

Statistics of the fluctuations of the kinetic energy of atoms in a solid (computer experiment)

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Fluctuations of the kinetic energy (E_k) in an fcc crystal at constant temperature and pressure have been investigated by computer simulation (molecular-dynamics method). The distribution of the instantaneous values of E_k and the magnitude distribution of the fluctuations of E_k are determined. It is found that these distributions correspond to the Maxwell–Boltzmann distribution. The average weighting time of the fluctuations of the kinetic energy of an atom was determined as a function of the magnitude of the fluctuations. © 1995 American Institute of Physics.

Fluctuations of the energies of atoms are the basis for thermally activated processes, such as diffusion, evaporation, plastic and highly elastic deformation, chemical reactions, electronic transitions, biological functioning, and so on. The duration of a fluctuation state of the atoms is short (of the order of the period of atomic vibrations). Therefore it is difficult to investigate fluctuations experimentally. Information about fluctuations is indirect and based mainly on the statistics of the elementary events of physical processes which they engender. Detailed information about the energy fluctuations themselves can be obtained at the present time only by the methods of computer simulation of the atomic dynamics.^{1,2} For example, in Refs. 3–8 an entire series of detailed information about fluctuations of the energy of atoms in one-, two-, and three-dimensional solids was obtained on the basis of the molecular-dynamics method. The first data on the statistics of the fluctuations of the energies of atoms were also obtained in Refs. 3, 6, and 8. It should be noted that questions concerning the statistics of fluctuations are especially important for the analysis of many thermal-activation processes.

In the present paper we use a much larger statistical sample than previously^{3,6,8} to analyze questions concerning the distribution of energy over atoms in a crystal lattice. The analysis is based on an examination of the time dependence of the energy of the atoms that is obtained in the course of computer modeling. In the present paper, only fluctuations of the kinetic energy of the atoms is discussed.

1. PROCEDURE OF THE COMPUTER EXPERIMENT

The molecular-dynamics method consists of a numerical integration of the classical equations of motion of the atoms and prescribed interatomic interaction potentials with prescribed initial and boundary conditions.

In the present work a model of a three-dimensional fcc crystal, containing 864 atoms, was chosen. The Stillinger–Weber interatomic interaction pair potential was used with parameters corresponding to nickel. Periodic boundary conditions were prescribed in order to eliminate surface effects on the dynamics of the atoms. All calculations were based on the Andersen–Nosé algorithm, which makes it possible to

model the behavior of a system at constant temperature and pressure, i.e., under conditions very close to real conditions.^{10,11} The calculations performed corresponded to zero pressure. Initially, the atoms occupied sites of the crystal lattice and they were given momenta chosen at random. The total energy distributed to the atoms was such that it corresponded to a temperature of the system of 500 K (so that the average energy of an atom was $3 kT$, where k is Boltzmann's constant).

The period τ_0 of the vibrations of the atoms was calculated from the coefficient of linear elasticity in a given potential and for a given mass of the atom. For the case at hand, $\tau_0 = 1.02 \cdot 10^{-13}$ sec.

The equations of motion of the atoms were integrated with an integration step of $0.05 \tau_0$.

The system was thermalized over a time equal to 25 periods of the atomic vibrations, after which the phase trajectory of the system was analyzed over a time of $150 \tau_0$. As a result, a series of instantaneous values (every $0.05 \tau_0$ of the kinetic energy of an atom

$$E_k(t) = \frac{1}{2} m \sum_q [\dot{x}_q(t)]^2,$$

where m is the mass of an atom and $\dot{x}_q = dx_q/dt$ is the component of the velocity of the atom along the coordinate q , where $q = 1, 2, \text{ and } 3$, was obtained for each atom.

The computational accuracy was checked according to the conservation of the integrals of motion during the computational process.

The effectiveness of the model in describing the dynamical behavior of atoms in a real solid was checked by performing calculations of characteristics such as the values and temperature dependences of the thermal expansion coefficient, the bulk modulus, and the Debye–Waller factor. The computed characteristics agreed satisfactorily with the experimental data for nickel.⁶

2. RESULTS OF COMPUTER SIMULATION OF THE FLUCTUATION DYNAMICS OF ATOMS

A fragment from the time dependence of the kinetic energy of one atom of a model crystallite over approximately

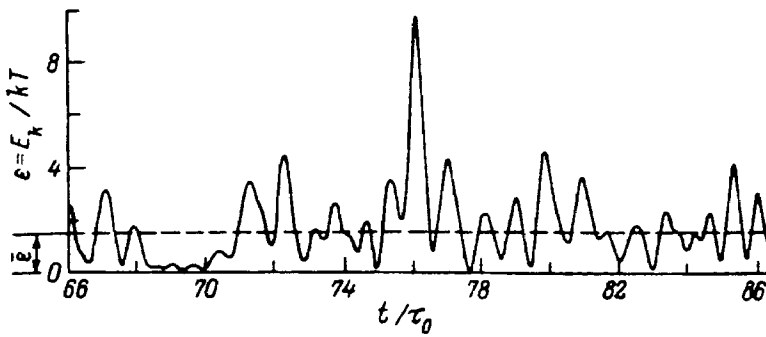


FIG. 1. Portion of the thermal life of an atom. Three-dimensional model. 864 atoms. Stillinger-Weber potential with parameters for nickel. The period of the oscillations of the atoms is $\tau_0 = 1.02 \cdot 10^{-13}$ sec. $T = 500$ K. Section with strong fluctuation of the kinetic energy.

20 periods of the atomic vibrations is displayed in Fig. 1. The kinetic energy (ε) is measured in units of E_k/kT . Among a large number of small fluctuations, one can see in the figure a quite strong fluctuation of the energy $\varepsilon \approx 10$. The duration of this fluctuation is short — approximately one period of the atomic vibrations. The short lifetime of the fluctuations of the energy of atoms is characteristic of solid-state systems. This question has been examined in detail in Ref. 8. One can see from Fig. 1 that the values $\varepsilon = 0$ are relatively rare. This seems to be natural for three-dimensional systems. For a one-dimensional system with one-dimensional vibrations there is no way to avoid double passage of the kinetic energy through zero over each period of the vibrations. In a three-dimensional system it is unlikely that phases of oscillations with different polarizations will coincide, and consequently zero values of the kinetic energy are observed quite rarely.

The temporal realizations of the kinetic energy for each atom in a crystallite containing 864 atoms over all 150 periods of the atomic vibrations are, in general, similar to those displayed in Fig. 1. Only the magnitude and number of fluctuations observed are different.

1) *Distribution of the instantaneous values of the kinetic energy of the atoms.* The distribution of the instantaneous values of the kinetic energy was determined after each half-period of atomic vibrations over a total 150 periods. The results were averaged over the 300 sets of data. As a result, we obtained the integrated distribution function, i.e., the fraction of the number of atoms $n(\varepsilon)/n_0$, where $n_0 = 864$, having instantaneously energies which are higher than the prescribed values $\varepsilon = E_k/kT$, were obtained. The values of ε ranged from $\varepsilon = 0$ to 11.5 with a step of 0.5. The results obtained are displayed in Fig. 2a. The variance for a large part of the dependence is small and increases somewhat only for high values of ε .

As one can see from the plot, the function $\ln [n(\varepsilon_0)/n_0]$ is slightly, but palpably, curved: The slope is smaller for low values of ε and increases toward high values of ε , approaching the value -1 (the slope equal to -1 corresponds to the Boltzmann factor). The differential distribution $n(\varepsilon)/n_0$ presented in Fig. 2b was also estimated from the integral function $(1/n_0) [dn(\varepsilon)/d\varepsilon]$. One can see that the differential distribution function is nonmonotonic and has a maximum near $\varepsilon = 0.5$.

The main question of a quantitative analysis of the distribution function is this: Does the dependence obtained in the computer experiment correspond to the theoretical distribution, when the fundamental principles of the statistical

physics of the distribution of subsystems over the energy are applied to a system of atoms, where each atom is a subsystem? We note that not only is the validity of such an extension not obvious, but it also appears to be "illegal," since a separate atom in a solid does not match the thermodynamic concept of a subsystem.

In a condensed system particle distributions over the kinetic and potential energy are separated.¹² The probability that a particle has a kinetic energy close to $\varepsilon = E_k/kT$ is given by the expression¹²

$$dW(\varepsilon) = \frac{2}{\sqrt{\pi}} \varepsilon^{1/2} \exp(-\varepsilon) d\varepsilon. \quad (1)$$

Then the probability that a particle has a kinetic energy greater than ε is

$$W(\varepsilon) = \int_{\varepsilon}^{\infty} dW(\varepsilon) = \frac{2}{\sqrt{\pi}} \int_{\varepsilon}^{\infty} \varepsilon^{1/2} \exp(-\varepsilon) d\varepsilon. \quad (2)$$

Since $n(\varepsilon)/n_0 = W(\varepsilon)$, it is this function that should be compared to the results of the computer experiments, displayed

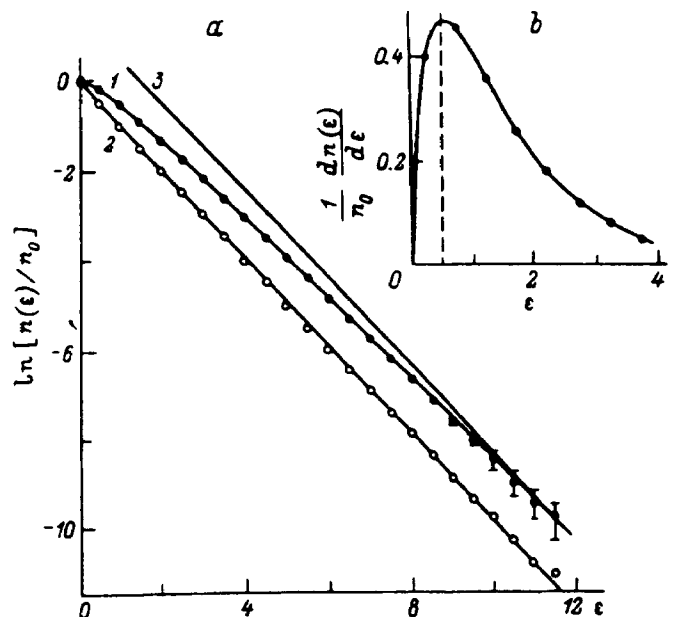


FIG. 2. Distribution of the instantaneous values of the kinetic energy of the atoms. a — Integral distribution: 1 — direct distribution of the values of the kinetic energy of the atoms; 2 — $F(\varepsilon)$ — recalculation of the function 1 using the formula (3); 3 — corresponds to the slope of the function proportional to $\exp(-\varepsilon)$. b — Differential distribution.

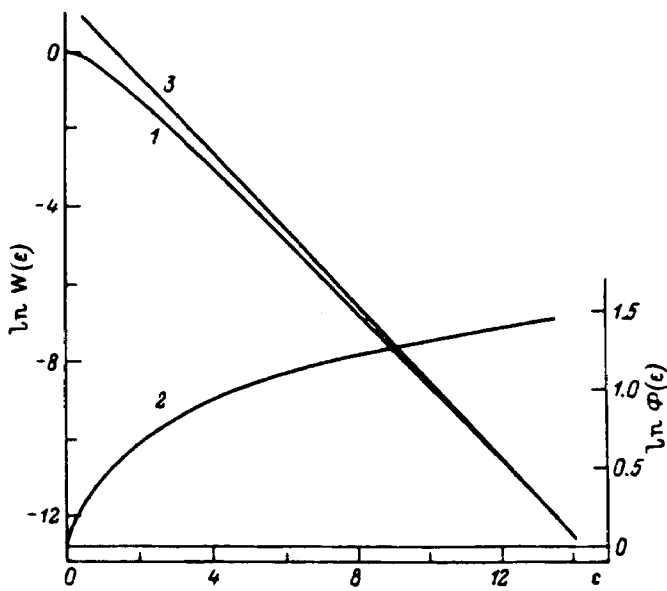


FIG. 3. Results of the numerical integration of the theoretical integral distribution function of the kinetic energy of the atoms. 1 — $W(\varepsilon)$, 2 — the factor $\Phi(\varepsilon)$, 3 — slope of the function, proportional to $\exp(-\varepsilon)$.

in Fig. 2a. The expression (2) cannot be integrated in terms of elementary functions. The result of the numerical integration is displayed in Fig. 3 (curve 1). It is convenient to represent this function in the form of a product

$$W(\varepsilon) = \frac{2}{\sqrt{\pi}} \int_{\varepsilon}^{\infty} \varepsilon^{1/2} \exp(-\varepsilon) d\varepsilon = \Phi(\varepsilon) \exp(-\varepsilon).$$

A plot of the function $\Phi(\varepsilon)$ is presented in Fig. 3 (curve 2). We can now check whether or not the computer calculations correspond to the expression (2). One can see that the form of the function $\ln [n(\varepsilon)/n_0]$ in Fig. 2a is similar to that of the function $\ln W(\varepsilon)$ in Fig. 3 (curve 1).

To make a quantitative check, we restructure the data of Fig. 2a using the function $\Phi(\varepsilon)$. A plot of the resulting function

$$F(\varepsilon) = \ln \left[\frac{n(\varepsilon)}{n_0} \right] - \ln \Phi(\varepsilon) \quad (3)$$

is displayed in Fig. 2a (curve 2). It is evident that the function is linear over the entire range and its slope is equal to -1 ; extrapolation of the plot to $\varepsilon=0$ gives a value equal to 0. In other words, the relation (3) is described well by the function $\exp(-\varepsilon)$, and therefore the equality $n(\varepsilon)/n_0 = W(\varepsilon)$ holds.

In summary, the distribution of the instantaneous values of the kinetic energy of the atoms obtained in the computer experiment, agreed well with the theoretical Maxwell-Boltzmann distribution. This means, in turn, that the thermodynamic limitations on Gibbs's theory are not strict with respect to the kinetic energy of the atoms in a condensed system. This has been known for a long time for the distribution of the kinetic energy of atoms in a gas (Maxwell's formula) and has been directly confirmed experimentally. With respect to condensed systems, however, no such direct

experimental data have been obtained; for this reason, the results of the computer experiments could be quite important.

The correspondence established between the computer and the theoretical distribution (2) makes it possible to calculate the energy ε_m corresponding to the maximum of the differential distribution. For the function (1) $\varepsilon_m=0.5$. As we have already mentioned, the position of the maximum of the distribution in Fig. 2b is close to $\varepsilon=0.5$; this agrees with the theoretical values.

This agreement, in turn, makes it possible to determine an important characteristic: the ensemble average kinetic energy $\bar{\varepsilon}$ of the atoms. For the function (1) $\bar{\varepsilon}=3/2$. We recall that we introduced into the system an energy corresponding to an energy corresponding to an average total energy per atom equal to $3 kT$. The average kinetic energy $\bar{\varepsilon}=3/2$ is shown in Fig. 1.

2) *Distribution of the fluctuations of the kinetic energy of the atoms in time.* As we have already mentioned, this question is very important for the description of the kinetics of physical processes. The issue is the average waiting time of the fluctuation of the energy of an atom as a function of the magnitude of the fluctuation. In this case, the fluctuations are regarded as events, the interval between which is described by a corresponding temporal distribution function. The data presented above for the instantaneous distribution of the kinetic energy of the atoms do not alone make it possible to answer the question of the temporal distribution of the fluctuations. In addition to the distribution of the instantaneous values of the energy, considered above, it is necessary to have data on the duration of the fluctuation states to resolve this issue. These data can be obtained from the time dependence of the kinetic energy of the atoms, which is similar to the dependence displayed in Fig. 1.

On the other hand, a calculation of the number of fluctuations can be made directly during the computer experiment. The question of the self-consistency of the model can be clarified by comparing the two distributions.

The word "fluctuation" comes from the Latin "fluctuatio" — vibration. In this sense any time-dependent values of the energy of an atom can be called fluctuations. For the further analysis, however, it is useful to use the term fluctuation for the extrema (peaks or valleys) in the time dependence of the energy of the atoms, similar to the dependence displayed in Fig. 1. Then the concept of the duration of a fluctuation state of an atom as the width of a peak or well at a certain height becomes meaningful. It is also useful to measure the energy of a fluctuation from the average energy. Then the values of the energy below the average value appear as negative fluctuations and energies above the average value appear as positive fluctuations. Of course, strong, positive energy fluctuations are of greatest interest. It is because of these fluctuations that the elementary events of many physical and chemical processes occur.

In the computer experiment the number of fluctuations n_{fl} of the kinetic energy of the atoms about the average kinetic energy $\bar{E}_k = (3/2)kT$ was calculated over 150 periods of the oscillations: for positive fluctuations — above prescribed energy levels — $\varepsilon = E_k/kT$ from $\varepsilon=3/2$ (average value of ε)

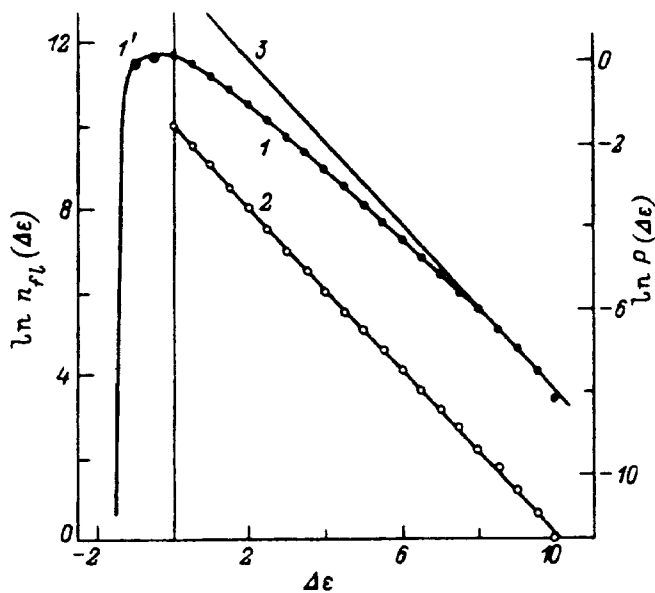


FIG. 4. Integral distribution of the fluctuations of the kinetic energy of the atoms. Calculation over 150 periods of the oscillations. 1 — Direct distribution of the positive fluctuations of the kinetic energy of the atoms, 1' — direct distribution of the negative fluctuations of the kinetic energy of the atoms, 2 — $P(\Delta\epsilon)$ — recalculation of the function 1 according to the formula (4); curve 3 corresponds to the slope of the function proportional to $\exp(-\epsilon)$.

to 10 with a step of 0.5; for negative fluctuations — below prescribed energy levels — from $\epsilon=3/2$ from 0 with the same step.

The number of fluctuations was calculated according to the number of two successive crossings of a given energy level by the curve of the time dependence of the kinetic energy of an atom. The residence time of an atom above a prescribed energy level [$\delta t(\epsilon)$] was also determined. In addition to this method, the number of positive fluctuations “along humps” was also calculated: according to the number of local maxima in the time dependence of the kinetic energy of an atom. For negative fluctuations, correspondingly, the residence times below a given energy level and the number of local minima were considered. Both methods for calculating the number of fluctuations gave similar results. The values of $\delta t(\epsilon)$ were averaged over all atoms and over the total computational time.

The integral distribution function so obtained for the fluctuations over the magnitude of the fluctuations is displayed in Fig. 4. The deviation of the kinetic energy of an atom from the average energy $\Delta\epsilon = \epsilon - \bar{\epsilon}$ is plotted along the abscissa. As one can see from Fig. 4, the distribution of the negative fluctuations lies in a narrow interval from $\Delta\epsilon=0$ to $-3/2$ and it has an n -shaped form. The range of values of the positive fluctuations is much wider. Here, the function $\ln [n_{fl}(\Delta\epsilon)]$ has a similar form to the function $\ln [n(\epsilon)/n_0]$ for the instantaneous values (Fig. 2a). However, there are quantitative differences. The function $\ln [n_{fl}(\Delta\epsilon)]$ has a greater curvature than the function $\ln [n(\epsilon)/n_0]$, and the slope of $\ln [n_{fl}(\Delta\epsilon)]$ for small values of $\Delta\epsilon$ differs more strongly from -1 .

As we have already mentioned, the integral distribution

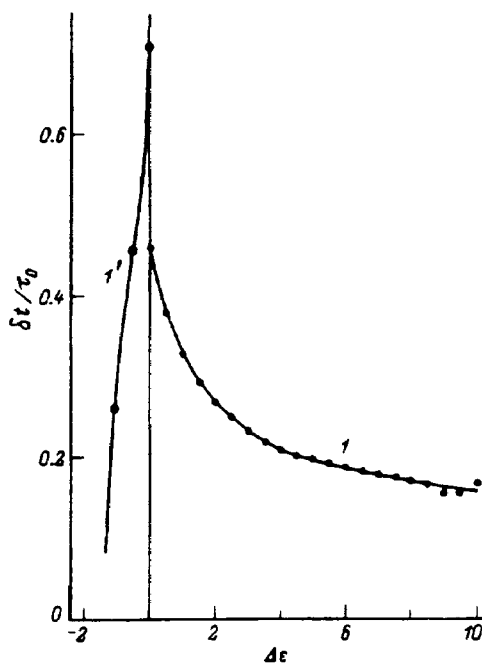


FIG. 5. Average residence time of an atom with kinetic energy different from the average energy. 1 — Above prescribed energy levels, 1' — below prescribed energy levels.

function for the instantaneous values and fluctuations of the energy are related with one another and can be converted into one another if the residence time of an atom above prescribed energy levels (or below levels for negative fluctuations), i.e., the values of $\delta t(\Delta\epsilon)$, is known. Such data obtained for positive and negative fluctuations in the computer experiment are displayed in Fig. 5. One can see that the curves are monotonically decreasing. For positive fluctuations, the slope of the curve decreases as $\Delta\epsilon$ increases.

We now employ the data displayed in Fig. 5 to compare the two integral distribution functions $n(\epsilon)$ and $n_{fl}(\Delta\epsilon)$ for positive fluctuations. Once again, the probability that an atom has a kinetic energy greater than ϵ is

$$W(\epsilon) = \Phi(\epsilon) \exp(-\epsilon) = \Phi(\bar{\epsilon} + \Delta\epsilon) \exp(-\bar{\epsilon}) \exp(-\Delta\epsilon).$$

Then, the relative time t_{fl}/t during which an atom will be in a state with high kinetic energy, greater than $\epsilon = \bar{\epsilon} + \Delta\epsilon$, is

$$\frac{t_{fl}(\Delta\epsilon)}{t} = W(\bar{\epsilon} + \Delta\epsilon).$$

Using the data on the average time $\Delta t(\Delta\epsilon)$ that an atom resides in a state with energy above $\bar{\epsilon} + \Delta\epsilon$ can be written as

$$t_{fl}(\Delta\epsilon) = \frac{\delta t(\Delta\epsilon) n_{fl}(\Delta\epsilon)}{n_0}.$$

Let us take $t = N\tau_0$, where N is the number of periods of vibrations over the computational time, in our case, $N=150$, and the number of atoms in the model crystallite to be $n_0=864$. Then,

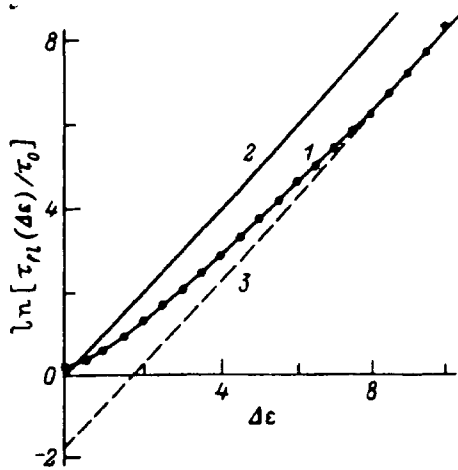


FIG. 6. Average waiting time of positive fluctuations of the kinetic energy of the atoms as a function of the value of the fluctuations. 1 — According to the data of Fig. 4 (curve 1), 2 — corresponds to Frenkel's formula, 3 — linear approximation with unity slope, refining the preexponential factor in Frenkel's formula.

$$\frac{\delta t(\Delta \varepsilon) n_{\bar{n}}(\Delta \varepsilon)}{\tau_0 N} = W(\bar{\varepsilon} + \Delta \varepsilon) = \Phi(\bar{\varepsilon} + \Delta \varepsilon) \exp(-\bar{\varepsilon}) \exp(-\Delta \varepsilon). \quad (4)$$

Hence the resulting function is

$$\ln P(\Delta \varepsilon) = \ln[n_{\bar{n}}(\Delta \varepsilon)] + \ln \frac{\delta t(\Delta \varepsilon)}{\tau_0} - \ln(N n_0) - \ln \Phi(\bar{\varepsilon} + \Delta \varepsilon) + \frac{3}{2} = -\Delta \varepsilon. \quad (4a)$$

The function $\ln P(\Delta \varepsilon)$ constructed according to the data in Figs. 3–5 for positive fluctuations is displayed in Fig. 4 (curve 3). One can see that 1) the dependence has become linear in the entire range; 2) the slope is equal to -1 ; and 3) extrapolating the plot to $\varepsilon=0$ (or $\Delta \varepsilon=-1.5$) gives zero.

Therefore, the equality $\ln P(\bar{\varepsilon}) = -\Delta \varepsilon$ does indeed hold; i.e., the relation (4) is satisfied. This shows that the results obtained in the course of the computer experiment are consistent.

We now consider the average waiting time of the fluctuations of the kinetic energy. The average waiting time $\tau_{\bar{n}}$ of the fluctuation with a magnitude of $\Delta \varepsilon$ or greater is equal to the average time between two such successive fluctuations of the particle energy. This definition makes it possible to find $\tau_{\bar{n}}$ by using directly the data obtained in the computer experiments on the number of fluctuations.

Obviously,

$$\tau_{\bar{n}}(\Delta \varepsilon) = \frac{N \tau_0}{n_{\bar{n}}(\Delta \varepsilon) / n_0} = \tau_0 \frac{N n_0}{n_{\bar{n}}(\Delta \varepsilon)}.$$

Hence

$$\ln \left[\frac{\tau_{\bar{n}}(\Delta \varepsilon)}{\tau_0} \right] = \ln(N n_0) - \ln[n_{\bar{n}}(\Delta \varepsilon)]. \quad (5)$$

A plot of this function, where data on $n_{\bar{n}}(\Delta \varepsilon)$ from Fig. 4 (according to positive fluctuations) were employed, is displayed in Fig. 6. Naturally, the plot of $\ln[n_{\bar{n}}(\Delta \varepsilon)]$ retains its

features (nonlinearity and deviation of the slope from 1).

At high energies ($\Delta \varepsilon \geq 8$) the slope approaches 1, but for intermediate and small positive fluctuations the deviation of the slope from 1 becomes appreciable. The form of the function shows a deviation from Frenkel's formula for the average waiting time of the energy fluctuations¹³

$$\ln \left[\frac{\tau_{\bar{n}}(\Delta \varepsilon)}{\tau_0} \right] = \Delta \varepsilon. \quad (6)$$

It can be concluded that Frenkel's formula is a first approximation, which is valid [according to the slope of Eq. (6)] in the region of quite large fluctuations. As one can see from Fig. 6, however, a linear extrapolation of the function $\ln[\tau_{\bar{n}}(\Delta \varepsilon)/\tau_0]$ to $\Delta \varepsilon=0$ leads to the value $(\tau_{\bar{n}}/\tau_0)|_{\Delta \varepsilon=0} = 0.2$ and not 1, as follows from Frenkel's formula.

The form of the function $\tau_{\bar{n}}(\Delta \varepsilon/kT)$ is an important issue because the activation energies of the most diverse processes are determined on the basis of the form of this function. A more accurate determination of the form of this function could lead to corrections to the activation energies determined and hence to conclusions about the details of elementary events of these processes.

In conclusion, we emphasize that it is the kinetic energy that dominates in the strong fluctuations of the energy of atoms in solids⁸ and thereby plays a leading role in the kinetics of thermally activated processes. At the same time, of course, the analysis of only fluctuations of the kinetic energy does not exhaust the topic of fluctuation dynamics of atoms. It is also necessary to study the statistics of fluctuations of the potential energy and then also the total energy of the atoms.

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