following arguments. We consider some segment of an MD trajectory. Let its calculation using the scheme (8) require M_1 steps. Let the same accuracy (with respect to the fluctuation of the total energy, see Section 2.3) be achievable by using a scheme of a higher order over M_2 steps, $M_2 < M_1$. However, at each step the calculation of the forces acting on atoms (the most resource-consuming part of the program) is repeated m_2 times. It turned out that for standard, close to the maximum, values of numerical integration steps $M_1 < m_2M_2$ (for scheme (8) $m_1 = 1$) for all the schemes studied in [85, 86]. That is why the schemes of type (8) proved to be the most cost-effective for the MD problems. The situation only changes when the numerical integration step decreases several times or more, then $m_2M_2 < M_1$. However, such degrees of accuracy are not used in the standard MD calculation.

When choosing the integration step Δt such physical characteristics of the system must be taken into consideration as the maximum frequency of oscillations arising in it. Another physical restraint is due to the fact that the interaction energy must change little over the length, on which the particles are displaced during time Δt. This is not an averaged characteristic as it concerns every particle. In this connection, a variable integration step can be used.

1.3. MD Simulation

1.3.1. Molecular dynamics experiment. MDM can be classified as a computer experiment; i.e., it can refer to numerical methods that, the same as real experiments, can be divided into an experimental setup and diagnostic tools.

The solution based on numerical schemes gives us comprehensive information on the trajectories of the particles, i.e., completely defines the system under study; it is an analog of the experimental setup, which comprise a research object. In our case, such an object (a model of a substance) is a set of particle trajectories that is calculated using MDM. Sometimes the model of the substance is understood as the mere set of interparticle interaction potentials.

The calculated particle trajectories contain comprehensive information about the system and all the data about its properties. It is only important to learn how to extract this information, i.e., to develop diagnostic tools for every property. For this purpose, MDM uses the most general, *strict relations* of statistical physics and physical kinetics. Specific diagnostics depends on the experimental setup.

The MD method is employed to investigate a variety of systems and for their adequate description, various interparticle potentials are used. Pure substances are simulated, as well as their mixtures, solutions, alloys, etc. All aggregate states are explored, both stable and metastable. Three main directions of modeling can be singled out, i.e., equilibrium states, relaxation, and controlled MD.

1.3.2. Simulation of equilibrium states. In these calculations, the initial state is more or less arbitrary. Then, the system is brought into equilibrium. Since this transition segment of the MD trajectory is auxiliary and excluded from further consideration, the initial conditions are chosen to reduce this section as far as possible. With the same purpose in bringing the system into equilibrium, various workarounds are employed not related to the real processes in the system under study.

The criteria for bringing simple systems into equilibrium can be quite trivial, i.e., achieving the constant value of the average particle temperature T and the stationarity of its fluctuations. The value T is related to the average kinetic energy

$$T = \frac{2}{3(N-3)}\left\langle \sum_{i=1}^{N} \frac{m_i \mathbf{v}_i^2}{2} \right\rangle \tag{11}$$

in the absence of the motion of the mass center $\sum_{i=1}^{N} m_i \mathbf{v}_i = 0$. However, we must ensure that the energy (velocity) distribution of the particles should become Maxwellian, which would enable us to derive its temperature. The agreement between the results of these two methods for obtaining the temperature indicates that the equilibrium has been established in the system with respect to this parameter. In the case of a crystal or liquid, we can additionally calculate the dispersion of fluctuations over a certain section of the equilibrium trajectory. If we extend the MD calculation to the section of the same length, we can repeat the computation of the dispersion. The coincidence of the two results will show that equilibrium has been also attained with respect to fluctuations. We can ensure the establishment of equilibrium by checking the stationarity of all the calculated parameters. In the case of biomolecules, the criteria can be quite sophisticated [87].

After the system has been brought into equilibrium the generation of the MD trajectory is continued and this stage is considered equilibrium. All information obtained in the calculation is found from this stage and only applies to the equilibrium state. The pressure is derived from the virial relation

$$P = \frac{NT}{V} - \frac{1}{3}\left\langle \sum_{i}\sum_{i<j} r_{ij} \frac{\partial U}{\partial r_{ij}} \right\rangle, \tag{12}$$

which follows from the general relations $P = -(\partial F/\partial V)_T$ and $F = -T \ln Z$, where F is the free energy and Z is the statistical sum. There are, however, unresolved issues in the calculation of the pressure [88, 89]. The heat capacity is obtained as the difference between the mean square U and the square of the average of U, etc. The transport coefficients are calculated both by the Green–Kubo formulas and from the Einstein–Herzfeld relations. For example, the diffusion coefficient D can be found at the velocity autocorrelator

$$D = \frac{1}{3}\int_0^{\infty} \langle \mathbf{v}(0)\mathbf{v}(t) \rangle \, dt, \tag{13}$$

or directly observing the particle displacements r

$$\overline{r^2} = 6Dt + C. \tag{14}$$

The agreement between the results obtained by those two methods enables us to verify the operation of the program and the establishment of equilibrium in the system. Some subtleties arising in this case are illustrated by the example of the diffusion coefficient in [90–95]. More information about the formulas for other transport coefficients can be found, for instance, in [96].

MDM allows us to study fluctuations. In the case of electron-ion nondegenerate plasma, fluctuations of different nature are possible. Modeling within a single calculation, as in the real plasma, involves all kinds of fluctuations. MDM provides a unified approach to the fluctuations in the density of free charges, pair electron-ion fluctuations, electron states localized in the long-wavelength density fluctuations, and other possible fluctuations. However, investigation into the fluctuations of each type requires special diagnostics. A method for the diagnostics of density fluctuations is presented in [97]. The pair electron-ion fluctuations (pair fluctuations or simply pairs) are considered in [98–100]. It is discussed there how these pairs pass into states that can be associated with highly excited atoms as they become less collisional and

their binding energy and life time increase. The understanding of the spectrum part adjacent to the ionization limit is refined. Fluctuations of plasma pressure are studied in [101].

The calculation of all quantities by MDM assumes that averaging is performed. Thus, the accuracy of averaging can simultaneously be determined. The analysis of the diagnostic accuracy in MDM also points to the analogy with the real experiment.

Standard requirements to equilibrium MD calculations are briefly summarized in [102].

1.3.3. The proof of the ergodic hypothesis in MDM. In the strict expressions (11)–(14) based on the first principles employed in MDM, averaging $\langle \ldots \rangle$ means averaging with respect to the Gibbs distribution. It had been found, however, rather long ago, that such averaging can be replaced by averaging over time along the MD trajectory. In view of the fundamental importance of such a replacement, its reliability was verified in various ways.

Thermodynamic quantities, such as pressure (12) and heat capacity can be calculated by the Monte Carlo method, which only uses averaging with respect to the Gibbs distribution. The same values for the same multiparticle system and under the same conditions can be found by the MD method using time averaging along the MD trajectory. The results computed using the two methods coincided with each other within the accuracy of the calculations, see, for instance, [103].

Averaging with respect to the Gibbs distribution can also be performed within MDM, see, for instance, [39, 104]. The results coincided with the time averaging. The space averaging (14) was compared with the time averaging (13) [105]. The choice of a particular averaging method when MDM is used is determined by the consideration of the calculations' convenience in each specific case.

Thus, while the ergodic hypothesis remains the subject of study in a rigorous mathematical theory [106, 107], the replacement of space averaging by time averaging along the MD trajectory has long become [105] a common diagnostic tool in MDM.

1.3.4. Simulation of relaxation. In early works [1–6], MDM had been designed as an instrument for studying equilibrium states. At the same time, by its very nature, MDM is a powerful tool for exploring the dynamics of relaxation and transition processes in dense media, including highly nonequilibrium states of such media that are inaccessible to theoretical approaches based on the smallness of the deviation from equilibrium.

In the study of relaxation, all the information should be drawn from the initial, nonequilibrium part of the MD trajectory, i.e., just from the part that is truncated in the MD simulation of equilibrium states. In contrast, on approaching the MD equilibrium the calculation stops. Thus, the simulation of the real relaxation process starts with the physically adequate choice of the initial state, or, more precisely, of an ensemble of initial states, which differ from each other microscopically but are equivalent macroscopically. The diagnostics tracks the time variation in all the system parameters, including those that can only be found with the help of time averaging along the stationary MD trajectory at constant parameters.

Standard requirements for the MD simulation of relaxation are presented in [102].

1.3.5. Controlled molecular dynamic experiment. In this case, the initial state is brought into equilibrium, just as in the equilibrium MD. Further, this state is exposed to a controlled physical action and the dynamics of the system's response to the applied action is studied comprising variable action and including feedback [108–112]. By way of example, we recall the unfolding and folding of protein molecules, the dynamics of stretching and compression of other systems, and shock waves.

1.3.6. Nonconservation of energy. The consistency of MDM's results with the experimental data had been maintained for years, although MDM's capabilities were expanding with the development of computer facilities and the progress in experimental techniques led to the enhancement of the database used for comparison. All this allowed the professionals working in the field of MDM applications not to pay attention to the fundamental issues.

At the same time, concerns were raised at the start of MDM's development. It was found that the total energy of the system $E = E_{kin} + U$ fluctuated during MD's calculation; $E_{kin} = \sum_{i=1}^{N} m_i \mathbf{v}_i^2/2$ is the kinetic energy of the particles system. In some numerical schemes, the researchers even observed a drift of the total energy E. The conclusion was made empirically without analyzing the causes; i.e., schemes were selected based on (8), which did not involve any drift in E and in which E fluctuations with respect to the mean value are of a stationary character. Only in [11] a requirement was found for the difference schemes for MDM, i.e., approximation of the second derivative was to be even with respect to time.

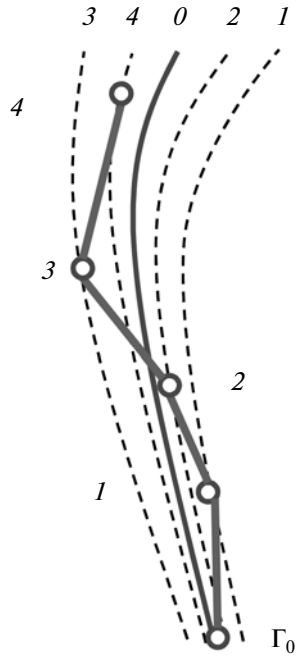

Fig. 1. Schematic illustration of the initial portion of the trajectory calculated in MDM from the initial state of system Γ_0. The solid curve shows the exact solution of the corresponding Cauchy problem. The dotted curves show the Newtonian trajectories of the MD system, on which there falls the solution of the finite difference approximation.

Thus, the massive popularity gained in MDM by the schemes (8)–(10) and their variations can be attributed not only to their best performance in solving MDM problems but also to their stationarity with respect to E.

The nonconservation of E, however, points to the fact that the particle trajectories calculated by MDM do not satisfy Newton's equations, because, for these equations, the total energy should identically be conserved along the trajectories obtained from the solution of the Cauchy problem. Thus, it appeared that the real MDM was not consistent with its original intent. However, this fact was largely overlooked. The fluctuations of E were considered a minor error of the method and their value was often not mentioned in publications.

2. CONCEPTS OF SUBSTANCE DEVELOPED IN MDM

2.1. Exponential Instability of Particle Trajectories

MDM consists in solving a system of ordinary differential equaltions (1) or (2) under the given initial conditions $(\mathbf{r}^0, \mathbf{v}^0)$ (point Γ_0 in $6N$-dimensional phase space), where $\mathbf{r}^0 = (\mathbf{r}_1^0, \ldots, \mathbf{r}_N^0)$ and $\mathbf{v}^0 = (\mathbf{v}_1^0, \ldots, \mathbf{v}_N^0)$. The forces acting on the particles are sufficiently smooth functions of the coordinates, while the theorem of the existence and uniqueness of the solutions of the Cauchy problem hold true. This implies that there exists an exact solution (trajectory) $(\mathbf{r}^d(t), \mathbf{v}^d(t)$ (d designates dynamical) shown in Fig. 1 by curve *0* starting from point Γ_0.

The solution of system (1) or (2) can only be found numerically (starting from $N \geq 3$). The numerical scheme and the integration step uniquely determine the function $\{\mathbf{r}(k\Delta t), \mathbf{v}(k\Delta t), k = 0,1,\ldots\}$. The finite-difference solution is shown in Fig. 1 by the polygonal line. Since the solution is approximate, point 1 following point Γ_0 does not lie on the original trajectory *0*. Another trajectory can be drawn across point 1, i.e., the exact solution of the system, denoted by the digit 1. Point 2 falls on the new Newtonian trajectory 2, etc. The lines *0*, *1*, *2* etc., cannot cross because of the uniqueness and unambiguity of the Cauchy problem solution. It is obvious from Fig. 1 that the total energy must fluctuate along the MD trajectory because every subsequent point on this trajectory *0*, *1*, *2*, etc. belongs to a new Newtonian trajectory, which corresponds to a different value of the total energy. In Section 2.5.2, we will study why and for which schemes the mean value of the total energy is still preserved.

It becomes clear from Fig. 1 how the "coarse-graining" procedure of the Newtonian trajectory takes place in MDM. And it is coarse-graining that is required for the emergence of irreversibility, which is one of the central questions; we will repeatedly return to different aspects of this.

All points on the MD trajectory are described by numbers, whose number of digital places is finite and determined by the computer used. All the remaining points on trajectories *0–4* are irrational because they belong to the exact solutions of the system of equations (1). Therefore, the points *0–4* and all subsequent points on the MD trajectory belong to different solutions of the system of equations (1). By itself, this fact would be commonplace for the numerical method, if the solution remained in a small ε-neighborhood of trajectory *0*. However, due to the Lyapunov instability, the Newtonian trajectories calculated from the initial conditions close to point Γ_0, but not coinciding with it exponentially, diverge with time. The same character of divergence with the same value of the parameter can be expected on average for the MD trajectories along the Newtonian trajectories.

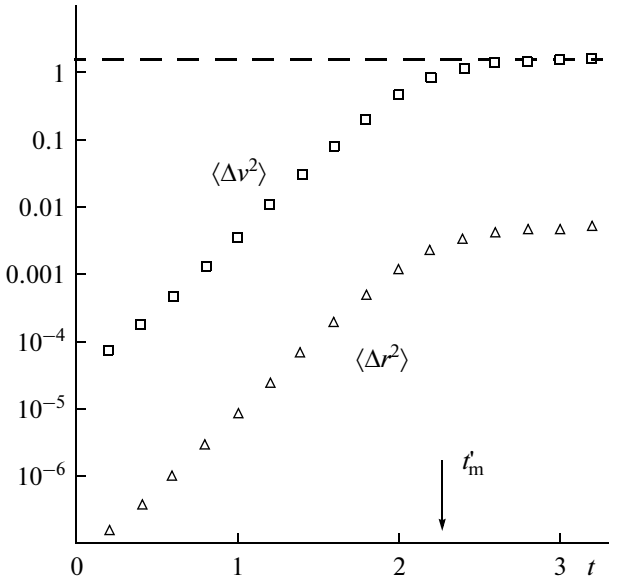

Fig. 2. Normalized averaged divergences of coordinates $\langle \Delta r^2(t) \rangle$ and velocities $\langle \Delta v^2(t) \rangle$ on two trajectories calculated from identical initial conditions with the steps $\Delta t = 0.001$ and $\Delta t' = 0.0001$ ($N = 64$, $\rho = 0.5$, $T = 0.44$, Lennard–Jones potential).

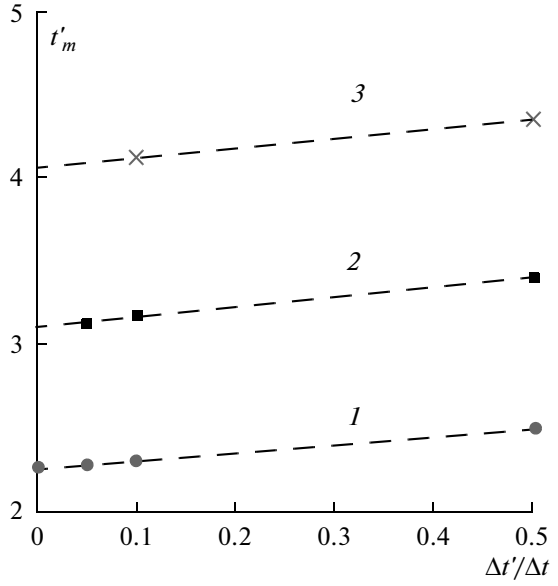

Fig. 3. Dependence t_m on $\Delta t'/\Delta t$ for different values of Δt: (*1*) $\Delta t = 0.01$, (*2*) 0.005, (*3*) 0.001, (the leftmost point on the line 1 corresponds to $\Delta t' = 0.00001$); ($N = 64$, $\rho = 0.5$, $T = 0.44$, Lennard–Jones potential).

While there is only a general statement about the divergence of the Newtonian trajectories, the divergence of the MD trajectories can be verified directly. We consider two trajectories calculated from the same initial conditions but with different numerical integration steps Δt and $\Delta t'$. Let $(\mathbf{r}_i(t), \mathbf{v}_i(t))$ designate the 1st and $(\mathbf{r}'_i(t), \mathbf{v}'_i(t))$ designate the 2nd trajectory. The trajectory-averaged differences of the coordinates (velocities) of the first and second trajectories at coinciding instants of time $t = (k\Delta t) = (k'\Delta t')$

$$\left\langle \Delta r^2(t) \right\rangle = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i(t) - \mathbf{r}'_i(t))^2, \tag{15}$$

$$\left\langle \Delta v^2(t) \right\rangle = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{v}_i(t) - \mathbf{v}'_i(t))^2 \tag{16}$$

are shown in Fig. 2. They exponentially increase with time

$$\left\langle \Delta r^2(t) \right\rangle = A \exp(Kt), \quad \left\langle \Delta v^2(t) \right\rangle = B \exp(Kt), \quad t_l < t < t_m, \tag{17}$$

where t_l is some transition time (of the order of the inverse frequency of interparticle collisions), A, B, and t_l depend on the numerical scheme, Δt and $\Delta t'$. K are the values of K-entropy (Krylov–Kolmogorov entropy, maximum Lyapunov index averaged over the phase space). In this and the subsequent figures, the time is expressed in terms of $(m\sigma^2/\varepsilon)^{1/2}$, where σ and ε are the parameters of the Lennard–Jones potential NS m is the mass of the particles. $(m\sigma^2/\varepsilon)^{1/2} = 2.16$ ps for argon. After the period of time

$$t_m \approx \frac{1}{K} \ln\left(\frac{6k_B T}{m} \frac{1}{B} \right) \tag{18}$$

$\left\langle \Delta v^2(t) \right\rangle$ becomes constant and $\left\langle \Delta r^2(t) \right\rangle$ passes to the diffusion mode

$$\left\langle \Delta v^2(t) \right\rangle = 2\left\langle v^2 \right\rangle = 2v_{th}^2, \tag{19}$$

$$\left\langle \Delta r^2(t) \right\rangle - \left\langle \Delta r^2(t_m) \right\rangle \sim D(t - t_m), \tag{20}$$

where $v_{th} = \sqrt{3k_B T/m}$ is the thermal velocity and D is the diffusion coefficient. Large-scale divergence is no longer possible for $\left\langle \Delta v^2(t) \right\rangle$.

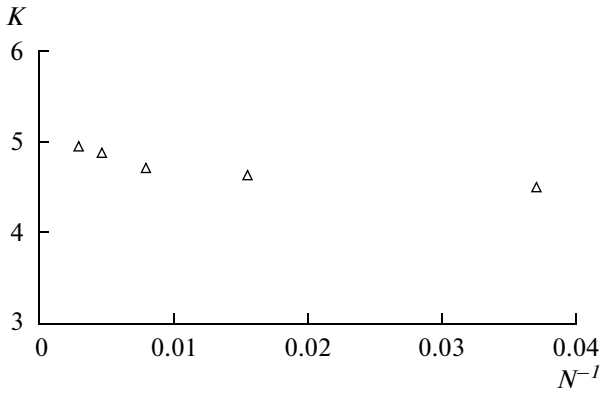

Fig. 4. Dependence of the K-entropy on the number of particles N ($\rho = 0.5$, $T = 0.44$ Lennard—Jones potential).

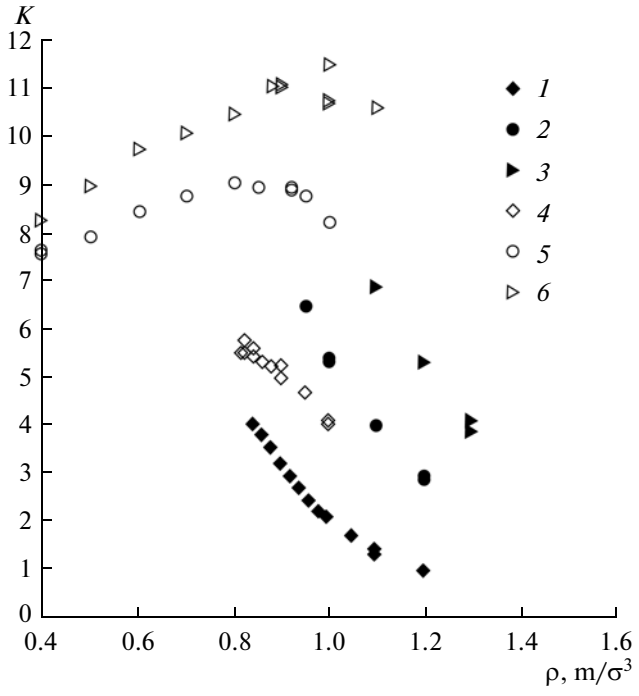

Fig. 5. Dependence of the K-entropy on the density ρ at different temperatures: crystal (*1*) and liquid (*2*) at $T = 0.5$; crystal (*3*) and liquid (*4*) at $T = 1.2$; crystal (*5*) and liquid (*6*) at $T = 2.0$.

The time t_m (18) is the *memory time*, i.e., the time, during which the MD system remembers the fact that the initial configurations on the both trajectories coincided at the time instant $t = 0$. We introduce the *dynamic memory time* t_m^d that characterizes the period of time, over which the correlation is lost between the solution of the finite-difference approximation $\{\mathbf{r}^n(k\Delta t), \mathbf{v}^n(k\Delta t)\}$ and the exact solution of the system of differential equations (1) or (2) $\{\mathbf{r}^d(t), \mathbf{v}^d(t)\}$ for the same initial configuration. In order to find the value t_m^d, calculations of t_m are performed for one and the same value of Δt and different values of $\Delta t'$: $\Delta t/2$, $\Delta t/5$, $\Delta t/10$, etc. (Fig. 3). The limiting value of t_m at $(\Delta t/\Delta t') \to 0$ is the time t_m^d for this scheme and the selected numerical integration step Δt. In the course of the numerical integration after time t_m^d the system of particles completely "forgets" its initial conditions and the calculated MD trajectory loses any correlation with the original Newtonian trajectory. Similar calculations were carried out in [113] for the embedded atom method potential .

Calculations of the type shown in Figs. 2 and 3 allow us to determine the values of $\hat{K}$ and t_m^d for various states of the system. The values of K weakly depend on N [114] starting from $N \sim 10$ (Fig. 4), because the determining factor for quantity K is the strong close collisions. The same happens also for t_m^d. As an example of the numerical values, Fig. 5 shows the dependences of K on the density for a liquid and crystal calculated for the Lennard–Jones system at $N = 4000$ in [115] for the region of equilibrium and metastable parameters for the stability boundaries. In the case of a crystal, the K-entropy changes monotonically and increases as it approaches the spinodal. For a liquid, isotherm $K(\rho)$ passes through the maximum at rather high temperatures.

The quantity Kt_m^d increases logarithmically with the decrease in the numerical integration step. Such a result can be obtained from (17)–(19), assuming that $A \sim (\Delta t)^n$, where n is the order of the scheme's accuracy. Indeed, at the time instant $t = t_m^d$,

$$6k_B T/m = 2\left\langle v^2 \right\rangle = \left\langle \Delta v^2(t_m^d) \right\rangle = A\exp(Kt_m^d), \tag{21}$$

and by taking the logarithm of (21) we obtain

$$Kt_m^d = -n\ln(\Delta t) + \text{const}. \tag{22}$$

From the fact that the numerical integration is approximate, it also follows that energy E is only constant on average. The value of E from step to step fluctuates around the mean value. Therefore, the trajectory calculated in the MD method is not on the surface $E = \text{const}$, as it should be for the solution of Newton's equation, but is located in some layer of thickness $\Delta E > 0$ near the surface $E = \text{const}$ [11, 42]. The

value ΔE is determined by the accuracy and scheme of the numerical integration [11, 42, 69, 116, 85, 86], while $\left\langle \Delta E^2 \right\rangle \sim \Delta t^n$. It follows from (22) that

$$Kt_m^d = -\ln\left(\left\langle \Delta E^2 \right\rangle\right) + \text{const}. \quad (23)$$

The calculation results for the Lennard–Jones system [31, 32] and for the collisional plasma [117] illustrating the fulfillment of relations (22) and (23) are presented in Figs. 6 and 7. The good agreement is obvious. Expressions (22) and (23) can be rewritten as

$$K(t_{m1}^d - t_{m2}^d) = n\ln(\Delta t_2/\Delta t_1) = \ln\left[\left\langle \Delta E_2^2 \right\rangle \Big/ \left\langle \Delta E_1^2 \right\rangle\right] \quad (24)$$

where t_{m1}^d and t_{m2}^d are the memory times for two values Δt_1 and Δt_2. Expression (24) connects the K-entropy and dynamic memory time with the noise level in the dynamic system. This expression is consistent with the concepts of [117–120].

So far, we have considered a single-component system. In [121] plasma is studied consisting of electrons and singly charged ions. For time less than t_m^d for electrons, trajectories of both electrons and ions had the same K-entropy. The value of K dropped sharply for ions at large times. Preliminary calculations for macromolecules and their systems show an exponential divergence also for angular variables. In this case, there arise other constraints on the limits of such divergence.

2.2. Decay of Correlations

In [48] the value K for monatomic systems is connected with the rate of change in the entropy S as a result of the dynamic mixing of trajectories, and to the quantity K^{-1} the meaning of the correlation decay time τ is assigned (see also [122, 15]). Let us compare these statements with MDM. Let the system preliminarily be brought into equilibrium. Further, we consider some small singly connected element of the phase volume $\Delta\Gamma_0$. We compare its evolution $\Delta\Gamma_0(t)$ during the motion of its points according to Newton's equations and along the MD trajectories. In the first case, by virtue of the Liouville theorem

$$\Delta\Gamma_0(t) = \Delta\Gamma_0. \quad (25)$$

Trajectories, for which the initial conditions are located close points inside $\Delta\Gamma_0$, exponentially diverge with time. Since the value of the volume is preserved, its structure becomes increasingly rugged and stretched. The envelope of this structure encloses the increasing volume $\Delta\Gamma(t)$. A good schematic drawing illustrating this process is presented in §1.5 [48].

The character of expansion of the phase volume envelope is also preserved in the case of motion

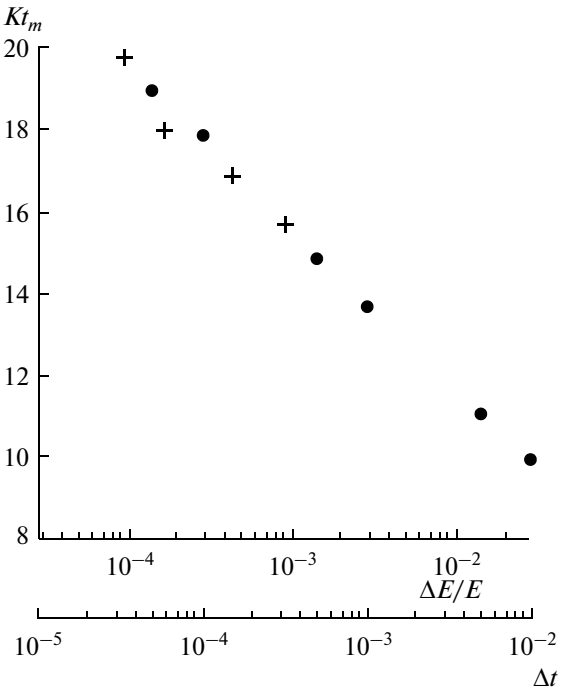

Fig. 6. Dependence of the quantity Kt_m^d on the relative fluctuation of the total energy of the system $\langle \Delta E^2 \rangle^{1/2}/E$ and integration step Δt (implicit Euler scheme (9)): crosses – Lennard–Jones system $N = 64$, $\rho = 0.5$, $T = 0.44$; crosses – collisional plasma [121] (plasma only corresponds to the energy axis).

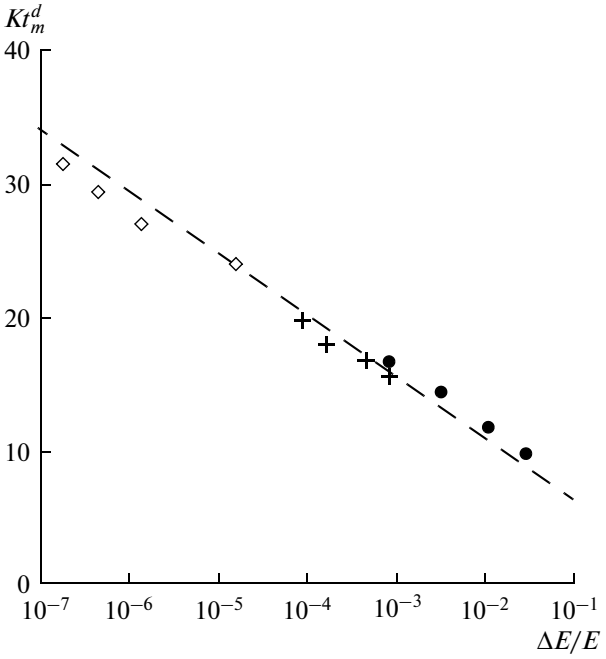

Fig. 7. Dependence of the dimensionless product Kt_m^d on the relative fluctuation of the total energy of the system: circles and crosses – Lennard–Jones system and collisional plasma, respectively (implicit Euler scheme (9)); diamonds – Lennard–Jones system (Runge–Kutta scheme of the fourth order of accuracy). The dashed line corresponds to (23).

along the MD trajectories. However, the phase trajectories that are obtained in the MD calculations are coarse-grained because of the numerical errors. Each point of such a trajectory passes through the new Newtonian trajectory. Therefore, identity (25) is violated, the phase volume swept by MD trajectories grows, and the entropy increases. The process takes place even in the case where only one MD trajectory is considered, i.e., when $\Delta\Gamma_0 = 0$.

The time t_m^d restricts the period of exponential divergence of the trajectories. The quantity $\Delta\Gamma(t)$ reaches the maximum value of $\Delta\Gamma_{\max}$ and the entropy $S = k_B \ln \Delta\Gamma(t)$ rises to its maximum. The reference point for this process can be chosen arbitrarily on the MD trajectory. For any segment of the trajectory with length t_m^d the procedure of filling the volume $\Delta\Gamma_{\max}$ is repeated again and again.

In other words, the time t_m^d is the time of filling the phase volume, in which a phase point is wandering, representing an MD cell at the given temperature T. And $\Delta\Gamma_{\max}$ is the size of the phase space region where the system remains in equilibrium most of the time. We can say that this region is an attractor for all MD trajectories. This region makes up a very small fraction of the phase volume. The MDM carries out significant sampling of that part of the phase space which determines the properties of the system, just as the Monte Carlo method performs the essential sampling in the coordinate space.

By implication of the calculation, t_m^d is also the time of the correlations' decay τ (in terms of [48]), i.e., $\tau = t_m^d$. Contrary to the assumption made in [48] that $\tau = K^{-1}$, the values K^{-1} and t_m^d can differ drastically. In addition to quantitative there is also some qualitative difference between K^{-1} and t_m^d.

The time K^{-1} is a physical characteristic (such as pressure, diffusion coefficient, etc.) of the studied multi-particle system and does not depend on the accuracy or the scheme of the numerical integration. The values of t_m^d are determined by both the state and properties of the system and also by the numerical integration's accuracy, which in this case serves as the coarse-graining procedure. However, the latter dependence is very weak, logarithmic, as is evident from Figs. 6 and 7. Since the noise of the numerical integration can be compared with the real noise in physical systems (see below), the time t_m^d also appears to be a physical characteristic although less is so far known about its value than for K^{-1}.

In [48], the roughening parameter ε was introduced and it was proposed at the end of the derivation to let ε tend to zero. Moreover, it was assumed that the result of the passage to the limit for the correlation decay time did not depend on ε and remained finite for $\varepsilon \to 0$. Let us recall that, according to [48], $K(t_{m1}^d - t_{m2}^d) = 0$ for the correlation decay time at small ε and is independent of the noise level. In MDM the role of ε is performed by the accuracy of the numerical integration. It is clear from relations (22)–(24) and Figs. 6 and 7 that, unlike in [48], $t_m^d \to \infty$ when $\varepsilon \to 0$. As in [48], the K-entropy is a metric invariant and does not depend on the roughening method under $\varepsilon \to 0$.

Along with the equilibrium states there can exist metastable ones. In this case the volume $\Delta\Gamma_{\max}$ practically ceases to be simply-connected. Such states arise both for simple systems and for macromolecules. The latter ones require special consideration.

2.3. Time of Computational Memory

The results of Section 2.1 still hold out hope that by improving the accuracy of the numerical integration, it would still be possible to extend, even if logarithmically slowly, the equilibrium trajectory satisfying Newton's equations. There is, however, another factor that limits this hope. An additional error arises due to the finite accuracy of the computer representation of real numbers [123, 124]. For example, in the case of pair potentials, the force acting on the ith particle is the sum of the contributions made by all its neighbors

$$\mathbf{F}_i = \sum_{k=1}^{n_i} \mathbf{F}_{ij_k}, \quad j_k \in G_i, \tag{26}$$

where G_i is the ordered sequence of indices. The structure G_i depends on the algorithm for particle sorting in calculating the forces. In computer summation with a finite accuracy of number representation (the fixed number of decimal digits), different orders of summation in (26) yield different result for $\mathbf{F}_i$.

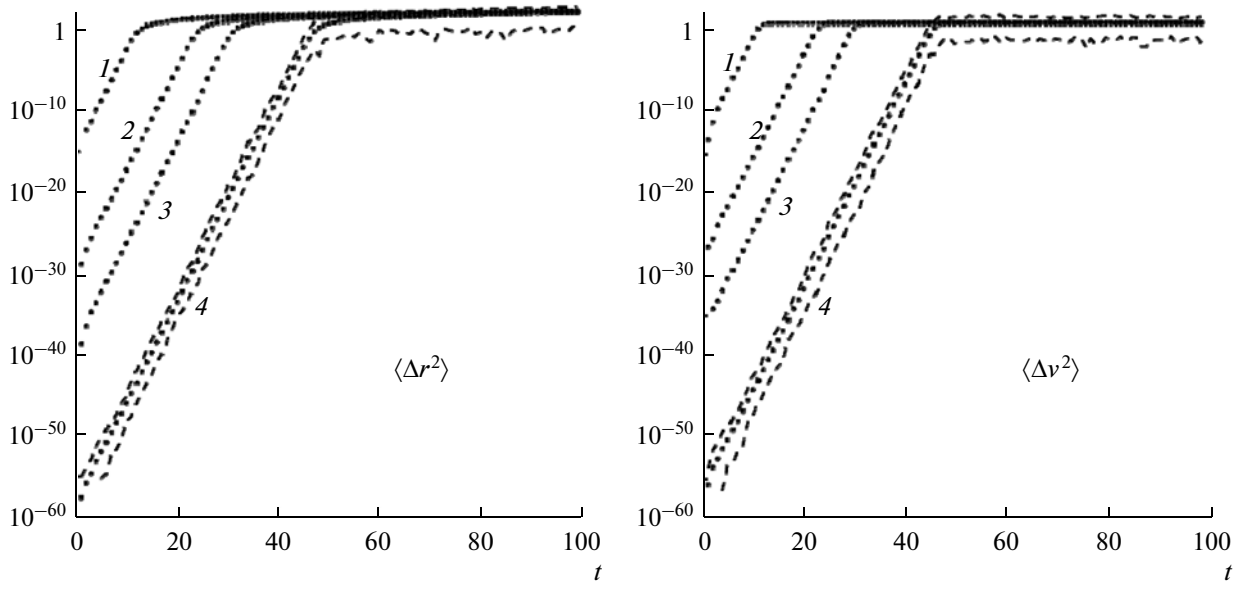

Fig. 8. Dependences on time t of the divergences of the coordinates $\left\langle \Delta r^2(t) \right\rangle$ and the velocities $\left\langle \Delta v^2(t) \right\rangle$ for two trajectories calculated from the same initial conditions under different summation orders of sums such as (26). The data are presented for different computer representations of real numbers: (*1*) float PC (4 bytes), (*2*) double Cray SV1 (8 bytes), (*3*) long double PC (8 bytes), (*4*) long double Cray SV1 (16 bytes). For the case of the most accurate representation of numbers (case 4), the dashed line shows the maximum and minimum divergence of individual particles at a given time instant t: $\max_i \Delta r_i^2(t)$ and $\max_i \Delta v_i^2(t)$ $(i = 1,\ldots,N)$.

Numerical rounding errors are a weak uncontrollable source of disturbance in the calculation of MD trajectories. In order to study their effect on the calculation result, we used the *procedure of artificial permutation of indices*. By the random permutations of the order of summation in (26), different versions of rounding errors and, therefore, different values of $\mathbf{F}_i$ are implemented.

Let two trajectories $\{\mathbf{r}^1(k\Delta t),\ \mathbf{v}^1(k\Delta t),\ k = 0,1,\ldots\}$ and $\{\mathbf{r}^2(k\Delta t),\ \mathbf{v}^2(k\Delta t),\ k = 0,1,\ldots\}$ be calculated from one and the same initial configuration, with one and the same numerical scheme, at one and the same step Δt, using one and the same computer, but let the order of summation in the calculation of the sums (26) be different. The trajectories diverge exponentially (Fig. 8). In this case we will refer to the memory time as the *time of computational memory* t_m^c. This time depends on the accuracy of the machine representation of real numbers. From the condition $t_m^d = t_m^c$, we can find the value of the numerical integration step which can provide the longest time of preserving the correlation of the MD trajectory with the true Newtonian trajectory for a given machine accuracy and finite-difference scheme.

Figure 9 is an example of the expected limitation of the time t_m^d by the finite accuracy of the machine representation of real numbers. For the values of numerical integration steps employed in MD calculations (of the order 0.01–0.001 of the inverse frequency of particle oscillations), the time t_m^d is only several factors less than t_m^c. Thus, the finite accuracy of the computer representation of real numbers makes it hopeless in the foreseeable future to integrate Newton's equations exactly over times characteristic of MDM.

2.4. Solution of Cauchy Problem in MDM. Irreversibility

Divergence is shown in Fig. 2 on a logarithmic scale. For most of the time less than t_m, the absolute value of the divergence is small and, on a linear scale, the divergence would be noticeable only in the vicinity of t_m (Fig. 10). In contrast to Fig. 1, where only one MD trajectory is shown, Fig. 10 presents four MD trajectories under the same initial conditions Γ_0; their polygonal character is smoothed due to the great number of the assumed integration steps. In Fig. 10a the trajectories 1–4 are calculated with increasing

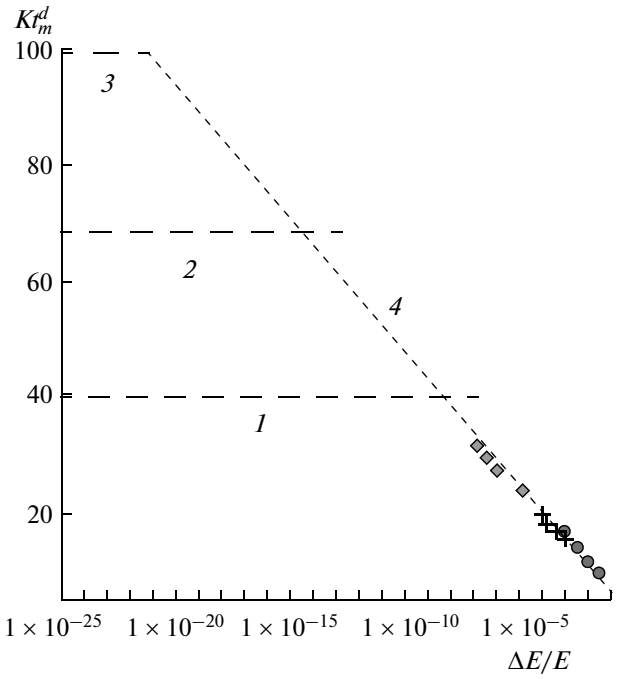

Fig. 9. The expected restriction of the limiting values Kt_m^d by the number length in a computer: *1*, *2*, and *3* correspond to 7, 16, and 31 decimal places in the machine representation of real numbers. 4 is taken from Fig. 7.

accuracy at the expense, for instance, of a reduction in Δt or raising the order of accuracy of the scheme. The logarithmically slow (Section 2.1) increase in t_m^d is schematically represented in Fig. 10a. In Fig. 10b the trajectories 1–4 calculated with the same accuracy diverge, for instance, due to the different order of the forces summed in (26). In this case, the values t_m^d prove the same for all trajectories.

Figure 10 illustrates an important feature of the MDM, which was designed as a solution to the Cauchy problem, i.e., instead of a single solution corresponding to the initial conditions Γ_0, MDM yields a bundle of trajectories emanating from Γ_0. These trajectories exponentially diverge from each other over time t_m^d. However, for times shorter than t_m^d, the solution of the Cauchy problem is, nevertheless, practically obtained.

The fact that MDM only enables finding the solution of equations of motion for short periods of time τ was mentioned in [29, 30, 125]. It had still been unclear why MDM yielded such successful results by averaging over trajectories, the lengths of which were by several orders of magnitude greater than τ, although in [30] the way to the answer had already been shown. Statements were repeatedly made (see, for instance, [10, 40, 41, 125–127]) proclaiming that MDM simulated a microcanonical ensemble; i.e., the MD trajectories lay on a hypersurface of constant energy in the phase space.

It was repeatedly stated that if the equations of motion were correctly solved, the MD trajectories had to be reversible in time [10]. However, from Fig. 10 it follows that trajectories calculated in MDM are irreversible if the length of the trajectories exceeds time t_m^d. To prove this, it is sufficient to calculate the forward trajectory with one accuracy and the backward trajectory with a different one.

The research [68] was commissioned by Lebowitz. Its authors, unfortunately, replaced the concept of the reversibility of a trajectory by the reversibility of the MD algorithm. Earlier, a similar mistake had been made in [128]. In this connection, as early as in [11], it had been pointed out that according to some opinions, the trajectories obtained by symmetrical difference schemes were reversible; it is true if for reversing a trajectory not one finite point of the forward trajectory is used but two, which was proposed in [128, 68]. It should be remembered that in MDM, it is impossible to find two neighboring points belonging to one and the same Newtonian trajectory. At the same time, if only one end point is used, as required by the Cauchy problem, for any difference scheme trajectories will not be reversed due to the instability of the

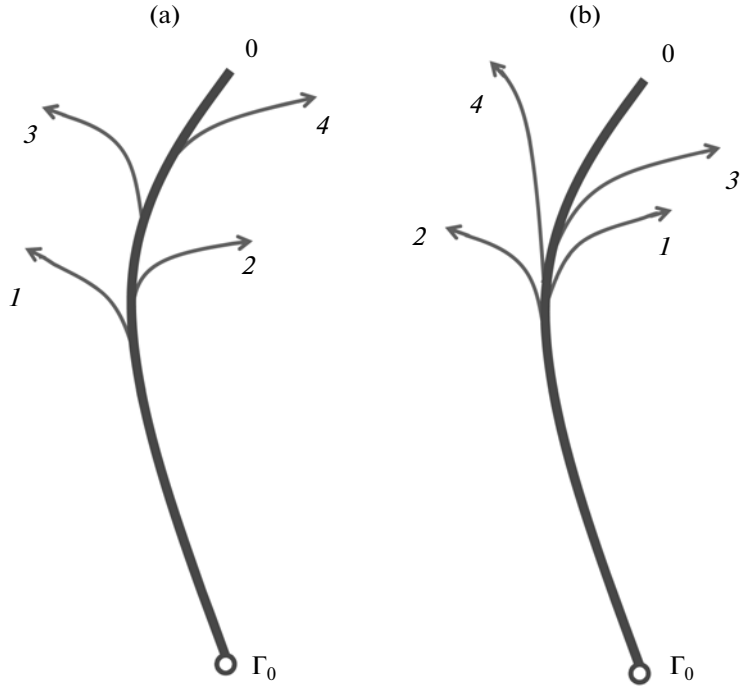

Fig. 10. Schematic illustration of the linear scale of divergence of MD trajectories (shown by fine lines) against the hypothetical exact solution of the Cauchy problem (continuous curve 0). MD trajectories are calculated with monotonically increasing accuracy when passing from trajectory *1* to trajectory *4* (a) and with one and the same accuracy for all trajectories (b). Both the trajectory 0, and the trajectories *1–4* have the same initial conditions Γ_0. The moments of MD trajectories' deviation from the exact solution correspond to different dynamic memory times t_m in the case (a) and to one and the same time t_m in the case (b). The linear time scale was selected; therefore, the initial coincidence of MD trajectories and the exact solution illustrates the fact that the relative error of the coordinates and velocities is still very small, although it increases exponentially (see Fig. 2).

equations of motion. The authors of [68] could verify the irreversibility of the MD trajectories by changing the step size for the backward trajectory.

The time t_m^d is sometimes called the horizon of predictability. In a dynamic problem of forecasting the weather, the predictability horizon limits the time of the reliable forecast [34–36]. The prediction of atomic trajectories is possible in the picosecond range, a reliable weather forecast is possible for a few days, but the mathematical nature of limiting predictability is one and the same.

At the same time, there is also a significant difference. Of practical interest in the weather forecast is a single trajectory and the deviation of the predicted one due to an unexpected small disturbance is perceived by the general public as the prediction error. In MDM, on the contrary, the individual trajectory is not of practical interest but rather the result of averaging over the total distribution of the trajectories. And this result proves to be stable and does not depend on the scheme, the step of numerical integration, or on the computer [102].

We also note the difference between the problems of MDM and dynamic chaos [50, 48, 51, 70–72], which is defined as an "irregular, aperiodic state change (movement) of a dynamical system possessing the basic properties of a random process" [129]. This result arises in the absence of random factors. In the problem of dynamic chaos, a unique trajectory is considered to be determined by the initial conditions. While in the problems of dynamic chaos, we can expect to obtain the characteristic of random processes after averaging distributions rigorously conserving energy over a single dynamic trajectory; all the more so, such distributions are attained in the MDM when averaging is performed over an ensemble of tragectories only conserving energy on average and located in the hyperlayer $E \pm \langle \Delta E \rangle$.

In star clusters and other systems of gravitating bodies, the distances between the bodies are huge compared to the size of the bodies themselves. Therefore, the motion of these bodies is determined by the gravitational potential r^{-1}. In molecular systems, there is also a long-range attraction potential, even if much

weaker, i.e., r^{-6}. The distances between particles in molecular systems are such that there necessarily occur close collisions resulting from short-range repulsion. It is these collisions that determine the instability of the motion of particles and trigger the exponential divergence of the trajectories. Krylov illustrated this by the simplest example of the collisions of balls [28]. In the theory of systems of gravitating bodies the situation is the reverse. The motion of bodies is usually described by standard cycles and the search for exceptional conditions is conducted when, despite the absence of close collisions, the instability of trajectories can still arise in the system [26].

The irreversibility in the numerical solution of equations of motion of exponentially unstable multiparticle systems is used for the construction of encryption algorithms [130].

2.5. Non-Hamiltonian Nature and Statistical Meaning of the MDM

We proceed to the conclusions that can be drawn from the basic features of the numerical integration in MDM analyzed in this work.

2.5.1. The accuracy of equilibrium MD calculations. *The first conclusion* [11] is that MDM for equilibrium systems is a method that (i) retains Newtonian dynamics only at times less than t_m^d and (ii) conducts statistical averaging over the initial conditions along the MD trajectory.

Hence, in particular, the dual meaning of the accuracy of MD calculations follows. On the one hand, dynamically independent points on the MD trajectory are separated by time intervals close to t_m^d. Thus, we estimate that the accuracy of averaging in the MD to be not worse than $(t_m^d/t_0)^{1/2}$, where t_0 is the length of the MD trajectory. On the other hand, the quantity t_m^d determined the time interval over which the solution of the system of Newton's equations is close to the exact one. Thus, by improving the accuracy of the numerical integration, we increase t_m^d but reduce the accuracy of averaging if we retain the same value of t_0. The value t_m^d is uniquely connected with the fluctuation of the total energy $\left\langle \Delta E^2 \right\rangle$. This implies that the latter is also a measure of the integration accuracy.

The comparison of the values of the dynamic memory time t_m^d with the characteristic times of the velocity autocorrelation function (VACF) shows that the interval when the VACF values normalized to 1 at $t = 0$ exceed 10^{-1} corresponds to the times less than the memory time t_m^d. Thus, the correlations in this area are dynamic correlations that follow from Newton's equations. Correlations for time greater than t_m^d are already of a stochastic nature rather than a dynamic one.

It would be of interest to find out whether the increase in the accuracy of the numerical integration affects the character of the correlations during the transition from dynamic to stochastic correlations. The available computing capability only enable the reduction in ΔE by several orders of magnitude even when refined numerical schemes are used [116, 85, 86]. This would only double t_m^d. Thus, the area of stochastic correlations would still be preserved in the time interval where VACF decreases exponentially [131].

2.5.2. Nonconservative equations of motion. Since Newtonian dynamics are only approximately retained in the MDM due to the impact of numerical errors, an inverse problem can be formulated consisting in finding equations satisfied by the trajectories of particles calculated by MDM [11, 42, 69]. Thus, the *second conclusion* is that these trajectories obey the equations

$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i(\mathbf{r}_1,\ldots,\mathbf{r}_N) + \eta_i(t), \quad \frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i + \xi_i(t) \tag{27}$$

for schemes with the explicit computation of velocity at each step or

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i(\mathbf{r}_1,\ldots,\mathbf{r}_N) + \mathbf{z}_i(t), \quad i = 1,..,N, \tag{28}$$

for schemes with the implicit calculation of the velocity. The quantities $\boldsymbol{\xi}_i$, $\boldsymbol{\eta}_i$ (or $\mathbf{z}_i$) are additional terms arising from the numerical integration of equations of motion (1) or (2), $m_i\boldsymbol{\xi}_i + \boldsymbol{\eta}_i = \mathbf{z}_i$. The errors of the numerical integration are made up of the scheme and rounding errors. The scheme errors are deterministic. Rounding errors in the computer are also formally deterministic. However, it is rounding that lays the foundation of the algorithms for obtaining pseudorandom number sequences in random-number generators. The repetition period lengths in these sequences are so large that random numbers actually turn out to be random, see, for instance, [132]. Therefore, for $\boldsymbol{\xi}_i$, $\boldsymbol{\eta}_i$ and $\mathbf{z}_i$, a probabilistic description can be introduced; i.e., we can use the concepts of a distribution function and correlation function.

The presence of additional terms having pseudorandom character makes the system of equations of motion (27) or (28) non-conservative. For the drift of the total energy to be absent and its fluctuations to be of a stationary character, the work of the force $\mathbf{z}_i$ must average zero

$$\langle \mathbf{z}_i \dot{\mathbf{r}}_i \rangle = 0. \qquad (29)$$

From (29) there follows the evenness requirement for the approximation of the second derivative [11, 42, 69]; i.e., only schemes of an even order are suitable for MDM. Those include Verlet schemes and leapfrog schemes. A stronger requirement for numerical schemes for MDM is their simplecticity, i.e., preserving the phase volume of the dynamical system (see, for instance, [133–136]). As applied to MD problems, the methods of geometrical numerical integration and backward error analysis are developed (see, for instance, [137]), enabling the construction of symplectic numerical schemes with stable preservation of the total energy of the system on average at large times. It should be noted that the use of symplectic schemes cannot affect the presence of the exponential divergence and stochastic entanglement of the MD trajectories. There is an opinion that the use of symplectic schemes is not always necessary in MD calculations [138].

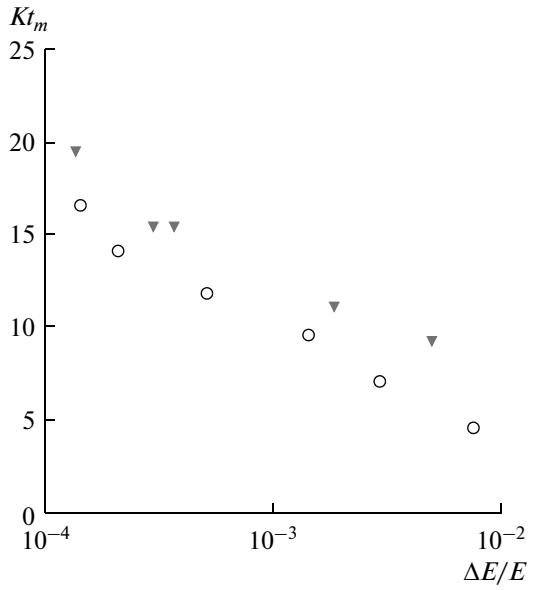

Fig. 11. Dependence (calculated by A.Yu. Kuksin) of the dimensionless product Kt_m on the relative fluctuation of the total energy of the system (Lennard–Jones liquid, $\rho = 1.0$, $T = 0.7$, Verlet scheme in the velocity form). Circles designate the Langevin thermostat, triangles denote the Berendsen thermostat.

Thus, the *third conclusion* is that MD systems are non-Hamiltonian. Attention is drawn in [139] to the fact that the system of dust particles in plasma is non-Hamiltonian caused by the stochastic background affecting the dynamics of dust particles and results from their collisions with electrons, ions, and atoms of the dusty plasma. Dusty plasma is nothing exceptional in this regard. The stochastic background is created already at the level of numerical integration errors (their physical counterparts are discussed below in Section 3.4) and can only be enhanced by other factors. Thus, any classical system of molecules, atoms, ions, and electrons is non-Hamiltonian. Only for time less than t_m^d these systems can be approximately Hamiltonian.

2.5.3. Ensembles in MDM. The result of the solution of the system (1) or (2) would be a phase trajectory $\Gamma = \Gamma(t;\Gamma_0)$, where $\Gamma = (\mathbf{r}_1,..,\mathbf{r}_N,\mathbf{v}_1,..,\mathbf{v}_N)$ is a point in the phase space and $\Gamma_0 = \Gamma(0)$ is the initial configuration. In this case, the total energy of the system would be identically conserved along the trajectory $E = E_{kin} + U = \text{const}$. The set of phase states of the system would correspond to the microcanonical NVE ensemble. However, making use of the finite-difference approximation for the numerical solution of equations of motion of a multi-particle system resulted in the fact that the value of the total energy E along the MD trajectory is not constant. The magnitude of the fluctuations $\langle \Delta E^2 \rangle$ depends on the selected numerical integration step and usually is relatively small, $\langle \Delta E^2 \rangle^{1/2} / E \sim 0.1\%$. However, the violation of the condition E = const significantly affects the dynamic properties of the MD system. Therefore, it makes sense to speak about a statistical ensemble $NV(E \pm \Delta E)$. MDM generated this ensemble and operates within its frame. This is the *fourth conclusion* from the performed analysis of the numerical integration in MDM.

The statistical ensemble $NV(E \pm \Delta E)$ originated in the theory of MDM from the empirical analysis of particle trajectories calculated by this method. However, it also has a complete analog in ergodic theory [107], in which we consider an ensemble of points in a phase space uniformly distributed in a thin layer near the surface of constant energy, i.e., the same ensemble $NV(E \pm \Delta E)$. It is such an ensemble, instead of a microcanonical one, that is used in this theory to prove the equality of two averages of the functions depending on the coordinates and momenta of all the particles of an isolated system. The first average is taken over time along the trajectories of the system in the phase space. The second average is the statistical mean over the ensemble of phase points in a thin layer $(E \pm \Delta E)$. The same method is used in § 112 [58]

for the proof of the Gibbs distribution in an isolated body. Thus, the ergodic theory provides an additional justification of the correctness of the MDM.

Distributions in small subsystems of a MD cell containing a large number of particles naturally comply with the standard statistical ensembles, i.e., canonical and grand canonical.

In the study of both macromolecular structures and single-atom systems, broad use is made of modified MDM versions such as Langevin and stochastic MD procedures for maintaining a constant temperature, the *NPT*-ensemble, the Nose–Hoover ensemble, and the Berendsen thermostat. In all these cases, Newton's equations are supplemented with additional terms maintaining the constancy of, say, pressure and/or temperature or some flow. Any addition further distorts the solution of Newton's equations in comparison with the standard numerical schemes described above. However, the duration of the dynamic memory time t_m^d can change insignificantly due to the semilogarithmic dependence of the value of t_m^d on the errors introduced in solving Newton's equations.

In Fig. 11 universal coordinates are selected analogous to Fig. 7, for which the intensity of disturbing sources is expressed through the value of the relative fluctuations of the total energy generated by them. The semilogarithmic dependence proved similar to Fig. 7. With excessively large $\Delta E/E$, the values of t_m^d are reduced so that the method loses its dynamic character and its capabilities are restricted to the level of the Monte Carlo method. The proposed analysis makes it possible to estimate the reliability of the approximated MDM variants and limits of their applicability in the study of dynamic properties.

3. SOME CONCLUSIONS FROM THE MDM RESULTS

MDM contains all the basic concepts of statistical physics and physical kinetics, i.e., irreversibility, the transition to the statistical description, and for equilibrium systems it also features Gibbs distribution and equality between time and space averages. MDM results are consistent with a variety of experimental data, including the macroscopic properties such as the equation of state, transport coefficients, ductility, and fracture dynamics, as well as microscopic properties, for example, the distribution function. MDM also demonstrated its predictive power.

Thus, MDM provides an adequate and internally self-consistent description of real substances. By description we understand the set of particle trajectories calculated in MDM. This set can be called a model of a substance or an object that is created by this method. Thereafter, within the MDM frame, various diagnostic tools are found that are used to study the properties of the created object. The agreement between the representations of the substance that are actually developed in the MDM and real substances suggests that these representations are a good approximation to describe real-world properties, processes and phenomena of classical physics. Let us turn to the conclusions that follow from the analysis of representations of a substance which is developed in the MDM. We will try to list therewith all items both consistent with the usual ideas of classical statistical physics [49, 58] and those that are at some variance with them.

3.1. Impossibility of Solving System (1) for Times Exceeding t_m^d

It is generally assumed that by treating a multi-particle system as a mechanical multi-particle system, setting up classical equations of motion for it, the number of which equals the number of degrees of freedom, and integrating these equations, you can get comprehensive information about the movement and properties of the system; however, this problem is practically unsolvable. MDM has shown that this problem is fundamentally unsolvable, because even for three particles it is impossible to solve the system of Newton's equations during the time required for averaging, as this time significantly exceeds t_m^d. The trajectories of the particles obtained in the MDM are close to the trajectories following from Newton's equations only over the time less than t_m^d. Therefore, the time interval of possible dynamic correlations on a microscopic level is limited by the value of t_m^d.

This already suggests the indication of irreversibility of the solution for the MDM system of equations of motion. It is not surprising, therefore, that the ideas developed in the MDM fit into the principles of statistical physics and its results both qualitatively and quantitatively agree with the experimental data. That is why the above-mentioned features of the trajectories calculated in MDM must be consistent with the specifics of particle trajectories in the real systems.

To avoid misunderstanding, we note that at the macroscopic level, the result of averaging over the distribution of trajectories is of interest rather than the trajectory of a single particle. Since this result is stable, the time interval of possible dynamic correlations at the level of a continuous medium by many orders of magnitude exceeds t_m^d for the trajectory of a single particle.

3.2. Choice of Particle Number

It is usually stated that the original so-called statistical laws, due to the presence of the large number of particles making up the body, cannot be reduced to purely mechanical laws. MDM has shown that this is true. However, the point here is not the large number of particles but the exponential Lyapunov instability and low noise. The boundary between the systems, for which a purely mechanical description is possible, and systems, for which statistical laws should be used, is a system of three particles. This is because systems of three and more particles are characterized by an exponential instability, which leads to qualitatively new laws and patterns.

We note that we are talking about statistical laws, which are manifested when the system is monitored over times significantly exceeding t_m^d or in the cases when averaging is performed over an ensemble of statistically independent initial conditions. The specificity of these patterns loses all content not only after transition to mechanical systems of two particles but also for systems with many degrees of freedom, when the dynamics of these systems is studied over times much smaller than t_m^d, and no averaging is conducted over independent initial conditions. Such problems, however, are beyond the scope of this survey.

Since the Lyapunov instability occurs in systems of three and more particles, the study of specific statistical laws can be started from three particles. Thus, for example, the equilibrium distribution can be obtained for three (even two) particles in a limited volume when averaged over time along the MD trajectory, the length of which is much greater than t_m^d. These distributions are getting increasingly closer to the Maxwellian distribution in a growing energy range with a rise in N [140, 141]. When similarly long trajectories are used, the properties of clusters and their dependence on N can be investigated, starting from three-particle ones [141]. Recently, the problem of clusters has significantly increased in importance in connection with the theoretical analysis and MD simulations of small clusters in dust plasma. The proximity to the Maxwellian distribution of particle velocities in such clusters has also been established experimentally (see [142] and references therein).

In the study of homogeneous systems in periodic boundary conditions (PBC), the error of this approach can be determined in relation to the infinite homogeneous systems and its dependence on the number of particles N (or N^{-1}) starting from $N = 3$. Certainly, for studying a variety of properties, unlike obtaining Maxwellian distribution, the choice of a small N can prove utterly meaningless. Thus, the choice of N is based not on the fundamental requirement of adherence to statistical laws, but is dictated by the size of the system characteristic of the problem to be explored; i.e., it is guided by specific physical considerations. At the same time, the increase in N enhances the wealth of properties and processes arising in the system. Accordingly, their investigation calls for an increasing variety of instruments.

The selection of the value of N (or MD size of cell L) which would be the minimum allowable for the posed problem is determined by the scale of the space and time correlations and inhomogeneities characteristic of this problem. Let us consider these aspects in greater detail.

Space constraints. If we calculate a pair correlation function $g(r)$, then $N \gg nr_c^3$, where n is the concentration of particles and r_c is the studied range of distances. The quantity r_c may correspond both to the distance to the first or some subsequent maximum or minimum, and to the region where $g(r)$ asymptotically tends to unity.

The correlation radii r_{ci} are determined not only by *g(r)* but also by other space characteristics, as there is a hierarchy of correlations $r_{c1} < r_{c2} < r_{c3} < \ldots$ in the system, which corresponds to the hierarchy $N_1 < N_2 < N_3 < \ldots$ where $N_i = nr_{ci}^3$. When choosing the value of N, we thereby cut the series of correlations to be studied in this MD calculation. The choice $N = nL^3$ limits the wavelengths $\lambda < L$ of the equilibrium fluctuations; i.e., it fixes the range of wave vectors for which we can calculate the variance in density fluctuations, such as phonons in condensed media and plasma waves in collisional plasma.

For long-range potentials, in particular the Coulomb potential, the contribution of particle interactions $\Delta U(r > L)$ at distances greater than L must be small compared to the interaction energy U. Other-

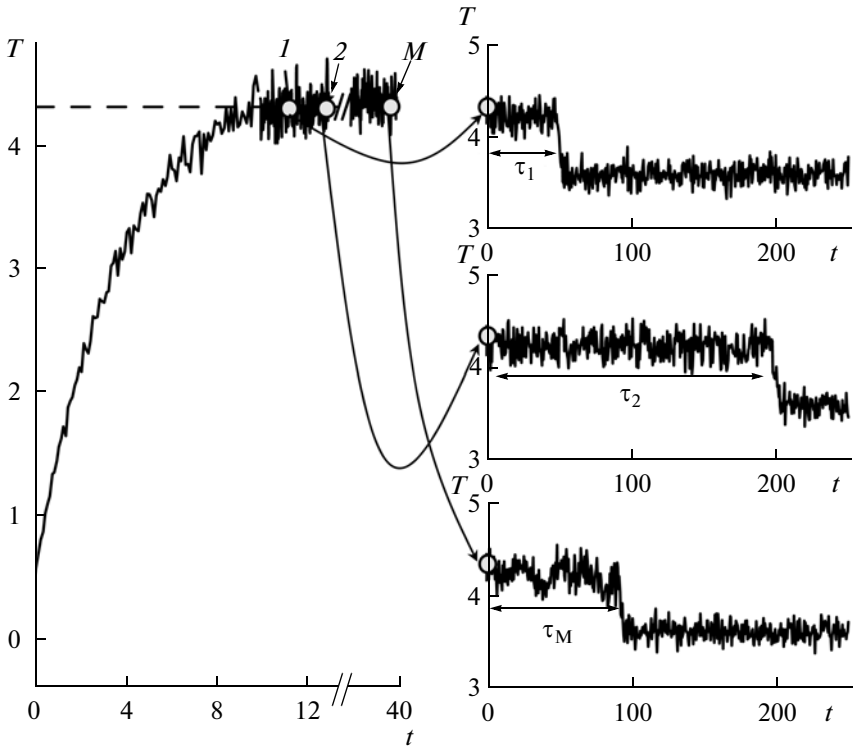

Fig. 12. On the left – dependence of the temperature on the time under heating to the required temperature with imposed restrictions on the movement of atoms. On the right – three examples of MD trajectories with removed restrictions on the motion of atoms each yielding its lifetime τ_j, $j = 1,2,\ldots,M$. The results are obtained for the Lennard–Jones system of $N = 500$ particles; the density is $1.2\sigma^{-3}$.

wise, nonphysical correlations can emerge in the system induced by PBC. N must be increased until its value reaches $\Delta U(r > L) \ll U$.

Time constraints. Alongside the hierarchy r_{ci}, there is a hierarchy of correlation times $\tau_{c1} < \tau_{c2} < \tau_{c3} < \ldots$. The choice of L cuts this series by two inequalities, i.e., $6D\tau_{ci} < L^2$ where D is the diffusion coefficient and $a_s\tau_{ci} < L$ where a_s is the sound velocity. The limitations imposed by the second inequality were identified in [131] for the velocity autocorrelation function calculated at different N and one and the same density for the system of hard spheres.

In the transition to relaxation processes, there are additional spatial and temporal characteristic scales and the corresponding requirements for N. The choice of N limits the range of the investigated characteristics for such cooperative phenomena as dislocations, and cracking.

The general conclusion is that the choice of the system size (number of particles) restricts the limiting values r_c, τ_c, λ, etc., and, consequently, the range of phenomena and processes that can be studied.

When MDM is applied using parallel computations on modern supercomputers, the time spent on the data exchange between computing nodes (cores and processors) is much smaller than the computation time within a single node. Initially, therefore, the performance increases almost proportionally to the number of nodes used, then the performance reaches its maximum and begins to decrease with the further increase in the number of nodes. M nodes is the optimal number of nodes, at which the performance is close to the maximum. The value of M depends on the architecture of the computed cluster or supercomputer and N, i.e., the studied property or process in the investigated system [143].

3.3. Probabilistic Nature of Classical Statistics

In the literature, it is still a matter of debate whether the findings and predictions about the behavior of macroscopic bodies based on statistics are of a probabilistic nature. The statistics might be different from classical mechanics, the conclusions of which are quite unique. MDM results made it possible to show

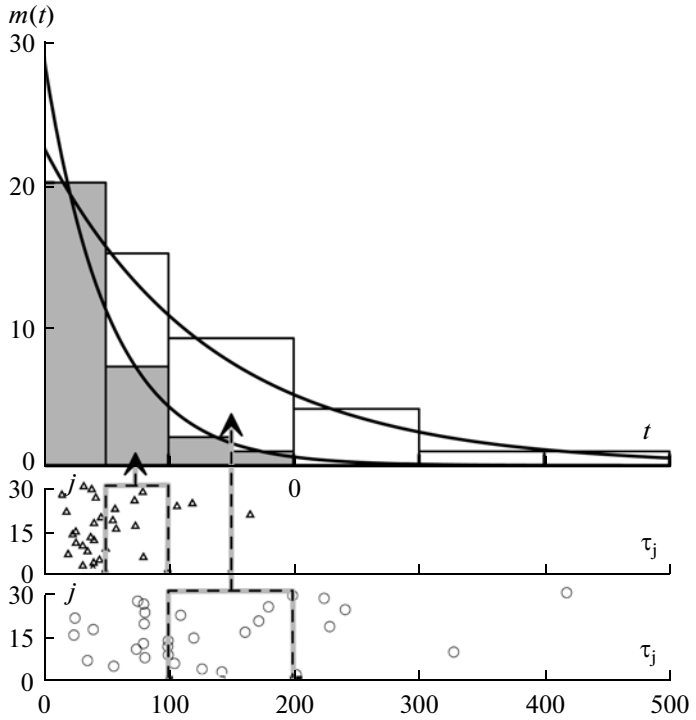

Fig. 13. Distribution of lifetimes for two temperatures; $m(t)$ is the number of MD trajectories for which the decay occurred within the time interval $(t, t + \Delta t)$ where Δt is the width of the histogram columns. The lifetimes themselves are presented in the two figures below, where j is the number of the trajectory in Fig. 11, $M = 30$, and τ is the respective lifetime. The results are obtained for the Lennard–Jones system of $N = 6912$ particles at density $1.0\sigma^{-3}$ for two temperatures $T = 1.6097$ (gray distribution) and $T = 1.58$ (white distribution). The solid line stands for $m(t) = (M\,\Delta t/(\overline{\tau}^2)\exp(-t/\overline{\tau})$.

that the probabilistic character of the results obtained by classical statistics lies in the very nature of the objects it studied; i.e., statistics are really fundamentally different from classical mechanics.

In the study of equilibrium systems, the cause of the above is the fact that the averaging time is much longer than t_m^d. The results of classical statistics are obtained on the basis of a much smaller amount of data than would be necessary for a full mechanical description. The data integrity required for the latter is essentially lost as the dynamics are developed for times longer than t_m^d.

The emergence of the probabilistic nature of the relaxation processes is illustrated below by an example of the decay of a superheated crystal. MDM allows us to study the decay of metastable states of condensed phases as close to the limit of stability as possible for their lifetime to be within the computational capabilities. First we must obtain the ensemble of initial states of the superheated crystal. Consider an example of this procedure [102]. Modeling begins with an equilibrium crystal at a temperature below the melting point. With further isochoric heating up to the required superheat artificial constraints on the movement of atoms are introduced, which prevent the disintegration of the lattice: each atom is surrounded by the Wigner–Seitz or sphere with reflecting walls. The system with these restrictions is brought to the equilibrium MD trajectory. Then, the ensemble of M independent points of this trajectory is used as an ensemble of initial conditions for the MD trajectories with no restrictions on the movement of particles.

Each of the M obtained trajectories gives its lifetime τ of the metastable state, as shown in Fig. 12. There is no correlation between the lifetimes of neighboring points because the initial states were selected as independent and the values of τ exceed the dynamic memory time t_m^d. This implies that the values of τ must be random, which is confirmed by the fact that the set of the values of τ forms an exponentially decaying distribution $\exp(-\tau/\overline{\tau})$ (Fig. 13). Moreover, $\overline{\tau}$ coincides with the average lifetime obtained by averaging the times τ of individual trajectories. Thus, the decay of metastable states appears to be a Poisson random process. The mean time $\overline{\tau}$ is stable and is a characteristic of the metastable state and the selected volume V. The quantity $J = (V\overline{\tau})^{-1}$ is physical—it is the rate of homogeneous nucleation.

Irreversibility in statistics based on the MDM equations occurs at the level of individual particle trajectories for systems of three and more particles (or two particles in a closed volume). The irreversibility of particle trajectories enables us to understand how dissipative processes arise in MDM. Indeed, Newton's equations do not contain any dissipation. At the same time, it is well known that MDM is an excellent tool for studying a wide variety of dissipative processes from thermal conductivity and viscosity to plastic deformation. The whole point is that the equations of motion corresponding to the particle trajectories obtained in MDM, are characterized by such additional terms which allow us to describe dissipation.

3.4. Quantum Origin of Stochasticity and Irreversibility Characterizing Trajectories of Particles of Real Substances

The description of a substance which is actually implemented in MDM can be compared with real systems, since there are physical factors that lead to finite t_m^d in real systems as well [118–121, 66, 144, 65]. Among such factors, we can name random effects in the interaction with a macroscopic system (thermostat). Errors of the numerical scheme in MDM qualitatively (but not quantitatively) correspond to such effects. Their value, however, does not play a significant role due to the logarithmic dependence of the value of t_m^d on the noise amplitude, and even a small trigger is sufficient to start mixing by the mechanism of the exponential instability.

We should, however, recall the view that the irreversibility must also arise in a completely isolated system when there is no thermostat [28, 57–59]. These authors saw the only way out in quantum mechanics. This viewpoint can be connected with the results of the classical MDM if we assume that the errors of the numerical procedure in the MDM qualitatively simulate the small but always finite quantum uncertainty inherent in any system that is considered a classical one. The quantitative agreement is not so important due to the logarithmic dependence of the dynamic memory time on the noise amplitude.

A rigorous consideration, especially with a decreasing temperature where the role of quantum effects is growing, requires the preservation of the lower corrections for $\hbar$ in the transition from the quantum to the classical description of the particles dynamics. In [65, 66, 144] the concept of quasi-classical trajectories is introduced and an attempt is made to obtain the equations of motion in the quasi-classical approximation

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} + \hbar^{1/2}\kappa_{ij}\chi_j(t), \quad \frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} + \hbar^{1/2}\beta_{ij}\phi_j(t), \tag{30}$$

where χ and ϕ are δ-correlated random functions of unit capacity. The corrections for Planck's constant were of the order $\hbar^{1/2}$. The random origins χ and ϕ take into account the spreading of wave packets and diffraction during elastic scattering. In [66, 143, 65] not all the lower corrections for $h^{1/2}$ were calculated. Apparently, the result has been over estimated and we do not present here the specific form of the tensor functions κ_{ij} and β_{ij}. In (30), the terms that could provide the constancy of the average total energy are also absent. The role of the weak inelastic processes was also noted by M. Gertsenshtein and Yu. Kravtsov [121], who considered the trajectory perturbation under the action of a thermal electromagnetic field and of spontaneous emission of low-frequency photons [118].

The approach of [65, 66, 118, 121, 143] dates back to Landau's hypothesis assuming that although the Schroedinger equation is symmetric with respect to time sign reversal, actually quantum mechanics essentially contain the nonequivalence of both time directions. The deep irreversibility in quantum mechanics is inherent in the measurement process [58, 62], which is probabilistic in nature. The measurement procedure is used in [66, 143, 65]. Equations (30) are incomplete and are presented in order to explain the problem of obtaining semiclassical equations of motion and their probabilistic character. We can assume that due to the logarithmic dependence t_m^d on the noise level, quantum uncertainty will lead to the values t_m^d for a real dense system of atoms in the area studied in the present work.

In the quasi-classical approximation, from a certain point $\{\mathbf{r}(0), \mathbf{v}(0)\}$ of the system's phase space, there emanates not a single classical trajectory but a bundle of trajectories, expanding at a rate of K^{-1}. Only the starting conditions of the divergence depend on Planck's constant, i.e., A, B, and t_l (see (17) and Fig. 2). Under the time reversal ($\mathbf{v}(t^*) \to -\mathbf{v}(t^*)$, $t \to -t$), at the time instant $t = t^*$ and point $\{\mathbf{r}(t^*), \mathbf{v}(t^*)\}$, a new bundle of phase trajectories emanates. The system will return to the initial point $\{\mathbf{r}(0), \mathbf{v}(0)\}$ with a certain

probability P_{rev}, which decreases exponentially with increasing t^* for $t^* > t_l$, $P_{rev}(t^* = t_m^h) = 0$. The values of t_m^h can be found after obtaining quasi-classical corrections for Newton's equation.

For complex potential reliefs $U(\{\mathbf{r}_i\})$ in (3), for instance, for polymers and biomolecules there arise new factors that lead to irreversibility.

In [144], a simple model of a chemical reaction is considered with a single reactant valley and two product valleys, i.e., with the topology containing a bifurcation point in the transition state area. It was shown that within the numerical solution of the corresponding mechanical model under the influence of random factors ξ, η (or z) introduced in (27) and (28) and analogous to the quantum uncertainty in (30), the system may behave either in a reversible or irreversible manner. In a more complex case, the trajectory's reversibility can be absent not only in the classical but also in the general sense; i.e., the reactants of the direct reaction can differ from the products of the reverse reaction due to the departure of the reverse trajectory to the valley of the potential relief U, different from the original one.

At the intersection of the potential surfaces, the adiabatic approximation is violated. In this case, there arise quantum points of bifurcation when in the vicinity of the intersection the notion of a trajectory loses its sense and the situation calls for consideration in the spirit of the Landau–Zener model and femtochemistry approaches.

Both the classical and quantum bifurcations impose additional restrictions on dynamic memory time by the transit time along the trajectory of the distance between two successive bifurcations.

The set of quantum effects can lead, in particular, to a violation of the principle of detailed equilibrium and the irreversibility of chemical and biochemical reactions, the dynamics of which take place at the complex potential reliefs with the points of the classical and quantum bifurcations. We imply both long sequences of processes as well as separate (elementary) stages.

3.5. Inequality, Providing Nonequivalence of Both Time Directions

According to Landau [58] "*Quantum mechanics does in fact involve an important nonequivalence of the two directions of time. This appears in connection with the interaction of a quantum object with a system which with sufficient accuracy obeys the laws of classical mechanics, a process of fundamental significance in quantum mechanics. If two interactions A and B with a given quantum object occur in succession, then the statement that the probability of any particular result of process B is determined by the result of process A can be valid only if process A occurred earlier than process B* (see also [62] § 47*)." "Thus in quantum mechanics there is a physical nonequivalence of the two directions of time, and the "macroscopic" expression of this may in fact be the law of increase of entropy... If this is indeed the origin of the law of increase of entropy, there must exist an inequality involving the quantum constant $\hbar$ which ensures the validity of the law and is satisfied in the real world."*

To obtain such an inequality, we use the following arguments. The quantum analog of expression (22) is

$$Kt_m^h = -a\ln(b\hbar), \tag{31}$$

where t_m^h is the quantum dynamic memory time. Due to the logarithmic character of (31), the values a and b are, apparently, of little significance. Since the value t_m^h is much less than averaging time $t_{\max}$ under the observation of the thermodynamical and transport properties of equilibrium systems, the inequality can be written as

$$-(a/K)\ln(b\hbar) \ll t_{\max}. \tag{32}$$

CONCLUSIONS

The molecular dynamics method was intended to determine the trajectories of interacting particles from the solution of the system of Newton's equations. It was implied that the theorem of existence and uniqueness of Cauchy problem was satisfied. However, the set of particle trajectories, which is actually calculated in MDM, is different. The analysis of these issues and the consequent effects were performed in the present study.

We analyzed the relationship between the dynamic and stochastic properties of the trajectories of particles due to the Lyapunov instability of Newton's equations and scheme and round-off errors of the numerical integration. The notion of the dynamic memory time (or predictability) t_m^d for the particle trajectories was considered. MDM approximately retains Newtonian dynamics only for times shorter than

t_m^d and further trajectories diverge. A bundle of trajectories on a Newton "stem" is formed instead of the unique solution of the Cauchy problem. The proposed approach allows us to check the degree of preservation of the dynamic properties of the trajectories in the modified MDM versions as illustrated by the examples of the Langevin and Berendsen thermostats.

The particle trajectories calculated in MDM correspond to the equations of motion, which differ from Newton's equations by small terms. These terms are stochastic in nature and, therefore, the particle systems considered in MDM are not Hamiltonian. Instead of a microcanonical ensemble, in MDM there arises an ensemble $NV(E \pm \Delta E)$, where ΔE is the fluctuation of the total energy E along the MD trajectory. Such an ensemble had been introduced earlier in ergodic theory.

MDM results contain all the basic concepts of statistical physics, such as irreversibility and transition to the statistical description, and for equilibrium systems they include the Gibbs distribution and equality of the time and space averages. From the analysis of the method for obtaining these results significant conclusions can be drawn. It is impossible to solve the system of Newton's equation during the time required for averaging in statistical physics, since t_m^d is much less than these times. Since Lyapunov's instability occurs in systems of three and more particles, the study of specific statistical laws can be started from three particles. The probabilistic character of the results of classical statistics is inherent in the very nature of the objects studied by it. From the probabilistic character there immediately follows irreversibility, which occurs at the level of the trajectories of individual particles.

Representations developed in MDM, give an adequate and internally self-consistent description of real materials and can be extrapolated to real systems because there are physical factors that lead to the finite values of t_m^d. For starting mixing by the mechanism of the exponential instability even a small trigger is sufficient. Its magnitude, at the same time, is of little significance due to the logarithmic dependence of t_m^d on the noise amplitude. The inequality is proposed containing the quantum constant $\hbar$, providing the validity of the law of an increase in entropy and holding true in the real world.

From the obtained solutions of the fundamental problems, there follow standard requirements to be met by the MD calculations for specific problems, both in studying systems brought into equilibrium and in exploring relaxation. The choice of the number of particles N is determined by physical factors, such as the dimensions of the system characteristic of the space and time scales of the problem to be studied. The selection of N, in turn, determines the optimal number of processing cores (CPUs), the excess of which is impractical for parallel computing. The accuracy of averaging in an equilibrium MD is not worse than $(t_m^d/t_0)^{1/2}$, where t_0 is the length of the MD trajectory. Thus, by improving the numerical integration accuracy, we increase t_m^d but reduce the accuracy of the averaging if we retain the same value of t_0. For relaxation processes, averaging is performed over an ensemble of statistically independent microscopic initial states that are equivalent to each other macroscopically.

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