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## NONLINEAR PROBLEMS OF MOLECULAR PHYSICS

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A survey on investigations of some nonlinear problems of molecular physics carried out by molecular dynamics simulations is given. Among them there are problems of elementary excitations in fluids, the dynamics of chemical reactions in solutions, dynamical properties of dilute plasma, dynamic phenomena in phase transitions in mesoscopic systems, structural properties of chains of nonlinear oscillators. Several new results about the distribution of clusters and of a method of identification of clusters are presented.

### 1. Introduction

The paper reviews some recent results of investigations of modern nonlinear problems concerning molecular physics, physics of condensed matter, plasma physics and others. All of them use the same method of the study - computer simulation based on the molecular dynamics method (molecular dynamics simulation, MDS) [1-3]. The paper does not claim for complete coverage of all problems of mentioned fields of science, the selection is restricted mainly to subjects of the researches performed within a collaboration between groups in Berlin-Moscow-Saratov. The purpose of the survey is to give an insight into modern problems of studies of nonlinear phenomena, observed, for example, in elementary excitations, in phase transformations of matter, in chemical reactions, in plasma processes. The main subject is preceded by brief explanation of the basic principles of intermolecular interactions and the molecular dynamics simulation method.

### 2. Interaction of molecules and molecular dynamics simulations

Let us first consider a problem: what is the minimal number  $N$  of particles of a substance necessary to explore its physical, chemical, thermodynamic etc. properties? On the first sight, billions and billions of molecules or atoms are required. However, there is a number of phenomena when ensembles of only a few thousand or even hundreds of particles exhibit almost the same properties as large volumes of a substance. Besides, study of processes in ensembles of rather small number of particles (clusters, mesoscopic systems (see, for example, [4])) and the observation of evolution of their properties with increasing number of particles often yield a key to understanding of what happens in real volumes of substances - macroscopic systems. These observations allow to offer a

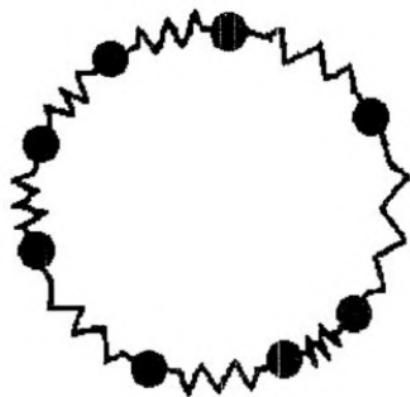


Fig. 1. A molecular system in a one-dimensional space with periodic boundary conditions

the average distance is  $\sigma$  (which plays the role of the specific volume) the simplest interaction model is a linear spring described by the parabolic potential (Fig. 2)

$$V^p(r) = \frac{1}{2}m\omega_0^2(r - \sigma)^2, \quad (1)$$

where standard notations are used. A standard model for a description of nonlinear interactions is the Toda model (Fig. 2)

$$V^T(r) = (a/b)[e^{-b(r-a)} - 1] + a(r - \sigma) \quad (2)$$

with constant parameters  $a$  and  $b$ . In higher dimensions the process is supposed to take place in a parallelepiped of sizes  $L_x, L_y, L_z$  in 3D model or  $L_x, L_y$  in 2D one, accordingly, and the space outside its limits is supposed to be filled with its precise copies immediately adjacent to each other (Fig. 3). Each particle has infinitely many copies in the space located on distances  $L_x, L_y, L_z$  in the relevant directions. If a particle abandons the field considered in a numerical modeling by crossing any boundary of the parallelepiped, its copy enters the field through an opposite boundary. In calculations of forces of particles interaction taking place in the vicinity of boundaries, the interaction with particles located outside of the field is taken into account if they are apart smaller

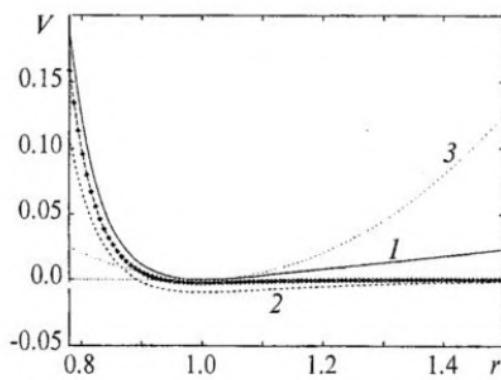


Fig. 2. Several models of the interaction potential  $V(r)$ : (1) - Toda potential, (2) - Lennard-Jones potential, (3) - harmonic oscillator potential and (↔) - Morse potential

method of the theoretical analysis based on the direct numerical simulation of a motion of particles in rather small ensembles and calculation of different macrocharacteristics by means of statistical treatment [1-3].

The important feature of molecular dynamics simulations is the application of periodic boundary conditions in studies of macroscopic systems. The influence of boundary conditions (requirements on a surface) should be minimal. Let us first consider a molecular system consisting of  $N$  particles in a one-dimensional (1D) space. In this case periodic boundary conditions are equivalent to placing the particles on a ring (Fig. 1). Let us discuss now the interaction of 2 particles at a distance  $r$ . If

$$V^p(r) = \frac{1}{2}m\omega_0^2(r - \sigma)^2, \quad (1)$$

$$V^T(r) = (a/b)[e^{-b(r-a)} - 1] + a(r - \sigma) \quad (2)$$

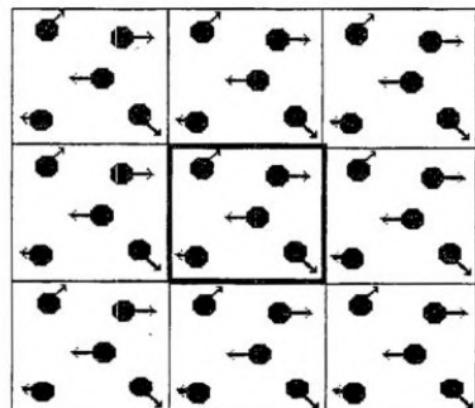


Fig. 3. A molecular system in a two-dimensional space with periodic boundary conditions

than some effective radius (see below). The periodic boundary conditions allow formally to assume  $N \rightarrow \infty$  already for  $N \sim 2^5 \cdot 2^{10}$ . In investigations of mesoscopic systems with limited number  $N$  the interaction space is considered as unbounded.

The kind of a theoretical model for an analysis is determined by physical properties of an explored system, and the type of forces of intermolecular interaction is principal among them. In this paper we consider only simple models with classical dynamics. The force of interaction between any two molecules is supposed to be depended only on the their distance  $r$ . The interaction potential in various models may be different (Fig. 2), but the methods of its calculation are not a subject of the analysis of this article. The models in which interaction of molecules takes place due to Van der Waals forces are defined by the Lennard-Jones potential

$$V^{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (3)$$

or its modification, more suitable for computer modeling, the finite-range Lennard-Jones potential

$$V^{FLG}(r) = A[(\sigma/r)^n - 1] \exp[(r/\sigma - 3/2)^{-1}] \quad \text{if } r < (3/2)\sigma, \\ V^{FLG}(r) = 0 \quad \text{if } r \geq (3/2)\sigma \quad (4)$$

are examined here (Fig. 2). Here  $\epsilon$  is a well depth in minimum of the potential well  $V(r)$ , and  $V(r=\sigma)=0$ . Also the models with particles interacting via conservative Morse forces described by the Morse potential

$$V^M(r) = (a/2b)(e^{-br} - 1)^2 - (a/2b) \quad (5)$$

are considered. In the models we study here parameters  $\epsilon$ ,  $\sigma$ , and a mass of interacting particles also are used as units of the relevant quantities, which are figured as dimensionless in the models. Note, the nonlinear potentials are «short-range» and  $V(r)$  is close to zero at  $r \geq 1.5$ . It allows to introduce an effective radius  $r_{eff} \approx 1.5\sigma$  so interaction of particles located more than  $r_{ij}$  from each other can be neglected. Therefore in calculations of, for example, complete potential energy of the system

$$U = \sum_{i,j=1}^N V(r_{ij}) \quad (6)$$

only those potentials of two-particle interactions, for which  $r_{ij} \ll r_{eff}$  should be taken into account. Here  $r_{ij}$  is a distance between particles number  $i$  and number  $j$ .

An initial position of particles and sizes  $L_x, L_y, L_z$  as yet depend on a type of a problem. If the system with random structure (gas, plasma) is studied, the sizes of the interaction space are chosen based on density at given number of particles  $\rho = N/(L_x L_y L_z)$ , and it is usually  $L_x = L_y = L_z$ . If the initial structure is a crystal lattice, for example, quantities  $L_x, L_y, L_z$  must match each other, depending on the type of symmetry of a lattice. Let us discuss now the problem how thermodynamic equilibrium for the system can be realized. The velocity distribution of the particles ensemble in a study of processes which proceed should be Maxwellian so that the average kinetic energy of particles defines temperature and is uniformly distributed among all coordinates, and the velocity distribution function of particles is Gaussian. Additional requirements to the problem are also possible. For example, for processes in a crystal lattice the average potential energy and the kinetic one should be the same at small temperature. To satisfy these requirements in computer experiments, the calculations of the «equilibrium» performances of the system are preceded by modeling of a nonequilibrium stage (stage of «heating»), when the trajectory of a motion of each particle obeys a Langevin equation ( $m=1$ )

$$v_i = dr_i/dt, \quad dv_i/dt = -\partial U(r, t)/\partial r_i - \gamma v_i + (2D)^{1/2} \zeta_i(t). \quad (7)$$

$$\langle \zeta_i(t) \rangle = 0 \quad \langle \zeta_i(t) \zeta_j(t_0) \rangle = \delta_{ij} \delta(t - t_0).$$

Here  $i$  is equal to  $x, y, z$  in 3D case,  $v_{x,y,z}$  and  $r_{x,y,z}$  are the velocities and coordinates of a particle,  $\gamma$  is a friction coefficient,  $D$  is a diffusion constant,  $\zeta_i(t)$  is a random function modeling a white noise. In order to bring the system to thermodynamic equilibrium at temperature  $T$ , the Einstein relation

$$D = k_B g T \quad (8)$$

should be satisfied. Here  $k_B$  is the Boltzmann constant. After reaching the given temperature, external sources are «switched off» and modeling of an equilibrium stage starts. It is possible to estimate precision of calculations at this stage based on precision of satisfaction of a conservation law of a total energy of a system  $E = T + U$ , where  $T$  is kinetic energy. In further, speaking about energies, we shall mean energy per one particle, if it is not stipulated other. Let us consider now specific applications of molecular dynamics simulations.

### 3. Elementary excitations in fluids

In fluids the typical dynamical phenomena are collective excitations in ensembles of particles. It is common to suppose that phonons and solitons are most important among them. Suitable model for investigation of their properties is the one-dimensional lattice (chain) of oscillators, in particular, of nonlinear Toda oscillators [5]. The Toda chain is chosen as one of basic models because many macroscopic characteristics can be calculated analytically due to unique properties of defined in section 1 Toda potential despite of the nonlinearity of the underlying processes [6]. In addition, such data can be served as a fine test instrument in computer simulations of processes in nonlinear chains.

In chains each particle interacts with two adjacent only, executing oscillations in a potential well formed due to interaction. The equation of motion (7) in combination with the Einstein relation (8) becomes

$$(d^2/dt^2)r_i = [V'(r_{i+1}) - 2V'(r_i) + V'(r_{i-1})] + \gamma^{1/2}[(2kT/m)^{1/2}\zeta_i(t) - \gamma^{1/2}(dr_i/dt)]. \quad (9)$$

At small oscillation amplitudes (small temperature) the potential is parabolic

$$V(r) = ab[(1/2)(r - \sigma)^2]. \quad (10)$$

In this case each particle executes simple harmonic motions, and the collective excitations of a chain are phonons. The frequencies and wave numbers of them obey the dispersion equation

$$\omega = 2\omega_0 \sin(k\sigma/2). \quad (11)$$

In the other limiting case, at high temperature, interaction of particles is mostly repelling, and the collective excitations are soliton-like. As a result the transformation of the thermodynamic properties of a lattice is observed in heating up. Most characteristics (the mean specific volume, the pressure, the specific internal energy, the mean potential energy et al.) can be calculated for an unlimited Toda chain analytically [5]. In particular, the specific heat per molecular at constant volume  $c_V$  as the function of temperature is represented in a Fig. 4. It shows that  $c_V$  varies from the value  $k_B$ , relevant to the ideal phonon gas, up to  $0.5k_B$ , relevant to the ideal soliton gas. There is the transition region near the temperature  $T_{tr}$ , defined by a relation  $c_V(T_{tr}) = 0.75k_B$  ( $c_V(T_{tr})$  is equal to average value of two limiting values), where a set of interesting properties initiated by interaction

of nonlinear collective excitations is observed. Some of them are explored by a molecular dynamics simulations in ring chains with quite small number ( $N=10-20$ ) of particles.

If  $N$  is even,  $N/2-1$  of waves (phonons), running on the right, and the same, running on the left, are excited in the ring at small temperature. Also, the phonon with frequency equal to an upper frequency of a phonon band and «a zero phonon» with a frequency and a wave number close to zero, corresponding to very slow rotation of a ring as a whole, are excited. So the frequency distribution of non-zero phonons modes contains  $N/2$  discrete peaks. When temperature increases and nonlinear effects are developed, the phonons begin to interact with each other, and then to transform to nonlinear (cnoidal) waves, also interacting with each other. The wave length of cnoidal waves on a ring is restricted by its length, and only at increasing number of particles they will differ ever less from solitons in a boundless chain.

The interaction of nonlinear excitations is most strong near to the transition temperature. In particular, it follows from the spectrum  $(FF)_{\omega}$ , defined as the Fourier transform of the time correlation function (ACF) of the force acting on a particle. The ACF is calculated from molecular dynamic simulations in order to identify thermally activated soliton-like excitations in the spectrum (Fig. 5). We can observe a noisy range of the spectrum near to a region containing frequencies of phonons, and also a broadband coloured noise of a  $1/f$  type at low frequencies. The last implies a hierarchy of beatings where periods with more energetic compression pulses are more probable to appear at longer time intervals. Its appearance is associated also with diffusion processes in the system and testifies an opportunity of transformation of white noise of a surrounding medium to coloured noise.

Some details of the process of interaction of nonlinear excitations are clarified by the analysis of a dynamic structure factor (DSF) of a chain [7]. It is defined as follows [8]

$$S(\omega, k) = 1/(2\pi N) \int_{-\infty}^{\infty} e^{i\omega t} \langle \rho(\mathbf{k}, t) \rho(-\mathbf{k}, 0) \rangle dt. \quad (12)$$

Here  $\mathbf{k}$  and  $\omega$  are a wave vector and a frequency,  $\rho$  is density of a particles ensemble, the angular brackets mean the operation of an average on a set of time series. DSF allows to judge time behaviour of spatial (collective) structures of specific scales, generated on a ring. Setting quantity  $k$ , defining a frequency composition  $S(\omega, k)$  and estimating breadth of spectrum lines, it is possible to judge a stability of structures (nonlinear waves) and velocity of their motion on a ring. In particular, in a ring

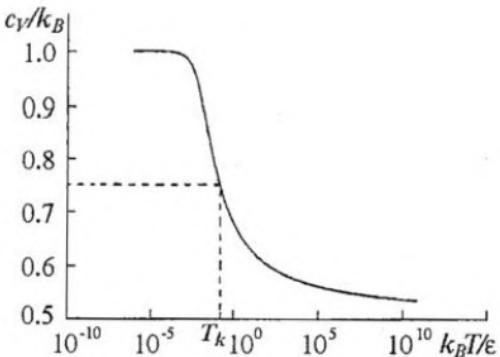


Fig. 4. Specific heat per molecular  $c_V$  at constant length of the Toda chain. In the region around the transition temperature  $T_{tr}$  (defined by  $c_V(T_{tr})=(3/4)k_B$ ) we observe the most interesting physical effects due to the interaction between solitary waves. For chosen parameters  $v=\sigma$  and  $b=100/\sigma$ , we obtain  $T_{tr} \approx 0.16 \text{ eV}$

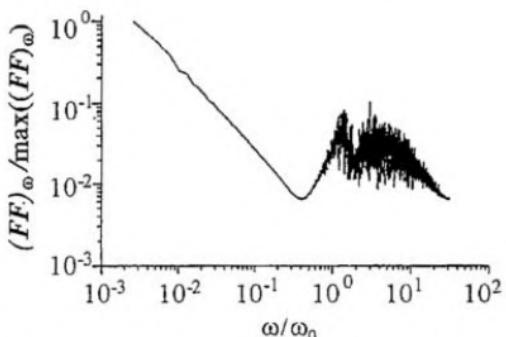


Fig. 5. Spectra  $(FF)_{\omega}$  of single-particle forces  $F$  in uniform rings of  $N=10$  (solid) and  $N=20$  (dashed) Toda oscillators with oscillation frequency  $\omega_0$  and stiffness  $b=100/\sigma$  in thermal equilibrium with a bath in the transition-temperature region  $(k_B T=0.26 \text{ eV})$  corresponds to  $c_V(T_{tr})=0.73k_B$ . The friction parameter is  $\gamma=10^{-3}\omega_0$ . The spectra were obtained by Fourier transformation of the auto-correlation function. We observe broad peaks around the second-phonon frequencies as well as  $1/f$  tails at the low end of the spectra

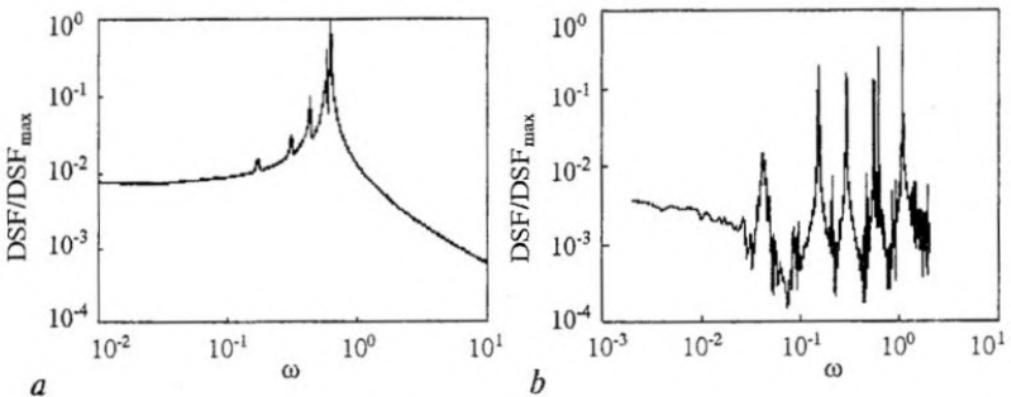


Fig. 6. The dynamic structure factor  $S(\omega, k) / \max S(\omega, k)$  versus frequency  $\omega$  for a Hamiltonian ring chain ( $N=10$ ,  $\gamma=0$ ) for the wave number  $k=k_{01}=2\pi/N$ : a) at low temperature, the particles interactions correspond to the cubic weak nonlinear (Fermi-Pasta-Ulam type) potential; b) in the transition-temperature region at  $T=T_{tr}$ .

with  $N=10$  it is possible to observe transformation of dynamics when reaching a stationary temperature and «switching-off» of an external environment by calculating a dynamic structure factor at different temperatures using MMS [9, 10]. It has been seen (Fig. 6, a), that at small temperature, when the nonlinearity is weak,  $S(\omega)$  at a wave number corresponding to the resonant structure of the largest scale - to the first phonon - contains combination frequency components in addition to the first phonon frequency  $\omega_1$ . They arise due to interaction of five phonons with frequencies  $\omega_i$ ,  $i=1,5$  on quadratic nonlinearity and have frequencies  $\omega_{ij}=\omega_{j+1}-\omega_j$ ,  $j=1,4$ . With increasing temperature the first phonon (and then others) transforms to a cnoidal wave with velocity more than velocity of a sound. In particular, at transition temperature it is approximately twice higher (Fig. 6, b). The nonlinear wave in this temperature range strongly interacts with other waves, but remains rather stable, as far as it is possible to judge from a spectrum  $S(\omega)$ , consisting of a small number of narrow discrete peaks. This tendency is specific under further temperature increase also, when the spectrum displaces to the right as a whole because of a velocity rise of nonlinear waves, and the region of combination waves is rare as the waves begin to resemble solitons more and more and their interactions weaken.

If the ring is not switched-off from external environment after reaching equilibrium temperature, the dynamic structure factor also indicates excitation of  $1/f$  of noise at low frequencies for small values of a wave number  $k$  (Fig. 7). However it is necessary to note, that the details of processes corresponding to  $1/f$  noise in the model described are still not clear and a more complete understanding of the matter calls for further study [5].

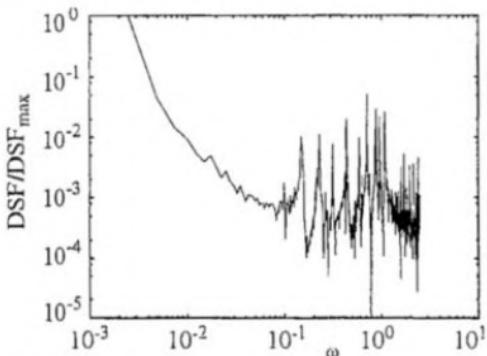


Fig. 7. The dynamic structure factor  $S(\omega, k) / \max S(\omega, k)$  versus frequency  $\omega$  for a ring chain in thermal equilibrium ( $N=10$ ,  $\gamma=10^{-3}\omega_0$ ) for the small wave number  $k=0.1$  in the transition-temperature region at  $T=T_{tr}$ .

#### 4. Dynamic structure factor of plasma

The problems of structure evolution arise, as a rule, in studies of phase transitions in gas-fluid, fluid-solid, gas-plasma and have many aspects. The distribution function,

certainly, is not the unique characteristic of such states. In particular, the use of the dynamic structure factor mentioned above (8) is effective in researches of spatial structures and their time behaviour both in plasma and fluid. An important advantage of DSF is that it can be defined experimentally and it is associated with several regular characteristics which on many occasions can be determined only as by means DSF. For example, having known DSF, one may find the plasma electric inductivity and dispersion, including the case of such density when it is very difficult to calculate these characteristics by other methods. Now let us discuss features of simulation of particles behaviour in plasma before we analyze results of DSF calculating.

Usually what is implied when one speaks about plasma, is the dense plasma. It is more similar to fluid than to gas by a number of properties. Really, Coulomb potential is more «long-range», than, for example, Lennard-Johnes potential, therefore in dense plasma each particle simultaneously interacts with several others particles, i.e. the interaction is collective. The definitions «isotropic», «homogeneous», «ideal» and so on are used for namely this kind of plasma. Its behaviour is oscillatory or wave, as a rule, and is studied within the framework of hydrodynamic or electrodynamic models. On the other hand, the density in dilute plasma is small and particles interact pairwise, as in gas. Therefore the dynamics can be investigated using models developed for studies of gas properties. However collective phenomena are exhibited more and more in dynamics of such plasma under increasing density (it can not be called dilute already). The application of MDS is most effective for study specifically these phenomena, evolution of their properties, changes in dynamics taking place when density grows. Moreover, there are situations, when MDS is the unique effective method of the analysis of behaviour of a plasma system.

Two stages can be identified in studies using MDS in the general case: the stage of determination of a potential share for each particular case of particles interaction and the stage of determination of the dynamics of the particles ensemble given by this interaction. First of them is not a subject of the present paper, we will not discuss that here. Note only, that a model of interaction of particles in plasma is developed as a rule based on concepts of a quantum mechanics. At the second stage the computer simulation of the particles interaction is carried out and the results obtained are used for determination of the different performances of a system. Usually a classical Coulomb potential is used for presentation of charged particles interaction in the theory. The point is that very high accelerations are developed when opposite-charged particles are coming together in the numerical model with the classical potential and calculations become illconditioned. As a matter of fact, the quantum phenomena come into force when particles close to each other at a distance exceeding that comparable an atomic scale, and they lead to a little bit other behaviour in comparison with «Coulomb» one. But the quantum models are very complicated and it is not efficiently to apply them to simulation of phenomena, in which «quantum» interactions take only a small part of a total duration of the process. That is why quasi-classical models are developed, in which the classical motion obeying the Coulomb potential force takes place, and only when particles are getting to close the specific shapes of a potential defined on the basis of quantum mechanics laws are applied [8]. We do not discuss details of those models, but the results obtained by a MDS in the frame of quasi-classical models, are very interesting.

In a Fig. 8 the data of calculation [8] of a certain coefficient  $R(k, \omega)$ , proportional  $S(k, \omega)$ , for plasma within the framework of a quasi-classical model developed in that work are represented. (The difference between  $R$  and  $S$  is not basic for our consideration, see the details in [8]). The cases of both moderate coupling ( $\Gamma=1$ ), when the autocorrelation function (ACF) falls monotonically to zero, and strong coupling ( $\Gamma=100$ ), when ACF shows oscillations with a frequency close to the plasma frequency  $\omega_p$ , have been explored. Here  $\Gamma$  is the coupling strength parameter. The results are given as

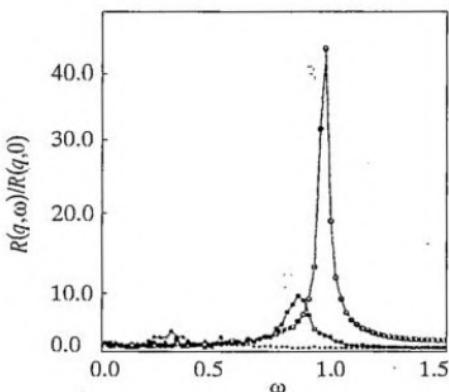


Fig. 8. The loss function  $R(q, \omega)$  versus frequency  $\omega/\omega_p$  for different wavevectors  $q$  at  $\Gamma=100$

magnitude as at small  $k$ . The peak is close to  $\omega_p$ , but under change in a wave number it is shifted distinctly. It allows to determine the dispersion that may be both positive and negative. The peak is identified even in the region of the strong Landau attenuation, where it is impossible in fact to determine dispersion by ordinary technique.

## 5. Distribution function of clusters and phase transitions

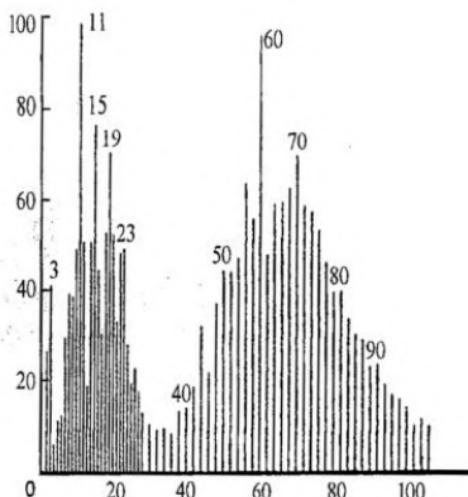
The big number of problems of molecular dynamics is associated with investigations of properties of clusters. In molecular dynamics the term cluster is used for designation of an aggregation of particles located close enough to each other and bound by forces of an intermolecular interaction, in particular, of the Lennard-Jones or Morse type. For example, clusters are formed in rings of particles interacting via Morse forces if density of particles is small [11]. The clusters are stable enough, i.e. their lifetime is long so that events in which clusters take part could be detected by spectroscopic methods, for example [4]. What the stability of a cluster depends on? Let's consider, for example, conditions at which two particles (the neutral molecules) will form a cluster. Apparently, this couple will be stable if its summary kinetic energy is less than the potential energy - they are in a potential well and can not overcome the potential barrier in the absence of an external excitation. It is likely that the cluster will be stable if the total energy of the system is negative:  $E=T+U<0$ . Therefore, the clusters are produced in processes when kinetic energy of particles decreases. For example, if to open the cock of a vessel containing hot gaseous carbon, clusters will be formed in jet discharged owing to abrupt cooling of the gas. The proportion of clusters containing given number  $n$  of particles (monomers, dimers etc.), is characterized by a distribution function  $f(n)$  (cluster size distributions, CSD [12]). Experimentally found  $f(n)$  for carbon, for example, under conditions mentioned above is given in Fig. 9 [13]. Note, the function characterizes a stationary, steady state. But there is a specific interest in evolution of clusters in processes of forming, dislocation, deformation, i.e. in the function  $f(n,t)$ . Let us now consider the procedure for theoretical calculation of the function, based on the geometric-energy approach.

For the configuration of the ensemble of particles obtained during MD-simulation at some instant «geometrical» clusters are determined first on the basis of the agreement that the particle is considered belonging to a certain cluster, if it is at a distance from any particle not exceeding the distance  $R \approx 1.2\sigma$ . The latter is taken as a characteristic size of a particle. Then, after each of particles has been identified as belonging to any cluster and

dependencies  $R$  as a function of dimensionless frequency  $\omega$  for different wavevectors  $q=ka$ , where  $a$  is a characteristic space scale of the system. As we see the peak at  $\omega \approx \omega_p$  (plasmon) is observed only for smallest  $q$  value (defined by the size of simulation space). The effect is not unexpected, as just the particles clusters of size comparable with big enough scale, corresponding to small values  $q$ , have an sufficient effect on motion of a individual particle at small coupling. Therefore the plasmon does not manifest itself really at small coupling in this case. However with increasing  $\Gamma$  (density) the plasmon peak rises although does not reach the same

Fig. 9. Mass-spectrum of the carbon clusters [13], i.e. relative intensity as a function of a number of carbon atoms in the cluster

the number of clusters has been counted, the total energy of each cluster is calculated. If it is subzero, the cluster is regarded to be stable (though, of course, it can be abandoned by some particles later on). If it is not, the fastest of particles is «extracted» numerically from the cluster until the energy of the stayed aggregation does not become negative. If the number of the particles discarded is small (it is less, say, 10) it may be considered as a stable one, i.e. it is a safe assumption that it does not break down. But if the number of them is big, we deal with a non-stationary phase - the phase of shaping or active deformation of clusters.



As an example of calculation of CSD in MD-simulation we will consider a problem about «spreading» of a «drop» of a fluid (big cluster (Fig. 10)) owing to such change of surroundings, that the drop energy became close to zero at some instant. Because of that the particles with high kinetic energy turned out to be a part of the cluster, and then they start leaving it. There is every indication that the result will depend critically on friction in the system. In Fig. 11 the plots  $f(n,t)$  for three cases of different values of a friction coefficient are represented. It is shown that at small friction the cluster in fact entirely collapses (Fig. 11, a) reaching fast the steady-state of big number of monomers, some dimers and insignificant number of clusters of big number of particles (Fig. 10). If the friction is appreciable (Fig. 11, b), the initial «big» cluster stays stable due to fast cooling (only some monomers and one-two clusters of a small number of particles break off). A steady state is established fast enough in this case also. And it is not a success to reach a steady state during carrying out of the computer experiment in the intermediate case (Fig. 11, c) - fragments of the cluster collapsed have not ceased to deform.

The phenomenon of transitions of matter from some phase to another one is associated also with the problems of clusters. A number of theoretical and experimental studies has been devoted to this problem having a great deal of aspects and items. Not

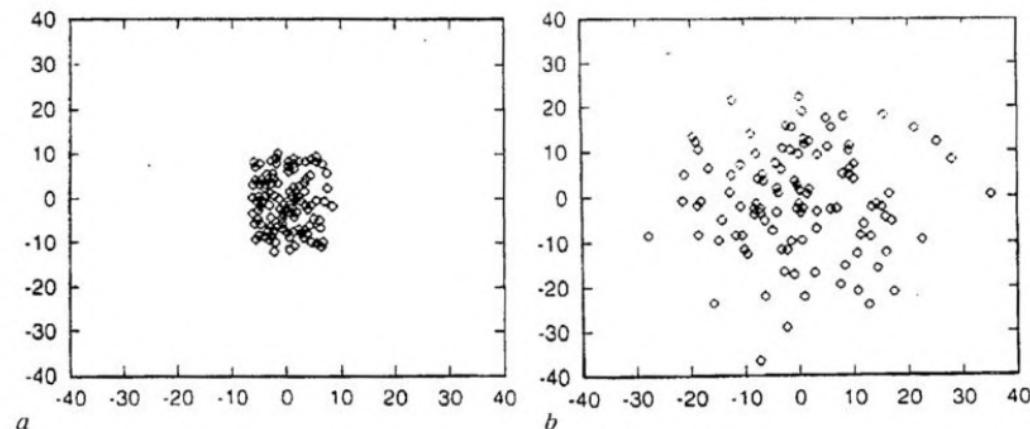


Fig. 10. Locations of interacting particles: a) at an initial moment («drop» of a fluid) and b) at stationary state at small friction

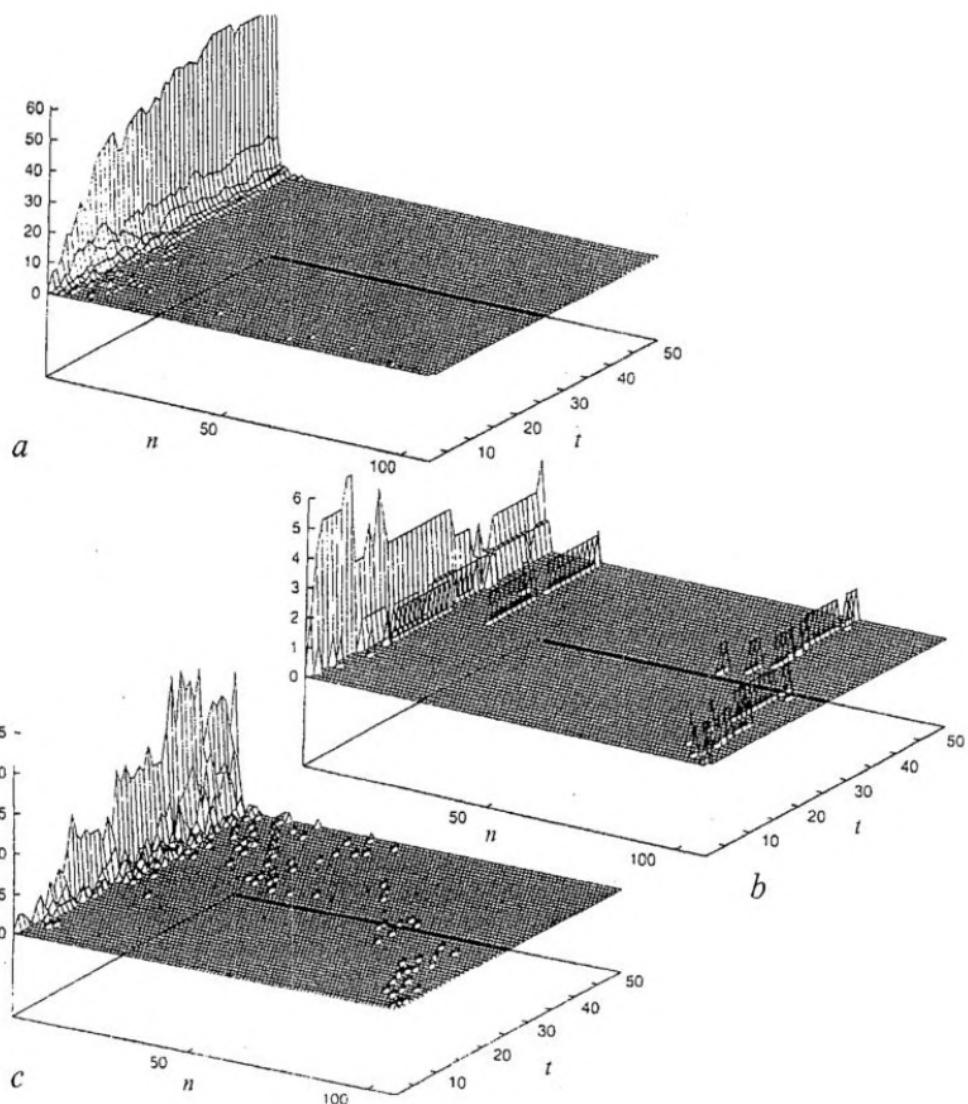


Fig. 11. Distribution function of clusters  $f(n, t)$  for three cases of different values of a friction coefficient:  
 a) small friction, b) appreciable friction, c) intermediate case

seeking to perform a complete overview and analysis of them, we will restrict ourselves to the discussion of only those of them, which are effectively explored by molecular dynamics simulation. In particular, this is a phenomenon that may be called as a problem about «fusion» of molecular clusters under heating. The difficulties of the analysis of phase transitions in real volumes of matter are accounted mainly by enormous number of particles taking part in the process and practical impossibility to analyze all created patterns of a uninterruptedly varying potential surface. However phase transitions of small enough (mesoscopic) objects - clusters - can be studied in detail. This problem is interesting by itself, as it appears, the phase transitions in clusters of a small particles number do not run as in extended volumes of matter. And on the other hand, increasing a number of particles, it is possible to trace evolution of properties in the transition from a «cluster» state of matter to a «volume» state. Note, mesoscopic systems take up an intermediate position between the macroscopic and microscopic of them. To investigate phase transitions in clusters the analysis of the shape of a potential surface established by

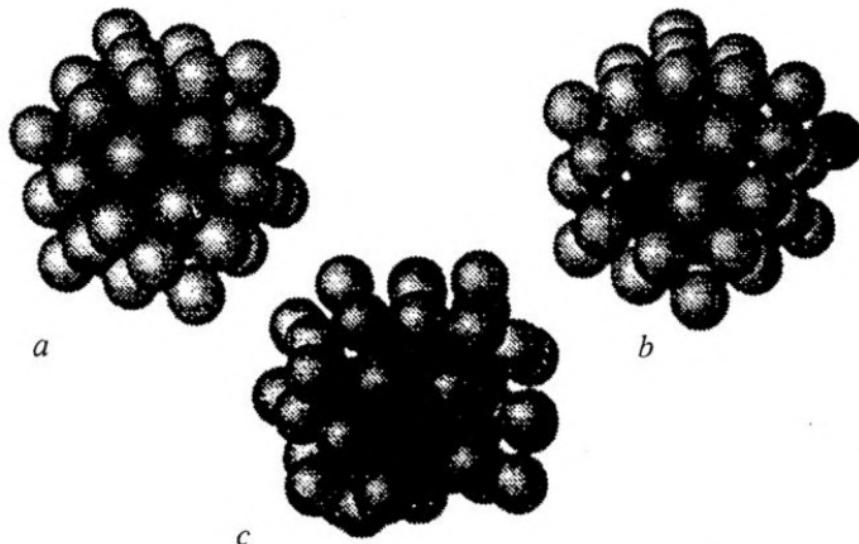


Fig. 12. Representative (quenched) structures of the coexisting phases in  $Ar_{55}$ : a) solid icosahedron, b) surface melted with one floater and c) homogeneously melted. The core atoms and the floaters are represented by dark spheres, the outer shell atoms by light one

cluster particles can be used as the very perspective approach [4]. The main item is the definition of location of local minimums of the potential and a depth of potential wells being in process of computer modeling by MD-method. The existence of a few phase states of a cluster may be regarded as the most interesting effect discovered recently. Three distinct phase states - microcrystalline (solid), homogeneously melted and solid kern with a melted shell - have been found by computer modeling [4] of isothermal dynamics of a three-dimensional cluster. At specific temperatures they can occur at the same time with a sense of such state is a little another, than in macroscopic systems. It has been revealed the certain, precisely distinguishable level of the potential energy corresponds to each phase. The simultaneous existence of several phases of a cluster means that it periodically goes from one state to another, and the residence time of each phase depends on a well depth and a width of transition between adjacent local minimums. In Fig. 12 the different states  $Ar_{55}$  (a - solid icosahedron (micro-crystal), b - with a melted surface consisting one «floater», c - with a homogeneous melted surface) and in Fig. 13 a time dependence of energy of a cluster are shown at different temperatures. There is no doubt that in a temperature range between  $T=30K$ , corresponding to a microcrystal, and  $T=40K$ , corresponding to melted matter, the states are established when there is periodic «switching» from one phase to another. Having determined levels of energy of each phase and their residences, one can calculate by means of statistical processing the probability distribution functions for different quantities, a diffusion constant for each phase, the entropy etc. Purposeful searching of states with given properties and methods of control in them may be carried out with help of characteristics mentioned. The field of phase transitions of mesoscopic systems are under active study now and discoveries of many interesting properties of such systems may be anticipated in future.

## 6. Transition processes and reactions

The model presented above is not sufficient for explanation of processes in several important and interesting cases. Let us consider, in particular, the problem about reaction

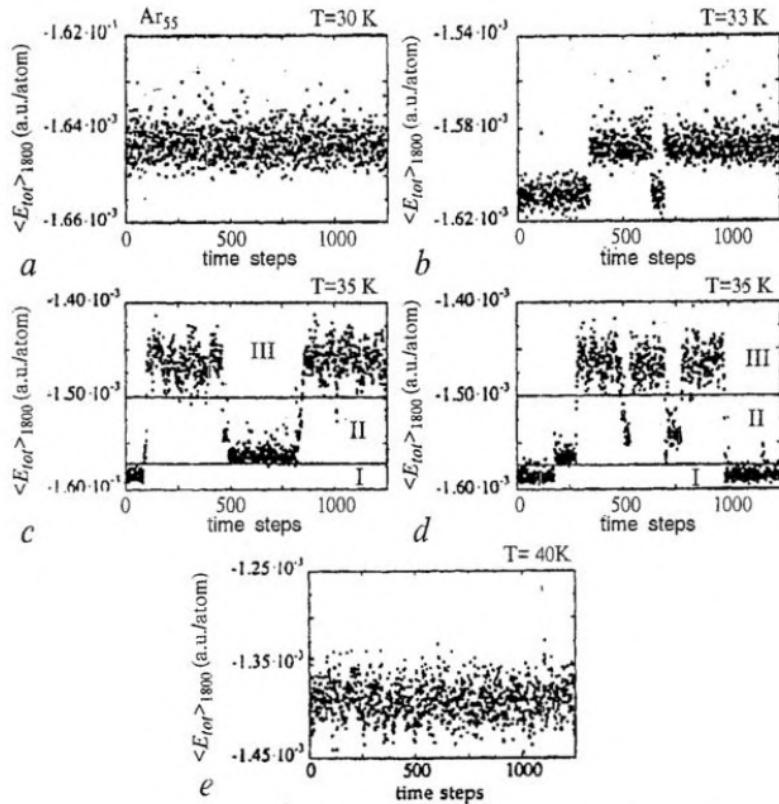


Fig. 13. The short-time averaged internal energy  $\langle E_{tot} \rangle_{\tau}$  of  $Ar_{55}$  for the temperatures  $T=30K$  (a),  $33K$  (b),  $35K$  [(c) and (d)], and  $40K$  (e). Each point represents an average over  $\tau=18000$  time steps of  $3 \cdot 10^{-15}$  s each. The solid lines in (d) correspond to the energy limits used in the simulations to distinguish between energy regions of the different phases, I denoting the solid phase, II the surface-melted phase, and III the homogeneously melted phase (e)

rates at different temperatures. As it is known, the rate of many chemical reactions is defined by the Arrhenius law

$$K = K_0 \exp(-\Delta U/k_B T), \quad (13)$$

where  $K_0$  is a reaction rate at  $T \rightarrow \infty$ ,  $\Delta U$  is the activation energy equal to a depth of a potential barrier, which should be overcome to split a bond,  $k_B$  is the Boltzmann constant. Arrhenius behaviour was marked for the first time more than hundred years ago and has been under an experimental test in different kinds of reactions. In 1940 Kramers developed the theoretical model becoming in the further the prototype of a statistical reaction theory. The Kramers-theory of reaction rates is based on a Fokker-Planck equation for the reactive molecule or on the corresponding Langevin equation with white noise sources (see [14, 15]). One of implications of this theory is the Arrhenius law. However recently it was clarified, that the Arrhenius-law is not always fulfilled precisely. Besides, it was revealed, that some other experimental data do not always correspond to behaviours following from the Kramers-theory [14, 15]. The search for the reason has lead to a presumption that one of basic assumptions of the Kramers-theory about lack of correlation of elementary exposure acts to other particles is disturbed in mentioned above cases. Indeed, it was shown in [16, 17] that if a noise source in the Langevin equation is assumed to be colored, it results in consequences leading to Arrhenius behaviour violation, in particular. But what is the reason for occurrence of preferred scales in the source? It has been hypothesized that it takes place due to specific exhibition of nonlinear

(and dispersive, to some degree) properties of systems of particles distributed in space [14]. We will leave the Arrhenius law for now and shall consider processes in solutions in more details.

As it is known, the solution is a mixture of particles of two sorts at least - a solvent and an impurity. The solvent concentration is much higher, for example, one molecule of the impurity is per 30 molecules of the solvent. It was found that the Arrhenius law is disturbed in such system if molecules of the solvent are «hard», and the others are «soft» [14]. It is implied that the interaction of «hard» molecules between themselves is much more restoring, than that of «hard» and «soft» molecules, and proceeds much faster. It has been supposed [14], that so-called local energy spots are formed in such system. They are located on soft particles and hard particles acquire the high potential energy. To verify this hypothesis the simple one-dimensional model of a solution in the form of a Toda chain has been considered [18]. As mentioned above, soliton-like local excitations of a density can exist in a homogeneous Toda chain (when the parameters  $a, b, \sigma$  are identical for all sites of a chain, see (2)). In the general case they arise, as known, under a certain relation of nonlinear and dispersion properties of a system. In a nonlinear chain soliton-like structures are excited for specific values of nonlinear potential parameters specifying both nonlinear and dispersion properties. If in a chain the small part of molecules are «soft», the soliton-like excitations formed by hard molecules can «stick» at the soft sites during some time, transferring coherently appreciable amount of energy to them. Indeed, the times of the interaction of the soliton with the «hard» and «soft» molecules are as  $\tau/\tau_0 = b/b_0$ , where the index 0 refers «soft» molecules. Moreover it is supposed, that the dynamics of «soft» molecules also obeys the potential of the same form (6), but with other parameter values. In particular,  $b_0 \ll b$ , so during relaxation the «soft» molecule can accumulate energy even more than that of one soliton. As a result the probability of overcoming of a potential barrier appreciably increases, and the reaction rate rises. It leads to a consequence that the fraction of high-energy soft molecules of the distribution as a function of the potential energy of the soft molecules increases, shifted to higher values and acquires longer tails. This conclusion is confirmed by the analytical calculations in [14]. But for systems with other kinds of a potential, furthermore for two-dimensional and three-dimensional systems, it is impossible to obtain the analytical results. That is why in [14] the molecular dynamics method has been used for calculation of the distribution functions.

The interaction of 32 particles, one of them was soft, was considered in 1D-, 2D- and 3D-models with the modified Lennard-Jones potential (4) which at  $A=28, n=8$  well approximates the real Lennard-Jones potential, but is much more suitable for numerical calculations. It is shown in a Fig. 14, *a* that the maximum of the distribution function  $f(U)$  for a 2D-case for soft molecules is really shifted to the range of high energy events relatively the maximum of the function for hard molecules and the fraction of high-energy molecules («a high-energy tail») is by an order of magnitude greater (fig. 14, *b*). Besides the average potential energy of soft molecules can be several times higher exceeding (fig. 15) average kinetic energy. (Note, at small temperatures, when interaction of molecules is in fact linear, these quantities are equal.) Results are the same for 1D- and 3D-models, and they do not change when the number particles is increasing. Taking into account this effect of formation of the energy spots, we shall return now to the Arrhenius law and consider specific systems, in which it is violated.

We shall consider the model of the dissociation of diatomic molecules [15]. The atoms in such molecule are bound by potential force arising from the Kramers bistable potential

$$V^K(x, y, z) = \varepsilon_x x(x^4 - 2x^2) + \varepsilon_y y^2 + \varepsilon_z z^2. \quad (14)$$

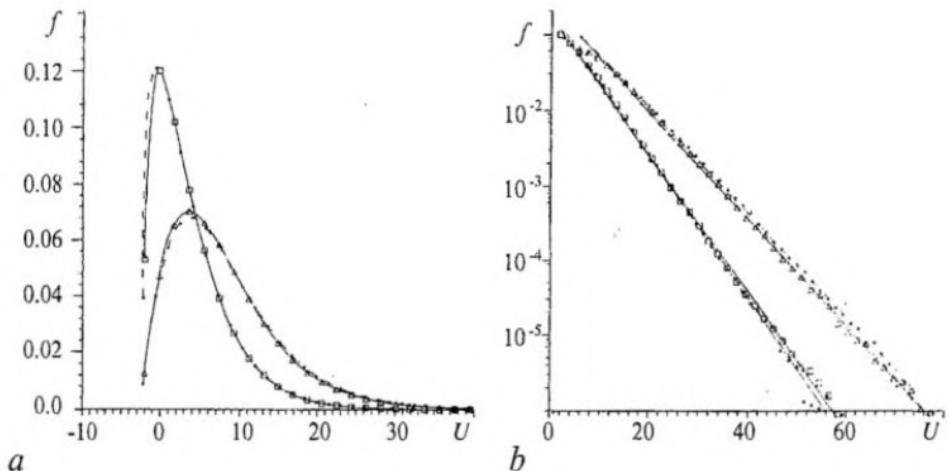


Fig. 14. The distribution function (a) and its tails (b) for  $T=7$  and finite size potentials in the two-dimensional system ( $N=32$ : triangles = soft, squares = hard molecules;  $N=200$ : stars = soft, fat stars = hard molecules)

Two minima of the potential correspond to two possible configurations of such soft molecule (Fig. 16). The potential barrier must be overcome to reach dissociation. The energy for overcoming is accumulated by a molecule owing to interaction with surrounding hard molecules, and the interaction force is given by the Lennard-Jones potential. The interaction potential of hard molecules with hard molecules is the same, but with parameters providing much more shorter time of relaxation. The study has been carried out within the scope of 2D-model with 100 particles. Initial positions of particles correspond to minima of the potential function, and then the system reaches the given temperature during a stage of «heating».

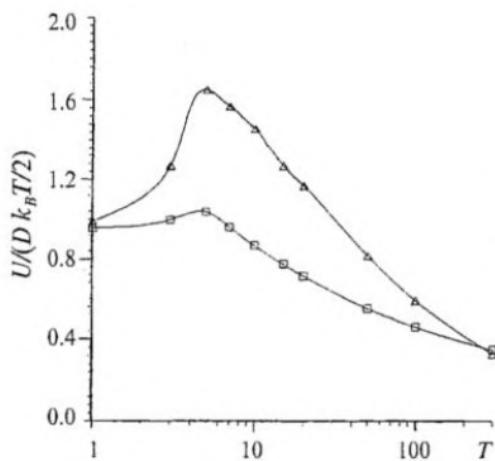


Fig. 15. The temperature dependence of the mean potential energy in  $D k_B T/2$  units for the two-dimensional case ( $N=32$ : triangles = soft, squares = hard molecules)

As it should according to the Arrhenius law, but it is parabolic instead. Similar results have been obtained in the simulation of a reaction with participation of the diatomic molecule, in which bond of atoms occurs by the Morse potential reads in the form

$$V_\mu(r) = \epsilon [(\exp(-6(r-\sigma_L 2^{1/6})) - 1)^2 - 1]. \quad (15)$$

$\ln \tau$  as a function of  $\Delta U/T$  at fixed  $\Delta U=50$  proves to be not linear again, and at a

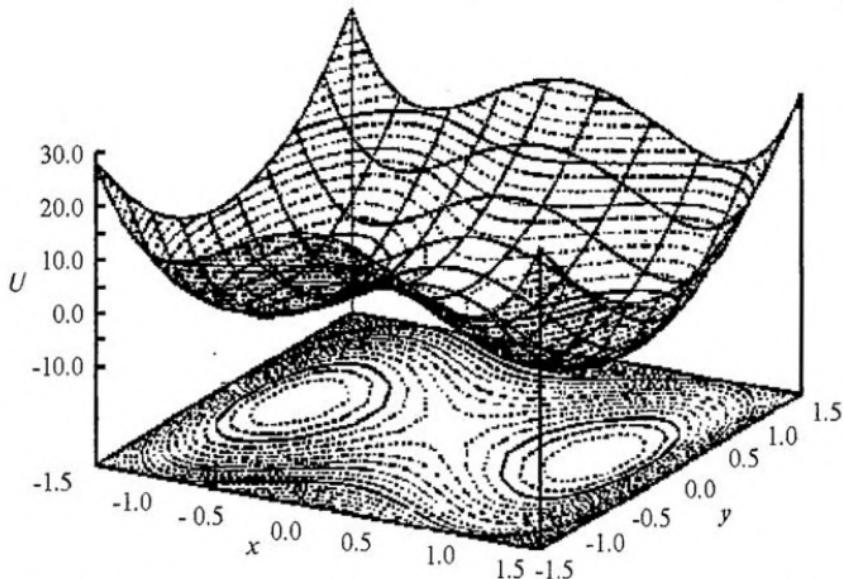


Fig. 16. The shape of a bistable 2D Kramers potential. The minima correspond to the stable states of the active molecule

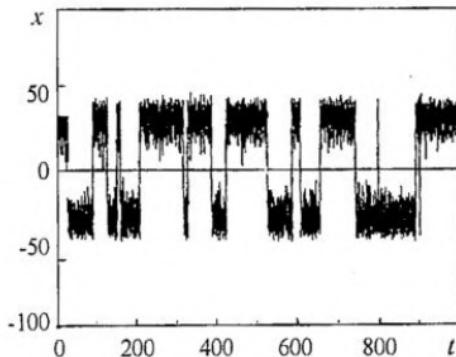


Fig. 17. Transitions between the 2 wells of the bistable Kramers potential caused by molecular collisions

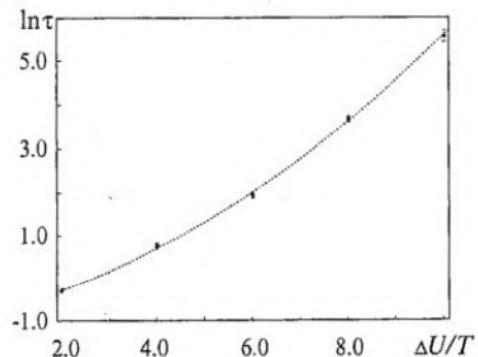
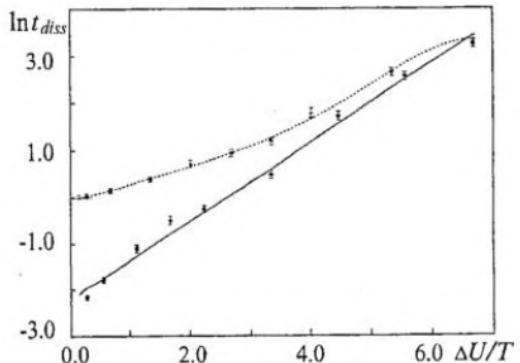


Fig. 18. The logarithm of the average time between transitions from one of the Kramers wells to the other one, as a function of the Arrhenius exponent ( $\Delta U/T$ )

fixed value  $T=7.5$  it is almost linear, but with a slope 0.5 instead of 1, as it should be in agreement with the Arrhenius behaviour (Fig. 19). Thus, the effective temperature of the system is not in agreement with the actual, classically defined temperature of a solution, because of the noise excited in collisions of molecules, is not white and effective temperature depends on its spectrum. Currently it is impossible to

Fig. 19. The logarithm of the dissociation time for a Morse molecule as a function of the Arrhenius exponent. The full line corresponds to a fixed value of the potential barrier  $\Delta U=50$  and the dashed line to fixed temperature  $T=7.5$  and variable potential barriers. All energies and temperatures are given in the Argon-units used in [15] (i.e.  $T=1$  corresponds to 119K)



finally conclude that phenomena considered are explained entirely by existence of local energy spots [15]. Nevertheless, this explanation is believed to be the most probable, and further researches in this lead are still in progress.

## 7. Nonequilibrium phenomena

There is an ample class of problems about various flows and instabilities in fluids. They are solved usually within the framework of hydrodynamic models. The results of many of them are well known (see, for example, [19]). In particular, it is known, that at low gradients of temperature and pressure the flow of a fluid is laminar, i.e., for example, the flow velocity is the same at all points of a jet. However this statement is valid only for spatial scales much more than characteristic sizes of molecules and a free length. The trajectories of a motion of molecules corresponding microscales remain chaotic. What is the way to structure unordered motion of individual molecules to collective motion of big ensembles? The molecular dynamics simulation allowing to calculate trajectories of molecules and then to carry out averaging complying with various scales plays an invaluable role in studies answering this question.

Let's consider for an example a motion of molecule of a fluid under conditions, at which the instability of Rayleigh-Benard is harnessed [20]. The results of simulation of motion of 5000 particles in a fluid layer in a rectangular vessel to be heated up from below are presented there. It is known [19] from the analysis of this system taking a hydrodynamic approach, that the type of collective motion of particles depends on a value of a non-equilibrium parameter - the Rayleigh number

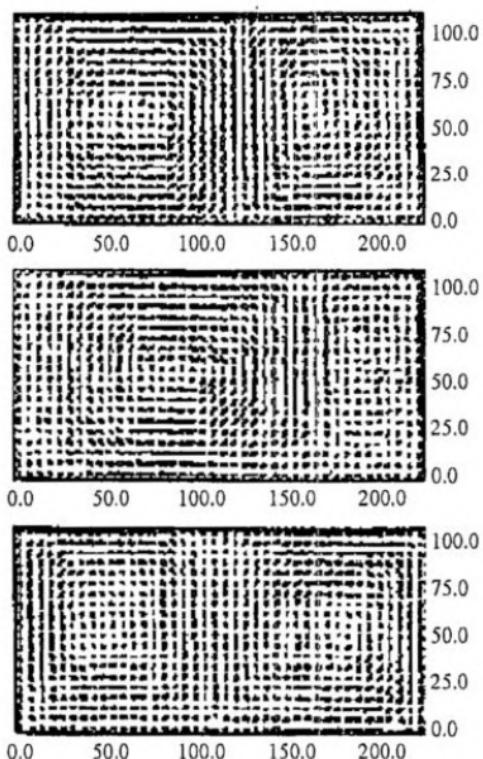


Fig. 20. Velocity field of molecular dynamics simulation with 5000 particles and aspect ratio = 2; (a) and (b) show transient states after 8000 and 10500 steps respectively; (c) displays the final state after 20000 steps (averaged over the last 10000 steps)

Here  $\alpha$  is a thermal expansion coefficient,  $\nu$  is kinematic viscosity,  $D_\tau$  is a coefficient of thermal diffusion,  $l_x$  is a width of a vessel,  $T_U$ ,  $T_L$  are temperatures on a top and a bottom, accordingly. As known, at small values of the Rayleigh number collective motion is laminar - this result confirms in [16] also. To obtain this a space averaging over small ensembles containing about 6 particles was carried out. The simulation field was divided into 800 «statistical» cells and an averaging was performed over all particles residing in of each cell at instant, and then a time averaging was carried out. The result was interpreted as a velocity of fluid at the centre of a cell. Increasing of the temperature gradient (the Rayleigh number) causes loss of stability of a homogeneous state and vortexes arise. Their «portrait» is represented in a Fig. 20. Vectors obtained by an average of velocities of all particles belonging to a given cell are shown in it by arrows. The vortexes are stationary inconvertible structures, and this deduction

is well in accord with known «hydrodynamic» one. However authors noted, that an average over an ensemble of only 6 particles is crude enough. For example, plots of the velocity distributions obtained by MDS and in hydrodynamic approximation, differ in details, being the same qualitatively (Fig. 21). In this connection in [20] the chance to research effects of birth of small-scale vortexes and, in the long run, the turbulence, by MDS is estimated skeptically enough. The point is that a rising number of «cells» and the particles number in a «cell» for obtaining of data up to acceptable accuracy is required with growth of number of vortexes under the Rayleigh number increasing (i.e. under decreasing of characteristic scales). However, it seems likely that this problem will be overcome with computer efficiency increasing. At all events, it is early to put an end to further investigations.

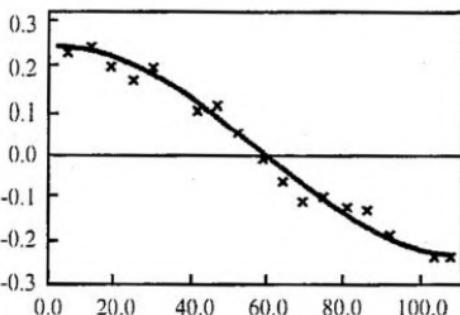


Fig. 21. Horizontal component of the velocity as a function of  $z$ , for a vertical slice located at  $x=L/4$ . The curve refers to the hydrodynamical calculation where as the crosses represent the molecular dynamics data averaged over the last 10000 steps. Both axes are scaled in system units

## 8. Conclusion

The molecular dynamics simulations (MDS) based on numerical solving of equations of motion for a small ensemble of particles, is effective for studies of properties of both a bulk state of matter (macroscopic systems) and states formed by clusters (mesoscopic systems). In both cases a main field of application of a method is in the systems which are nonequilibrium or are in a state of phase transitions «gas - fluid», «fluid - solid», «gas - plasma». For many problems MDS is the only research instrument. The models are used both with a classical nonlinear potential (Lennard-Johnes, Morse, Toda etc.), and semiclassical, in which individual events of particles interaction occur potentials determinated on the basis of quantum mechanical calculations. It is implemented effectively not only for three-dimensional models, but also for two-dimensional and in particular one-dimensional. It is possible in the last case to compare computer simulation data with analytic results. Among the problems related to properties of bulk states, problems concerning origin and evolution of structure transformation in ensembles of particles used in studies of properties of chemical reactions, dilute plasma, near-boundary fluids, processes of ionization etc., are assumed as most interesting. The development of technique of determination of quantitative characteristics of structure transformations (distribution functions, dynamical structure factor, probability distributions and others) is very important. In researches of mesoscopic systems the data can be highlighted on availability of some phase states of clusters with a small number of particles and opportunity of simultaneous existence of them. It seems likely that studies of connection of properties of potential surfaces, created by cluster particles, with nonlinear dynamics of particles and collective cluster performances are highly promising. The examinations of transformation of the performances of mesoscopic systems under increasing of a particles number are interesting because they lay a bridge between mesoscopic and macroscopic systems.

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## НЕЛИНЕЙНЫЕ ПРОБЛЕМЫ МОЛЕКУЛЯРНОЙ ФИЗИКИ

A.P. Четвериков, B. Эбелинг

Представлен обзор исследований некоторых проблем молекулярной физики, проведенных методом молекулярной динамики. Среди них проблемы элементарных возбуждений в жидкостях, динамика химических реакций в растворах, динамические свойства разреженной плазмы, динамические явления при фазовых переходах в мезоскопических системах, структурные свойства цепочек нелинейных осцилляторов. Обсуждаются также некоторые новые результаты исследований распределений кластеров и метод идентификации кластеров.



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