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# Microscopics of fluctuations of the energy of atoms in solids

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Abstract. Internal atomic-molecular vibrational dynamics of solids gives rise to short-lived localised states of atoms with a much higher energy or amplitude of vibrations, i.e. it gives rise to fluctuations. These fluctuations play the dominant role in a variety of physical processes, which include diffusion, evaporation, plastic deformation, highly elastic deformation of polymers, fracture, chemical reactions, electronic transitions, biological functions, and many others. The essentials of the fluctuation origin of these processes are given in the classical papers of Ya I Frenkel'. The microscopics of fluctuations of the energy of atoms has begun to develop successfully. The present paper provides a brief historical introduction, which is followed by the first results (obtained by computer simulation) that can account for the detailed characteristics of fluctuations: the lifetime of a fluctuation state of atoms, the size of a fluctuation region, and migration of fluctuations. Special attention is given to the mechanism of formation of energy fluctuations. Investigations of fluctuation dynamics in condensed media, regarded as a new and to some extent independent part of the physics of liquids and solids, have been given a decisive start by the fundamental work of Yakov Il'ich Frenkel'. He began his investigations back in the twenties and continued them with outstanding success throughout his life. The study reported below represents the attempt by the present authors to continue the development of the fruitful ideas of Yakov Il'ich.

### 1. Introduction

The very important role of internal dynamics of bodies, i.e. the motion of particles composing these bodies (atoms, molecules, or quasiparticles such as phonons), in determination of the physical properties of these bodies and of the processes occurring in them is self-evident.

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Received 22 December 1993 Uspekhi Fizicheskikh Nauk **164** (4) 357–367 (1994) Translated by A Tybulewicz The average values of the dynamical characteristics (energy, mean free path, frequency, etc.) account satisfactorily for the following properties of both gases and condensed media: the specific heat, thermal conductivity, velocity of sound, thermal expansion, temperature dependence of the elasticity, etc.

On the other hand, just the average values of, for example, the energy are insufficient to account for a very large number of processes. For example, the thermoluminescence of and ionisation in gases, or the evaporation, diffusion, plastic deformation, viscous flow, and many electronic processes in solids require for the occurrence of elementary events an energy at least an order of magnitude greater than the average.

If we ignore tunnelling (sub-barrier transitions †, it becomes clear that elementary events of atomicmolecular rearrangements occur only when a sufficiently high (much higher than average) energy is concentrated locally, in the region of an elementary event. Briefly, therefore, the realisation of elementary events in an enormous number of processes requires energy fluctuations, specifically it requires sufficiently large positive fluctuations.

The occurrences of such energy fluctuations in the internal dynamics of bodies follows naturally from a nonequilibrium energy distribution between components of a body (subsystems). The fundamental work of J Willard Gibbs on thermo-dynamics and the atomistic theory of J Clerk Maxwell and L E Boltzmann have established that a state of a body in a global equilibrium at a temperature T is characterised by a certain distribution function of the particle energy E in which a dominant position is occupied by the Boltzmann factor<sup>‡</sup>.

$$\exp\left(-\frac{E}{kT}\right).\tag{1}$$

<sup>&</sup>lt;sup>†</sup> The problem of the tunnel mechanism of atomic – molecular rearrangements in a condensed system has begun to attract serious attention recently and is an interesting trend [22].

<sup>&</sup>lt;sup>‡</sup> Dependences of the  $\exp(-A/T)$  type are also frequently called the Arrhenius laws. This is because in 1889 S Arrhenius established experimentally the temperature dependence of this type of rate of chemical reactions. A direct experimental confirmation of the Maxwell and Boltzmann distributions has been provided much later.

Eqn (1) represents essentially the distribution of energy fluctuations in a body.

It should be pointed out that the kinetic aspect is ignored in such a description of a steady equilibrium state of a system. The questions of the lifetime of local fluctuation states, nature of the time evolution of fluctuations, frequencies of fluctuations of the energies of atoms, etc. have not been analysed in these classical investigations.

These problems were formulated and considered for the first time by Yakov Il'ich Frenkel' in the twenties. He concentrated his attention on the processes of fluctuation origin in condensed systems, i.e. in liquids and solids, and continued to work on this problem right up to the fifties. The main results have been summarised by Frenkel' in his monograph *Kinetic Theory of Liquids* [1]. He has been planning to prepare a revised edition and call it the *Kinetic Theory of Liquids and Solids*, i.e. of condensed systems.

Frenkel' has introduced the concept of jump-like or hopping atomic-molecular rearrangements. He has introduced the concept of the average waiting time for such a rearrangement as "... the time necessary for the accumulation by a given atom of a kinetic energy equal to or greater than the potential barrier ... " [1]; he has proposed the hypothesis of 'instantaneous release' of the kinetic energy after overcoming a barrier. He has derived an expression for the average waiting time before a jump of an atom across a potential barrier [1] (this is known as Frenkel's formula, described below), which represents the waiting time for a specific fluctuation of the energy of an atom. This formula is used very widely. In fact, the ideas and work of Ya I Frenkel' represent a transition from the 'vibrational dynamics' usually considered before his work to the 'fluctuation dynamics' which determines many characteristic features of the thermal behaviour of condensed systems.

It was Frenkel' who started the development of the fluctuation dynamics, i.e. the task of obtaining detailed information on fluctuations of the energies of atoms such as their temporal statistics, evolution, degree of spatial localisation, etc. Yakov II'ich has thus formulated the problems of the microscopics of fluctuations.

The fluctuation states of atoms are themselves of physical interest. However, the role of fluctuations in an enormous number of processes already noted makes the study of fluctuations a particularly important task.

In dealing with fluctuations of the energy of atoms in condensed media we are faced not only with the task of obtaining detailed information on their characteristics, but also with the fundamental task of identification of the mechanism of formation of a fluctuation, i.e. the mechanism of concentration of a higher energy at an atom, which this atom can only obtain from other atoms. A phenomenological description of energy accumulation by an atom because of a directional energy flux from the environment has been proposed [2]. However, the dynamical reasons for such a flux (if it exists at all) have not been identified. In the case of a condensed medium the problem of energy transfer and its accumulation at a single atom is naturally difficult to deal with because in a system of this kind each atom interacts directly with a small number of neighbours (practically only in the first coordination sphere). In the case of a gas this situation is simpler. There each atom or

molecule can interact consecutively by collisions with a large number of atoms. A higher kinetic energy (an energy fluctuation) can be acquired if over a sufficiently long time there are no 'head-on' collisions with other atoms, but only 'side' impacts by these atoms. Then, if small energy portions are received from a large number of other atoms, the atom under investigation acquires a sufficiently high kinetic energy and becomes a possessor of a fluctuation energy. A situation of this kind, i.e. the feasibility of interaction with a large number of other atoms, does not exist in the case of condensed media and, therefore, the mechanism of concentration of a higher energy is obviously different and this requires elucidation.

It is not in fact possible to investigate by direct experiments the details of fluctuation phenomena on the atomic scale. In reality, large fluctuation affecting atoms are relatively rare and the lifetimes of fluctuation states are short, so that experimental studies of the evolution of fluctuations have not yet been carried out.

Nevertheless, it is possible to elucidate the details of the evolution of energy fluctuations of atoms and to identify the mechanism of formation of fluctuations. This can be done by the method of computer simulation, known as the method of molecular dynamics [4]. The first work on simulation of the dynamics was that of E Fermi [3]. Since then the number of papers on molecular dynamics has been rising rapidly. However, there have been no attempts to account for the physics of fluctuations. The application of this approach to the problems in fluctuation dynamics in solids is described below and the results obtained are the subject of the present paper.

### 2. Method of computer experiments

The method of molecular dynamics involves numerical integration of the classical equations of motion of atoms with given interatomic interaction potentials and subject to given initial and boundary conditions.

We considered various models of solids: onedimensional, two-dimensional, and three-dimensional crystals (Fig. 1), as well as three-dimensional amorphous structures. The number of atoms in the simulated systems was varied from 100 in a chain of atoms to 500 in threedimensional crystalline and amorphous systems.

In the case of one-dimensional systems we used three potentials: Morse, Toda [5], and harmonic, all with identical values of the equilibrium interatomic spacings, binding energy, and Young modulus (Fig. 2). In twodimensional crystals we used the Morse potential and in three-dimensional systems we employed the Stillinger-Weber pair potential [6].

We set the 'temperature' by random sampling of the initial values of the velocities of atoms, followed by subsequent thermalisation for approximately 20 periods of atomic vibrations. We defined the temperature in terms of the average kinetic energy of atoms.

We integrated the equation of motion for *N* interacting particles:

$$m \frac{\mathrm{d}^2 \boldsymbol{x}_i}{\mathrm{d}t^2} = -\frac{\partial U_i}{\partial \boldsymbol{x}_i},$$

were m is the mass of an atom,  $x_i$  are the coordinates of the *i*-th atom,



**Figure 1.** Lattice models used in computer experiments: (a) onedimensional; (b) two-dimensional; (c) three-dimensional (fcc lattice).



Figure 2. Atomic pair-interaction potentials for computer simulation experiments: (1) harmonic, (2) Toda, (3) Morse.

$$U_i = \sum_{j \neq i} \boldsymbol{\Phi}\left(r_{i,j}\right)$$

is the potential energy of the *i*-th atom, and  $\Phi(r_{i,j})$  is the interatomic interaction potential.

Integration gives the path of each atom in the phase space of the coordinates and velocities.

The integral of motion is the internal energy of the system. In all cases the integration of equations of motion was carried out using the Nordsieck algorithm of the fifth order of precision [7]. The integration step, which should be sufficiently small, was selected in the range from 1/20-th to 1/50-th part of a period of atomic vibrations. The precision was judged on the basis of conservation of the integrals of motion.

In this way we found for each atom in the simulated systems the instantaneous values of the coordinates

 $x_q(t),$ 

the instantaneous values of the velocities

$$\dot{x}_q(t) = \frac{\mathrm{d}x_q(t)}{\mathrm{d}t} \; ,$$

the instantaneous values of the potential energy (defined as the sum of the potential energies of the bonds of one atom with its neighbours)

$$E_{\text{pot}}(t) = \frac{1}{2} \sum_{i} U_j \big[ x_i(t) - x_j(t) \big] ,$$

the instantaneous values of the kinetic energy

$$E_{\rm kin}(t) = \frac{1}{2} m \sum_{q} [\dot{x}_q(t)]^2$$

and the instantaeous values of the total energy

$$E_{\text{tot}}(t) = E_{\text{pot}}(t) + E_{\text{kin}}(t)$$

The fitness of the models in respect of their ability to describe the dynamical behaviour of atoms in solids was checked by calculations based on the data, obtained in computer experiments, on such characteristics as the values and temperature dependences of the thermal expansion coefficient, bulk modulus, and Debye–Waller factor. For example, in the case of simulation of nickel we achieved a quite satisfactory agreement with the experimental data [12].

The ability to find the instantaneous values of the characteristics of the dynamics of atoms enabled us to analyse dynamical fluctuations, i.e. fluctuations of the energies of atoms.

The characteristics of energy fluctuations found in our computer experiments are shown in Fig. 3.



Figure 3. Strong fluctuation of the energy, *E*, of an atom.

We determined the main characteristics, which were: — the maximum energy of a fluctuation  $E_{\text{fl}}$  (separately kinetic, potential, and their sum);

—the excess of the energy of a fluctuation above the relevant average energy  $\Delta E$ ;

—the lifetime of a fluctuation  $\Delta t_{fl}$ ;

— the number of fluctuations as a function of their energy at different temperatures (statistics of fluctuations).

These and several other characteristics (spatial localisation, velocity of fluctuations, distance travelled by fluctuations, etc.) are the main elements of the microscopics of fluctuations.

# **3.** Results of computer simulation of dynamical fluctuations in atomic systems

The results reported below have been described earlier [8-13]. Fig. 4 shows a fragment of the 'thermal life' of one

of the atoms in a one-dimensional model (chain) with an anharmonic interaction potential (Morse potential). We simulated one-dimensional vibrations only along the chain axis. The fragment of a relatively 'quiet life' is identified in this figure. We can see fluctuations of the kinetic energy, but their amplitudes differ little from the average kinetic energy  $(\frac{1}{2}kT)$ . Strong fluctuations are not observed during this time interval (amounting to several fluctuation periods).



**Figure 4**. Fragment of the thermal life of an atom. One-dimensional model of 100 atoms with the Morse potential. The figure shows a fragment without strong fluctuations of the kinetic energy. Here (and later)  $\tau_0$  is the average period of the vibrations of atoms.

Fig. 5a shows a different fragment of the dynamics of the same atom. During this time interval we can see a fairly strong fluctuation of the kinetic energy of an atom. The data in Fig. 5a can be used to answer the question of the lifetime of a fluctuation state of an atom. We can see that a large energy fluctuation moves very fast. The whole fluctuation 'survives' for about one period of the atomic vibrations.

Similar results are obtained also for two- and threedimensional models (see below). In all cases the energy fluctuations appear as very sharp energy peaks. As already



**Figure 5.** Fragments of the thermal life of atoms. One-dimensional models with 100 atoms and with the Morse (a) and harmonic (b) potentials. The figure shows fragments with strong fluctuations of the kinetic energy.

mentioned, Frenkel' was the first to formulate the problem of evolution of fluctuations using the term 'accumulation' and for the dispersal of energy he introduced the hypothetical concept of 'instantaneous release' of energy. Yakov Il'ich wrote about this hypothesis as follows: 'Rigorous justification of this hypothesis represents a very complex problem, which nobody has yet attempted to solve'' [1]. We can now say that 'accumulation' is very fast. The energy rise is in the nature of a flash. The 'instantaneous release' hypothesis is seen to be fully supported.

Having established a strong time localisation of energy fluctuations, let us now consider the degree of their spatial localisation.

Fig. 6 shows a space-time diagram of the energy of atoms in a chain. The abscissa gives the values of the energy of each atom. The gaps, points, and numbers represent the corresponding energy values (caption of Fig. 6). The ordinate gives the time. Each row represents an instantaneous distribution of the energy between the atoms in a chain. The rows are spaced every one-sixth of the average period ( $\tau_0$ ) of the vibrations of an atom. This figure gives the total energy of atoms (the kinetic energy plus the half-sum of the potential energies of two adjoining bonds). The interaction potential is assumed to be harmonic (the reason for assuming the harmonic potential will be discussed later).

The data in Fig. 6 make it possible to identify the following properties of fluctuations of the energy of atoms: — the fluctuations are also localised strongly in space; an excess energy is concentrated usually at just one atom; the adjacent atoms are weakly excited; in a smaller number of



**Figure 6.** Space-time diagram of the total energy of atoms. Onedimensional model with 100 atoms and the harmonic potential.  $E_{\rm fl}$  denotes the magnitude of the fluctuation of the total energy of an atom. Gap:  $E_{\rm fl} < 1.5 \ kT$ , (•)  $E_{\rm fl} = (1.5 - 2.0) \ kT$ ; (1)  $E_{\rm fl} = (2.0 - 2.5) \ kT$ ; (2)  $E_{\rm fl} = (2.5 - 3.0) \ kT$ ; (3)  $E_{\rm fl} = (3.0 - 3.5) \ kT$ ; (4)  $E_{\rm fl} = (3.5 - 4.0) \ kT$ ; (5)  $E_{\rm fl} = (4.0 - 4.5) \ kT$ ; (6)  $E_{\rm fl} = (4.5 - 5.0) \ kT$ ; (7)  $E_{\rm fl} = (5.0 - 5.5) \ kT$ ; (8)  $E_{\rm fl} = (5.5 - 6.0) \ kT$ ; (9)  $E_{\rm fl} = (6.0 - 6.5) \ kT$ ; O:  $E_{\rm fl} > 7.0 \ kT$ .

cases and usually for weaker fluctuations the excess energy is spread out between two, three, or several neighbouring atoms; the energy fluctuations are mainly of monatomic scale;

— there is a definite migration of fluctuations; the diagram shows translation of an excess energy from one atom to another; the rate of this translation is close to the velocity of sound; it should be stressed that the motion of fluctuations is not of purely soliton nature (in a harmonic system there should be no solitons at all) when a local excitation travels with conservation of a constant energy; the magnitude of a fluctuation oscillates during its motion and the peak-to-peak amplitude of such oscillations is fairly large;

—the strongest fluctuations appear as a result of 'collisions' of moving fluctuations (when the lines of motion of fluctuations intersect).

Similar results are also obtained by simulation of the dynamics of an anharmonic chain. In two-dimensional anharmonic and also harmonic and three-dimensional systems there are equally strongly localised (on the scale of one atom) energy peaks (fluctuations). In two- and three-dimensional systems there is also migration of fluctuations along the lines of close packing of atoms.

Having demonstrated the strong temporal and spatial localisation of energy fluctuations, we shall now consider the problem of the mechanism of their formation. Computer simulation experiments were carried out with this particular aim in mind and in these experiments we considered not only realistic anharmonic potentials, but also harmonic potentials. For example, in addition to the Morse potential

$$U(x) = U_0[\exp(-2\alpha x) - 2\,\exp(-\alpha x)]$$

we selected the harmonic potential

$$U(x) = U_0 \, \alpha^2 (x^2 - 1).$$

Here, x is the deviation of the distance between two atoms from the equilibrium value. The parameters of both potentials,  $U_0$  and  $\alpha$ , were assumed to be the same so that the values of the potential and of its first and second derivatives with respect to the displacement x (i.e. the values of the elastic force and the linear elasticity coefficient) were the same at x = 0.

It was important to establish whether the nature of the fluctuation dynamics is similar or very different for the anharmonic and harmonic interactions. A comparison can be made by examination of Figs 5a and 5b the latter of which shows a fragment with fluctuations for a harmonic chain. It is evident that

(1) the 'peaks' of the energies of atoms are also observed for the harmonic interaction;

(2) the nature of the fluctuation pattern remains practically the same as in the case of anharmonic interaction.

Similar results, demonstrating a high degree of similarity of the dynamical behaviour of fluctuations in anharmonic and harmonic systems, were obtained for two- and threedimensional models. The similarity makes it possible to draw the following conclusions about the mechanism of formation of fluctuations.

In an anharmonic system two types of phenomena may lead to a local increase in the energy of an atom: an interference between elastic waves (normal vibrations);

a redistribution of the energy between different vibrational modes (energy transfer from some modes to others).

The second phenomenon is excluded in the case of a harmonic system and, therefore, only the interference of elastic waves is possible when the local phase matching of the waves leads to energy 'peaks'. †

The similarity of the fluctuation dynamics in the case of anharmonic and harmonic systems thus allows us to conclude that the mechanism of formation of fluctuations of the energy of atoms is in all cases the interference between the elastic waves. This conclusion is supported by the fairly large change in the energy of a fluctuation as it migrates, which is pointed out above (Fig. 6). Such a change is obviously due to different interference phase relationships along the path of a moving fluctuation.

The interference-wave nature of energy fluctuations allows us to call them characteristic 'wave packets'. Thus, if we assume that computer experiments do indeed simulate real thermal processes in solids, we may conclude that fluctuations of the energy of atoms in real bodies are the results of an interference between phonons. In this case we can say (without minimising the importance of phonons in many dynamical processes in solids) that probably the main role of phonons is to create fluctuations of the energy of atoms.

It is appropriate to mention here that the phonon origin of fluctuations has been postulated earlier. For example, Fabelinskii [15] says: "...Fluctuations are the results of the interference between Debye waves." The results of our computer simulation appear to support this treatment well.

There are thus grounds for concluding that fluctuations of the energy of atoms are the result of the wave nature of the internal dynamics of a solid. The overall picture may then be described as follows.

The normal vibrations (with their own frequency spectrum) represent extended (over many wavelengths or up to the dimensions of a body, and in an anharmonic system over the phonon path) travelling or standing waves. The interference between them creates solitary wave formations ('packets') which result in fluctuations of the energy of atoms. Computer simulations show that these packets may appear both as a brief increase in the energy only at a particular point (at one atom) or as a travelling solitary formation (migrating fluctuation) with a variable fluctua-tion energy mentioned above. Then, in addition to the inter-ference between extended waves of the normal vibrations (interference between the phonons themselves), there is a possibility of a characteristic interference between moving solitary waves (interference between packets representing fluctuations) when they collide. It is then (as is evident from Fig. 6) that particularly strong energy

† Strictly speaking, the results of wave interference in a harmonic system do not fit the concept of fluctuations as random events, but represent 'beats' which are determined by the initial conditions. However, since the criterion of stochasticity is related to the anharmonicity parameter and to the number of particles in a system in such a way that an increase in this number increases the anharmonicity needed for stochastic behaviour [14], it follows that if the number of particles is sufficiently large we can use the concept of fluctuations in harmonic systems in the same way as in the case of anharmonic systems. fluctuations are formed. Computer simulation makes it possible to obtain a detailed picture of the events.

Elastic waves in a solid are naturally related to density fluctuations. Mandel'shtam [16] has shown that density waves (components of a spatial Fourier expansion) introduced by Einstein [17] are identical with the Debye thermal elastic waves.

A change in the density of an elastic body is in one-toone relationship with a change in the potential energy at the same point. The motion of a density wave leads to the vibrations of atoms, which are periodic processes of conversion of the potential into the kinetic energy and vice versa. This applies to ordinary periodic processes. The situation is obviously somewhat different when solitary wave formations (fluctuations) appear. There is no periodicity (everything happens in one period) and in this case we can hardly use the concept of the phase (which determines the result of the interference of ordinary waves). Instead, for each specific packet we can determine whether a positive or a negative dilation predominates, i.e. whether elastic com-pression or elongation of the bonds between atoms takes place. The result of a collision of packets in the form of the ratio of the kinetic and potential energies of an atom at the moment of the 'combined' fluctuation then depends on the signs of the dilations of the colliding packets.

Fig. 7 shows the space-time diagrams of the fluctuation dynamics in anharmonic chain of atoms, but not of the energies of atoms (contrary to Fig. 6), separately for elongation and compression of fluctuations. We can see that the migration of dilations is of the same nature as the migration of energy fluctuations (compare with Fig. 6), which follows in a natural manner from the relationship between energy and density waves. We may point out some quantitative differences between the diagrams of the migration of compressions and elongations. They are related to the anharmonicity of a chain. In the case of a harmonic chain it follows from the simulation results that there are no differences. The influence of the anharmonicity will be discussed later.

Examples of computer results on the collisions of fluctuations with the same and opposite signs of the dilatation are presented in Fig. 8. We can see that a collision of two fluctuations with the same sign of the dilatation (elongation in Fig. 8a) leads to a strong energy fluctuation which is almost wholely a fluctuation of the potential energy. The kinetic energy represents only a small fraction of the total energy of the fluctuation.

In contrast, when two fluctuations with opposite signs of the dilatation collide (Fig. 8b), the resultant strong fluctuation of the energy of an atom is mostly a fluctuation of the kinetic energy. This is to be expected, since fluctuations with opposite signs of the dilatation moving towards one another have momenta directed in the same way (parallel) and in a collision the momenta are simply summed giving rise to a strong peak of the kinetic energy when the potential energy falls because of the mutual compensation of the elongation and compression.

Consequently, strong fluctuations of the energy of atoms may have different ratios of the kinetic and potential energies. It would be of interest to analyse statistically the fluctuations in order to identify characteristic ratios of the two types of energy in the total energy of the fluctuation of an atom. This was done by averaging over a number of realisations of the total, potential, and kinetic energies of atoms in a onedimensional system (seven realisations), a two-dimensional system (eight realisations), and a three-dimensional system (twenty-two realisations). For each of these cases we selected time scans of fluctuations with the same values of the total energy and averaged the component potential and kinetic energies.

The results obtaind are presented in Fig. 9 which shows the total and kinetic energies. The potential energy is the



Figure 7. Space – time diagrams of the strains experienced by interatomic bonds. One-dimensional model with 100 atoms and the Morse potential. (a) Tensile strain  $\varepsilon$ . Gap:  $\varepsilon < 10\%$ ; (•)  $\varepsilon = 10\% - 16\%$ ; (•)  $\varepsilon > 16\%$ . (b) Tensile strain  $\varepsilon$ . Gap:  $\varepsilon < 4\%$ ; (•)  $\varepsilon = 4\% - 7\%$ ; (•)  $\varepsilon > 7\%$ .

difference between the total and kinetic forms. All the systems are anharmonic. We can see that the nature of the average time scan of the total energy of an atom for systems with different dimensions is the same: the time 'core' of a fluctuation, occupying about one vibrational period  $(\tau_0)$ , and a somewhat longer pedestal (amounting to two





**Figure 8.** Collision of fluctuations. One-dimensional model, with 100 atoms and the Morse potential. (a) Fluctuations with the same sign of the strain (elongation) moving towards one another, snapshot at  $0.5 \tau_0$  before collision on one bond. (a') Moment of collision; a strong fluctuation of the potential energy of the bond ( $_{\odot}$ ) and a low kinetic energy of atoms ( $\bullet$ ).

(b) Fluctuations with opposite signs of the strain moving towards one another, snapshot at  $0.5\tau_0$  before collision of one bond. (b') Moment of collision; a strong fluctuation of the kinetic energy of an atom ( $\bullet$ ) and a low potential energy ( $\circ$ ).



**Figure 9.** Fluctuations of the energies of atoms in lattices with different dimensions: (1) total energy; (2) kinetic energy. (a) One-dimensional model with 100 atoms and the Morse potential, averaged over 7 realisations. (b) Two-dimensional model with 271 atoms and the Morse potential,

averaged over 8 realisations. (c) Three-dimensional model with 500 atoms, fcc lattice, Stillinger-Weber potential averaged over 22 realisations.

periods). We can also see that in all three cases the kinetic energy represents a major fraction of a fluctuation peak. In the case of a one-dimensional system this fraction is about 90%; for two- and three-dimensional systems it amounts to about 90% -95%. Consequently, the kinetic energy statistically dominates the fluctuations of the energy of atoms. This is evidently because the collisions of fluctuations with different signs of the dilatation are statistically more probable and, as demonstrated earlier, this leads to the predominance (on average) of the kinetic energy in a strong fluctuation of the energy of an atom. However, this problem should be analysed further.

It would be interesting to supplement the above information about fluctuations with the results obtained for a model of a different atomic structure. The results quoted so far have been obtained by computer simulation of the dynamics of systems with the crystalline order of the distribution of atoms. In simulation of an amorphous system we started with a three-dimensional fcc lattice (a crystallite of 500 atoms) and then this crystallite was 'melted' on a computer and rapidly 'cooled' (the equivalent cooling rate was  $10^{13}$  K s<sup>-1</sup>). This made it possible to determine the positions of atoms corresponding to an amorphous structure. This structure was confirmed by computer determination of the function representing the radial distribution of atoms. The dynamic characteristics of the atoms were determined for such a system at a number of temperatures, as was done earlier for crystalline systems. The amorphous system was also found to exhibit fluctuations of the energy of atoms.

Fig. 10 shows a time scan of a strong fluctuation of the energy of an atom averaged over 43 realisations. The overall nature of the time scan of the total energy is quite close to the scans for crystalline systems (compare with Fig. 9). However, it should be noted that in this case the fraction of the kinetic energy is considerably less: it is below 50%. Computer experiments show that this may be related to a difference in the behaviour and state of the surrounding atoms at moments preceding a strong energy fluctuation at a given atom and at the moment of a fluctuation peak at this atom. The results show that in the case of amorphous



**Figure 10.** Fluctuations of the energy of an atom in an amorphous system. Three-dimensional model with 500 atoms and the Stillinger–Weber poten-tial, averaged over 43 realisations: (1) total energy; (2) kinetic energy.

systems a fluctuation excitation extends over a somewhat larger number of atoms than in crystals. Once again, a further clarification is needed.

The results of our computer simulation of systems with the anharmonic and harmonic interactions allow us to estimate the role of the anharmonicity in the fluctuation dynamics.

As pointed out earlier, fundamentally the anharmonicity is not essential for the appearance of local energy peaks (fluctuations). The pattern of the fluctuation dynamics (time and space scans of the fluctuations for systems with all three dimensions) are basically similar for the anharmonic and harmonic models.

The nonlinearity of the interatomic interaction potential has the effect that for the same fluctuation of the potential energy the compression and elongation of bonds are different: the elongation is stronger than the compression (this naturally does not occur in a harmonic system). This is obviously the reason for the differences, revealed by computer experiments, between the characteristics of fluctuations obtained in the anharmonic and harmonic models, and also the differences between elongation and compression fluctuations considered in the anharmonic models.

If we use the concept of the lifetime of a fluctuation, which is the time during which the energy E of an atom exceeds the average energy  $E_{av}$  (see Fig. 3), we find that this lifetime  $\Delta t_{\rm fl}$  is considerably longer for the elongation fluctuations than for the compression fluctuations. For example, in the case of a chain with the Morse potential we find that when the fluctuation of the total energy is  $\Delta E/kT = 3$ , the lifetime of an elongation fluctuation is  $\Delta t_{\rm fl} = 1.7\tau_0$ , whereas the lifetime of a compression fluctuation is  $\Delta t_{\rm fl} = 0.8\tau_0$ .

The space-time diagrams of the type shown in Figs 6 and 7 can be used to estimate the path or the lifetime of a solitary wave formation (packet, fluctuation) along the line of motion of a fluctuation from the more or less reliably known point of its nucleation to the point of its dispersal. The average results are given in Table 1 for a chain of 100 atoms. We can see from this table that the lifetimes in a harmonic system are independent of the sign of a dilatation, whereas for an anharmonic system the influence of the sign is considerable.

 $\textbf{Table 1}. \ Life time of moving fluctuations with different signs of dilatation.$ 

Potential	Elongation fluctuation	Compression fluctuation
Harmonic	$(46 \pm 3) \tau_0$	$(46 \pm 3) \tau_0$
Morse	$(25 \pm 10) \tau_0$	(90 ± 10) $\tau_0$

Moving compression fluctuations are much more stable than elongation fluctuations. The latter have a lower (by a factor of 1.5-2) velocity, so that their 'mean free paths' are reduced even further compared with the paths of the compression fluctuations.

Our computer data allow us to consider also the problems of statistics of energy fluctuations. One aspect is the distribution of fluctuations in terms of their energy. This distribution can be found by calculating the instantaneous values of the energies of atoms. The total number of cases  $n_0$  when the average energy is exceeded is



**Figure 11.** (a) Distribution of the instantaneous values of the total energy of atoms in a two-dimensional model with 271 atoms and the Morse potential. (b) Dependence of the average waiting time of an energy fluctuation and its magnitude. One-dimensional model with 100 atoms and the Morse potential, averaged over 10 realisations with different initial conditions. (•) Kinetic energy of an atom; ( $_{O}$ ) potential energy of an interatomic bond.

determined for a system that has undergone a period of thermalisation. This corresponds to the number of atoms with positive energy fluctuations of different magnitude (from small to large) at a given moment. This is followed by finding the number of cases when higher values of the energy are exceeded, i.e. by finding the dependences  $n(\Delta E)$  (we recall that  $\Delta E = E_{\rm fl} - E_{\rm av}$ ; see Fig. 3). The resultant normalised dependences  $n(\Delta E)/n_0$  are then averaged over several tens of calculations of the distribution of the instaneous energies of atoms.

The results of determining the distribution function of fluctuations of the total energy of atoms for a twodimensional anharmonic model are presented in Fig. 11a. We can see that a linear dependence with a slope close to unity is obeyed fairly well when semilogarithmic coor-dinates are used. This means that the distribution is described by the function  $\exp(-\Delta E/kT)$ , i.e. it is the Boltzmann distribution.

These computer experiments show that the distribution is stable. It is not affected by changes in the initial conditions after the thermalisation period, i.e. after the system reaches a dynamic equilibrium. Since the Boltzmann distribution is to be expected for the energetics of an atomic dynamic system, its direct manifestation in computer experiments may be regarded as additional confirmation of the reliability of the method and of the satisfactory nature of the model results on the thermal state of real bodies.

We shall now turn to a different aspect of the statistical data which is the problem of the distribution of fluctuations in terms of the frequency of their appearance or in terms of the waiting time. It is understood that the frequency distribution and the steady-state distribution of the energy fluctuations are related. However, such a profile of the energy. Usually the waiting time of a fluctuation is the most important characteristic that governs the kinetics of those numerous phenomena which are based on fluctuation started Therefore, Frenkel'-who dynamics. the development of the microscopics of the fluctuation processes - paid special attention to this characteristic. He estimated theoretically the average waiting time of a fluctuation of the energy of an atom on the basis of a simple and natural assumption that the lifetime of the state of an atom excited by a fluctuation is close to the period  $\tau_0$  of the vibrations of the atoms. The ratio of the lifetime in a state with a higher potential energy  $(\Delta U)$  to the lifetime of the 'quiescent' state  $(\tau)$  is the reciprocal of the ratio of the probabilities of these two states described by the Boltzmann factor exp  $(-\Delta U/kT)$ . This leads to the Frenkel' formula

the fluctuations themselves; their lifetime and the time

$$\frac{\tau}{\tau_0} = \exp\frac{\Delta U}{kT} \,. \tag{2}$$

Since in the treatment by Frenkel' himself the 'jump' of an atom over a potential barrier of height  $\Delta U$  requires a fluctuation of the energy of an atom  $\Delta E \ge \Delta U$ , Eqn (2) leads directly to the expression for the average waiting time of a fluctuation  $\Delta E$  of the energy of an atom:

$$\tau \cong \tau_0 \, \exp \frac{\Delta E}{kT} \,. \tag{3}$$

It should be pointed out that the average waiting time of a fluctuation  $\Delta E$  of the energy of an atom is also the average time between two consecutive fluctuations of the same magnitude  $\Delta E$  at one atom. This interpretation of the waiting time makes it possible to check directly the validity of Eqn (3) by computer simulation. The assumptions made by Frenkel' determine, as pointed out already, the value of the preexponential factor to within the average period of the vibrations of atoms.

The dependence  $\tau(\Delta E)$  for a thermalised system was studied by calculating, over a fairly long time interval  $\Delta t = M \tau_0$  (*M* is the number of the vibrational periods), the value of  $n_{\rm fl}$  which is the number of energy fluctuations of magnitude exceeding a certain energy level beginning from  $E_{\rm av}$ . In this way we obtain the dependences  $n_{\rm fl}(\Delta E)$ which are used to determine the dependence of the average time between fluctuations of the kinetic energy of one atom and between the fluctuations of the potential energy of one bond on the fluctuation energy:

$$\tau(\Delta E) = \frac{M \tau_0}{n_{\rm fl}(\Delta E)N},$$

where N is the number of atoms or bonds in the model.

The results for a one-dimensional anharmonic system are presented in Fig. 11b. The dependence of  $\ln [\tau(\Delta E)/\tau_0]$ is linear with a slope practically equal to unity (when the argument is  $\Delta E/kT$ ); moreover, it is not only linear but very nearly directly proportional. Consequently, in the case of fluctuations of the kinetic energy of atoms and of the potential energy of bonds the following relationship is well satisfied:

$$\tau \cong \tau_0 \exp \frac{\Delta E}{kT}$$
.

This means that the results of computer experiments support directly the Frenkel' formula both in the functional (qualitative) and quantitative senses.

## 4. Summary

Computer simulation of the atomic dynamics in solids has thus provided a whole range of detailed data on fluctuations of the energy of atoms: the lifetime of such fluctuations, their spatial localisation, the ratio of the kinetic and potential energies at the moment of a fluctuation, the migration of fluctuations and their interaction, and the statistics of the energy fluctuations. The mechanism of formation of fluctu-ations of the energy of atoms has been identified: it is the inteference between normal vibrations (phonons). These results will be needed in the development of the micros-copic theory of fluctuation dynamics and of the processes that are based on elementary fluctuation events.

The results of computer simulation naturally leave many questions unanswered. These questions include whether the selected potential fields around atoms correspond to reality and also limitations of the description of the dynamics only by the classical approach. Moreover, the processes occurring in the electron subsystem of a body are ignored (atoms are regarded as hard spheres connected by springs) and so on. However, the computer simulation method makes it possible to vary quite easily the parameters of the models and thus approach the solution of at least a number of similar problems.

It is worth mentioning that computer simulation is used increasingly in an analysis not just of fluctuations themselves, but to an even greater extent in an analysis of fluctuation atomic-molecular rearrangements. Diffusion, evaporation, motion of dislocations, implantation of atoms, and other events have been simulated successfully [18-21].

We may assume that the appearance of detailed microscopic data on energy fluctuations and fluctuation parameters will lead to the solution of problems formulated long ago and relating to the activation energy of the processes in condensed bodies, the 'compensation effect' (which is the relationship between the pre-exponential factors and the arguments of the exponential functions in the expressions for the rates of the processes), the preexponential factors in the Boltzmann-type expressions, etc.

The continuing development of the problem of fluctuations in condensed systems has been stimulated decisively by the ideas and work of Yakov Il'ich. The range of fluctuation-type topics is increasing continually. They include mechanical fracture and electrical damage, decom-position of polymers, complex processes in glasses, etc. It is worth stressing particularly the increasing importance of fluctuation processes in biological functions. All this is enhancing the importance of the subject founded by Yakov Il'ich, the fluctuation dynamics, and makes it very desirable to develop this subject further.

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