Physics of the Solid State, 2025, Vol. 67, No. 3

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Free volume in the classical model of viscous flow during glass transition

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Received December 24, 2024
Revised March 3, 2025
Accepted March 5, 2025

A modification of the Eyring model is discussed, which takes into account free volume during viscous flow. It is proposed to include free volume directly in the structural model. In this model, repeated vacancies in the material are analogous to sets of edge dislocations on a single sliding plane. The displacement is a cooperative process involving successive „jumps" of groups of atoms (in the one-dimensional case, chains). An inverse proportionality between the Newtonian viscosity coefficient and vacancy concentration is determined. As temperature decreases, vacancy concentration decreases and kinetic unit size (or „structural") increases. This can lead to increased potential barrier and further slowing of glass transition.. Within the framework of the improved model, it has been shown that the frequency of asymmetric local oscillations at vacant positions should be considered as fluctuations of kinetic entities that determine viscosity and the glass transition process.

Keywords: viscosity, vacancy, local vibrations, relaxation, glass.

DOI: 10.61011/PSS.2025.03.60886.350

1. Introduction

One of the most important objectives in the solid-state physics that is often mentioned is the problem of substance transition from a fluid to a vitreous state and related fundamental patterns determining the properties of glass [1–5]. The process of substance vitrification and fundamental patterns that determine the concomitant characteristics and properties of the material are the object of the continuous research in connection with the need to solve the key objectives of condensed matter physics and material science. Vitrification, as is widely recognized, is not a classic phase transition and comes under a denomination of a relaxation transition [6–8]. Drastic decrease near the vitrification temperature in the time of molecular relaxation (time of structure rearrangement) causes the fixation in the solid state of the non-equilibrium structure of the fluid. Usually, for the glass-forming materials, two types of relaxation processes are discussed: (i) primary (also called α) relaxation, which is present near the vitrification temperature (T_g); and (ii) secondary (β) process, which has a smaller amplitude and is detected at temperatures below T_g [9–11]. β-relaxations and α-relaxations for the amorphous materials were observed on the basis of dielectric or mechanical spectroscopy. Temperature dependence of α-process is complicated, while the secondary β-relaxation is subordinate to Arrhenius temperature dependence. The research shows that β-relaxation is related to the localized atomic or molecular motion, while α-relaxation corresponds to more complicated and correlated motions of atoms or molecules. Relaxation processes in disordered media, in particular, determine the availability of bosonic peak phenomenon in them — abnormal rise of density of oscillating states in the material in the low-frequency area from several to several dozens of reciprocal centimeters (dozens−hundreds GHz). The microscopic nature of excitations, determining the nature of the bosonic peak, has been studied for several decades already, and recently this subject got „a second wind" in connection with the appearance of the new promising materials with the specified thermodynamic, optic and mechanical properties [12–22]. The possibility of the controlled modification and/or control of the material properties (for example, glass) using various methods is also of substantial interest from an applied perspective [23].

The relaxation nature of the vitrification process and the versatility of this phenomenon were effectively confirmed by production of amorphous metals and alloys [24,25]. After a classic experiment by P. Davez in 1960 the first amorphous metals were obtained, which were vitrified at cooling rates 10^8-10^{10} K/s. Transition to alloys vitrified at the rate of $1-500$ K/s, made it possible to widely use the unique properties of amorphous metals in most diverse pertinent arts.

Macroscopic process of frictional flow under various temperatures in the vitrification area makes it possible to

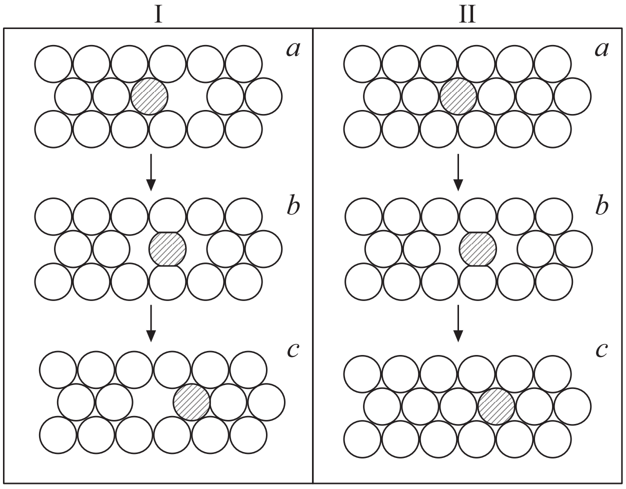

Figure 1. Two mechanisms of transition from initial state (a) via activated complex (b) to end state (c).

decide on the change in time of molecular relaxation in this area. Frictional flow is defined by thermofluctuational transitions of certain kinetic units into a new equilibrium position, in the adjacent more or less „vacant" areas of the structure making the so called free volume. In the unassociated simple fluids such kinetic units are atoms (molecules), in polymers and glasses — individual areas (segments) of the structure. Therefore, in all models and theories of vitrification and models of frictional flow the free volume is present in a certain form. It is also important to note that the free volume determines the frictional flow and self-diffusion in the material.

The value of the free volume to a certain extent depends on the physical process that it manifests itself in: in process of microindentation of inorganic glass the free volume makes it possible for the lattice of Si$-$O$-$Si to fold and compact; in the method of positron annihilation, a positron is captured by certain defects of the glass or polymer structure (free volume elements); in the experiments on gas permeability, the decisive role for the substance diffusion is played by the comparative size of nanopores, etc. At the same time there is an evident correlation between the values of the free volume obtained by different methods.

Bachinsky [26] demonstrated that viscosity of fluid at its permanent volume, despite pressure and temperature variations, practically does not change. This conclusion was confirmed experimentally and made it possible to assess the free volume at approximately 10$-$15%. The obtained results indicated the decisive role of the free volume in the frictional flow mechanism. However, the free volume in this process is interpreted by two different models.

In the models of the first type (Frenkel, Eyring etc., [27–30]) the fluid is seen as binary mix of molecules and vacancies. A kinetic unit changes to the neighboring vacancy, the vacancy moves to its place and is available for the transition of the next neighboring unit (Figure 1, a).

The volume of vacancies calculated from the experimental data on impact of pressure at viscosity, turned out to be equal for simple fluids to $1/6-1/7$ of the molecule size. This corresponded to the free volume of only approximately 3%, and A in total. Miller [31] was one of the first researchers who noted the uncertainty of the free volume concept. Accordingly, they started separating geometric („frozen") free volume and the one that determines viscosity, physical or fluctuation one [32,33].

The geometric free volume may be calculated using available methods [34], which take into account the atomic structure of the substance.

In the papers after Eyring (*for example*, [35–41]) they mainly analyzed the exponential component in the expression for the viscosity, reflecting the probability of elementary act of transition through the barrier. At the same time the attention was paid not to the structural model, but to thermodynamic relations. Simultaneously, empirical formulae were offered for dependence of viscosity on the free volume, based on a priori representations on the role of the latter. In the empirical equation of Doolittle [35] the free volume is included in the exponent parameter; accounting of free volume distribution by atoms and their groups added a small correction to its formula, equal to $\sqrt{2}$ [36]. In the valence-configuration theory by S.V. Nemilov [8,39,40] a matter of principle is considered — interaction of the elementary act of frictional flow with the environment, which made it possible to include deformation characteristics of the latter into consideration. Yu.S. Lipatov in the review [33] analyzed in detail various concepts of the free volume and their relation to empirical formulae, describing the vitrification process, including in respect to the amorphous polymers, and also contradictions that arise. New opportunities opened with the application of the method of molecular dynamics [41]. However, the Eyring model remains a basic molecular model.

Second interpretation of the free volume considers vacancies as continuously arising and disappearing fluctuations of the structure due to the oscillating thermal movement of the molecules. A molecule in this case may or may not have time to go to the vacancy it created (Figure 1, b). Therefore, these two approaches differ by the comparison of the vacancy life time and time of transition of the kinetic unit that created it therein.

According to the estimates of Eyring [27], for many substances the energy of vacancy generation is substantially higher than the energy of transition through a potential barrier, which the kinetic unit overcomes in transition. In our opinion, this makes the second variant of interpretation of the free volume role in the frictional flow more probable. The corresponding idea was implemented in the semiclassical model of vitrification as „freezing" for the specific frequency of kinetic unit oscillations [42]. The theoretical model of localized atoms was developed in series in papers by D.S. Sanditov et al. [43–45]. At the same time particular prominence is grained by the research of relaxation pro-

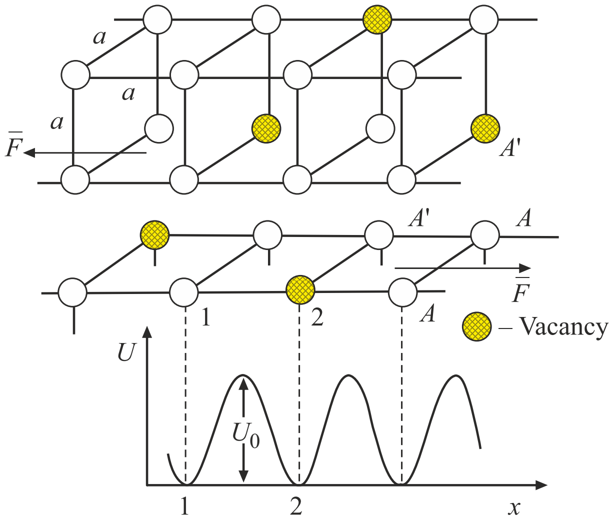

Figure 2. Shear of atomic plane $A_1 - A_1$ relative to plane $A - A$ due to independent transitions of atoms into vacancies, preferably in direction of the force, with transition over a potential barrier U_0.

cesses microscopy (see *e. g.,* review [41]), which explain, in particular, strength properties of solid bodies [46].

At the same time the discussed models contain some disagreements, related in our opinion to incomplete accounting of microscopic features of the free volume and its role in various processes (frictional flow etc.). In particular, Eyring theory predicts the rise in the medium viscosity with increase of the free volume, which seems to be a rather contradictory consequence of the model.

In this paper we offer the clarification, which makes it possible to introduce a free volume value directly into the structural model, which makes it possible to correctly describe the role of free volume in process of frictional flow.

2. Frictional flow model according to Eyring

In the kinetic theory of frictional flow by G. Eyring [27–29] the free volume in the form of vacancies is a principal element of the model, providing for thermofluctuational mechanism of frictional flow of solid body or fluid (Figure 2).

In an ideal crystal the shear should occur at the expense of simultaneous pulling of interatomic bonds between the sheared atomic planes, then their simultaneous break with a shear by value a and establishment of a new equilibrium distribution of atomic bonds, which is immediately damaged — the process continues. Thermal fluctuations play no role, the shear occurs at the stresses of more than a certain critical value — theoretical shear strength.

To simplify the calculations, in the Eyring model the atoms form a simple cubic lattice; for a fluid state the value a means the average value of interatomic distances. In the atomic chain selected for consideration, the potential energy of atoms 1, 2 and further is a periodical function of coordinate x.

The shear is accumulated due to independent transitions of atoms into the neighboring vacancies at their thermofluctuational transition over the potential barrier U_0. The role of the external force consists in increasing the probability of such transitions in direction of the force and decreasing the probability of the reverse process. At comparatively low shear stresses the theory yields a Newtonian flotation equation, and the process of such shear is possible at arbitrary small stress, but accordingly with the low deformation rate. The transmission ratio characterizing „success“ of the transition over the barrier, is assumed to be equal to one, and tunnel effects are neglected.

Newtonian viscosity coefficient η according to Eyring is

$$\eta = \frac{k_B T}{\nu_0 a^3} e^{U_0/(k_B T)}, \qquad (1)$$

where ν_0 — frequency of thermal oscillations of atoms equal by order of value to 10^{12}–$10^{13}\,\mathrm{s}^{-1}$ (infrared area); a — average interatomic distance; U_0 — potential barrier for atom transition from one equilibrium position to another (Figure 2).

In the original model [28]

$$\nu_0 = (2\pi k_B T/\hbar) F_1/F,$$

where F_1 and F — sums of stages of the activated complex (transition state at the top of the potential barrier) and the initial state of the atom.

However, the specific value of free volume (specific or per mole of solid body) in this structural model is not taken into account. At the same time, in various theoretical models of vitrification, as it was shown above, the value of the free volume is of fundamental importance for the viscosity value.

Eyring further introduces the free volume v_f in terms of one molecule via a sum of states F for the atom (kinetic unit) in the non-activated state and the sum of states F_1 of the activated complex (transition state). It is assumed that $F \sim v_f$, and in the number of states of the activated complex F_1 it is taken into account that one degree of freedom is excluded — forward movement by reaction coordinate. At the same time the subspace of coordinates is reduced, which causes certain doubts. As a result, the free volume is included in the expression for frequency ν_0, and as a result, the viscosity coefficient turns out to be dependent on v_f in the following manner [28]:

$$\eta = v_f^{1/3} (2\pi \cdot m_k \cdot k_B T)^{1/2} / a^3 \exp(U_0/k_B T), \qquad (2)$$

where m_k — mass of kinetic unit.

Therefore, in the Eyring theory the viscosity increases with the increase of the free volume, which contradicts the concept itself of its role in the frictional flow.

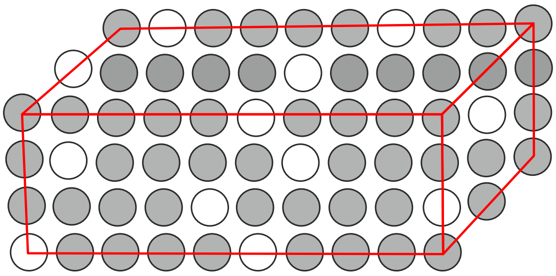

Figure 3. Model of 3D crystal with vacancies.

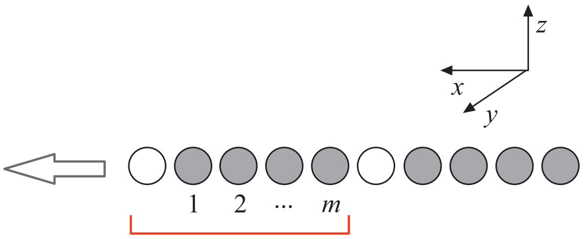

Figure 4. Recurrent „structure" of one vacancy and m atoms.

3. Confirmed structural model of frictional flow according to Eyring with account of the free volume value

Let us consider a simplified model, where the free volume in the form of individual vacancies is statistically, but comparatively evenly (at macroscopic scale) distributed in the crystal volume with a simple cubic lattice (Figure 3).

If the distance between the atoms is equal to a, then the number of lattice sites N in a single cube is a^{-3}. Let N_ν sites of those are vacancies, i. e. concentration of vacancies is $n_\nu = N_\nu/N$. Low concentration of vacancies in solid bodies up to fusion makes it possible to consider them as single, not interacting objects.

The Eyring model is actually unidimensional. Two planes are sheared relative to each other at the expense of an independent shear of atom chains, where atoms „transition" only to vacancies of this chain (Figure 2). The chain direction depends on the shear direction. Staying within this model, let us consider one of the atom chains.

At the strictly even distribution of vacancies the chain is a repeating structure from individual vacancies, alternating with atoms in the quantity of m (Figure 4).

In fact, m is an average value. Transitions inside each structure may be assumed independent. In the left structure they start from the transition of atom 1 to the vacancy on the left; then atom 2 may transition to the opened vacancy, etc. The right structure regardless of „performs" the same manipulation, but will only be able to move to the left by one interatomic distance only when a vacancy remains in the place of atom m of the first structure. That is when all structures in the chain and the chain as a whole will move to value a.

In the Eyring theory the effective number of transitions n of each atom in direction of the force action per unit of time, i. e. the difference in the number of transitions along with and opposite to the force action, with the Newtonian flotation is

$$n \approx \frac{\nu_0 a^3 \sigma_{\mathrm{sh}}}{k_{\mathrm{B}} T} e^{-U_0/(k_{\mathrm{B}} T)}, \tag{3}$$

where σ_{sh} is shear stress.

At the same time each transition is seen as a shear of the entire atomic chain by value a, and n matches the deformation rate. In fact, as it was shown above, a transition of one atom inside each „structure" is not sufficient for the shear of the entire chain — single transitions must accumulate in a certain way. So that „a caterpillar" moves one step ahead, all its „legs" must make the same step in turn. The situation is similar to the shear of crystal with a single edge dislocation. The dislocation line moves in the sliding plane, the shear area follows it, but nothing happens macroscopically. A shear in the form of a single-atom step on the crystal surface is only implemented when the dislocation line exits on the surface.

In our model the recurrent vacancies in the structure are similar to the set of dislocation lines in one sliding plane. They may be seen as unidimensional dislocations, and the shear is a cooperative process, as the movement of ordinary dislocations in the crystal. The principal difference consists in athermic mechanism of atomic structure rearrangement in process of dislocation movement and thermofluctuational one in case of frictional flow.

With our confirmation of the model, the shear of the entire chain by the value of interatomic distance will only occur after m transitions in force direction (independently in each structure), and the deformation rate is not n, but n/m. Accordingly, in the final formula for viscosity an additional coefficient will appear, the confirmed value of viscosity η_1 is

$$\eta_1 = \eta\, m, \tag{4}$$

where viscosity η is set by formula (1), and Eyring model actually assumes $m = 1$.

To determine value m, let us refer to the 3D model of cubic lattice with statistically even distribution of single vacancies (Figure 3). A single crystal with a cubic lattice, containing N atoms, contains $N^{2/3}$ atomic chains with length $N^{1/3}$. Among them, N_ν vacancies are randomly distributed. One chain in average contains vacancies $N_1 = N_\nu/N^{2/3}$, and the distance between them in average is $N^{1/3}/N_1 = N/N_\nu = n_\nu^{-1}$, where n_ν — concentration of vacancies.

Therefore, the average distance between vacancies is $a n_\nu^{-1}$, and

$$m = n_\nu^{-1}, \tag{5}$$

and with account of formulae (1) and (4) this provides the following expression for Newtonian viscosity in the confirmed model:

$$\eta_1 = k_{\mathrm{B}} T/(\nu_0 a^3 n_\nu) \exp\left(\frac{U_0}{k_{\mathrm{B}} T}\right). \tag{6}$$

Viscosity does not depend on dimensions of the crystal (i. e. N), therefore the free volume is included in formula (6) in the form of vacancy concentration.

It is possible to strictly calculate the average value m in the atomic chain, assuming probability W_ν to meet a vacancy in this site equal to $W_\nu = n_\nu$, and probability W_a to meet atom $W_a = 1-n_\nu$. In this case we receive the average value $\langle m \rangle = n_\nu^{-1}$, i. e. the same result.

The Eyring model does not consider the transitions of atoms into vacancies between planes of share and in this plane perpendicularly to shear (Figure 3). Now let us consider these opportunities.

For an atom in a chain directed along the shear (axis x in Figure 4) to transition to the nearest vacancy, it is necessary for it not to have an opportunity to transition to a vacancy of one of the neighboring chains, i. e. along axis y or z. At the same time, in our model the vacancies in these axes may only be located on one of the sides of the considered atom chain (which corresponds to really low density of vacancies). In both case the probability of vacancy absence along axis y or z is

$$W_y^1 = W_z^1 = m/(m+1) = 1 - 1/(1 + n_\nu^{-1}) \approx 1.$$

The probability of atom transition along axis x may now be recorded as the product of probabilities, and at the expense of low concentration of vacancies it practically does not change compared to the unidimensional case:

$$W_x = e^{-U/(k_\mathrm{B}T)}\, W_y^1 W_z^1 \approx e^{-U/(k_\mathrm{B}T)}, \qquad (10)$$

where according to the Eyring theory $U = U_0 \pm \delta A$; δA — elementary work of shear stress against the shear direction or along therewith.

Possible transitions of atoms and vacancies of neighboring chains perpendicularly to the shear direction increase or decrease the value m in this chain. However, value m is of statistical nature, and the probability of such „transverse" transitions does not depend on the value of the applied shear stress and does not impact viscosity directly.

Note that our confirmation relates not only to Newtonian viscosity, but to the entire Eyring model, including the area of Newtonian flotation.

The proposed geometric model is fair for the second interpretation of the free volume, uniting in a single process the occurrence of the vacancy and transition of a molecule therein, which „was affected by" a fluctuation (Figure 1, b). In this case value m changes not only from one „structure" to the other, but in time in every structure, but this does not affect our general conclusions.

As temperature falls, the concentration of vacancies decreases (even though the equilibrium structure has no time to settle), and m, i. e. structural unit length, increases. In opinion of some researchers, the increase in the size of the kinetic unit may lead to increase of the potential barrier U_0 and additional acceleration of the vitrification process. In our model, as in the Eyring model, the kinetic unit is an individual atom (a segment of the glass or polymer structure); transitions of kinetic units inside „the structure" into the vacacny are independent processes. In fact such change of the equilibrium position in the condensed medium must cause local elastic oscillation, disturbing the entire „structure" and making it a certain kinetic supraunit. The process „of the structure shear" by value of interatomic distance is a cooperative process with such approach, which covers all m atoms. Then the elongation of the „structure" we introduced with the decrease of the temperature is equivalent to the increase in the effective size of the kinetic unit. This correlates to the representations of Adams and Gibbs on the decrease of configuration entropy nearing the Kozman temperature at the expense of increasing the number of molecules within a kinetic unit [37,47].

4. Role of impurity local oscillations of lattice

The viscosity formulae (3) and (6) include a frequency of oscillations ν_0 of kinetic units responsible for the vitrification process. Above we noted that according to Eyring $\nu_0 = (2\pi k_\mathrm{B}T/\hbar)F_1/F$, where F_1 and F — sums of stages of the activated complex (transition state) and the initial state of the kinetic unit. Many researchers interpret ν_0 as the specific frequency of the lattice oscillations and is compared, for example, to the Debye frequency [45]. In fact the transition of the atom to the vacancy, i. e. the frictional flow mechanism, is determined by frequency of local oscillations at the vacancy and their peculiarities. Therefore, it is desirable to do certain estimates of value ν_0.

The interest in localized states on defects and disorder of the structure became active in the middle of XX century [48–55]. The reason was the understanding of the dependence of multiple properties of solid bodies on their real structure, as well as the appearance of new theoretical and experimental methods. Accordingly, the literature contains solved problems on local oscillations at vacancies close to our problem.

The first fundamental calculations on impact of defects at the crystalline lattice oscillations were made by I.M. Lifshits et al. [48].

For unidimensional crystals rather simple formulae were obtained in papers [51,52]. The authors, using the general method of Green's function that they developed, solved the problem of local oscillations in a unidimensional simple lattice with a single zero-dimensional defect that could be an atom of impurity (including isotopic one). Generally the defect differed from the atoms of the lattice either by mass or bond of abnormal elasticity. Using this result and formally believing that the defect mass was equal to zero, the authors [50] recorded the frequency of local oscillations at the vacancy as

$$\omega = 0.5\,\omega_L(\gamma_2/\gamma 1)/(\gamma_2/\gamma_1 - 1)^{1/2}, \qquad (11)$$

where ω_L — maximum value of acoustic frequency of oscillations in a unidimensional defect-free lattice, γ_1

and $\gamma_2 > \gamma_1$ — elasticities of bonds (in harmonic approximation), corresponding to the interactions of atom–atom in the non-distorted lattice and vacancy — neighboring atom. The problem is solved in the close-range interaction approximation by the successive approximation method. Impurity oscillation is characterized as a pulsating antisymmetric one (between the vacancy and the neighboring atom).

The assumption that the elasticity γ_2 of interaction between the vacancy and the neighboring atom is higher than between the atoms of the main lattice causes certain doubts. The authors justify it by the fact that the occurrence of the vacancy makes neighboring atoms get somewhat closer. However, it will change the forces of interaction, but not necessarily the elasticity. The elasticity of bonds as such at minor deformation may be treated as constant, and at the substantial distance between the atoms at both sides of the vacancy γ_2 as knowingly lower γ_1.

Madelung previously [49] demonstrated that in a unidimensional simple lattice with a single defect (impurity, vacancy) a local oscillation may occur with frequency detachment above the maximum acoustic one provided that the mass M_1 of the impurity atom is lower than the mass M of the main lattice atoms. For the vacancy with $M_1 = 0$ this condition is met.

In a lattice with a basis (for example, two atoms in a cell with masses M_2 and M_3) under the same condition (M_1 smaller than the mass of any atom in the cell), local oscillations occur above the optic branch. At the same time, as in the ordinary optic branch, at $k = 0$ the atoms in the cells oscillate in opposition, but the oscillation amplitude near the defect is higher.

Slit local oscillations arise at the boundaries of the first Brillouin zone between energy zones of acoustic and optic oscillations provided that $M_2 > M_1 > M_3$. For the vacancy with $M_1 = 0$ this condition is met. This case is illustrated in Figure 5, *b*.

Resonant local oscillations inside the energy zone of acoustic oscillations (at low value of wave vector) are characterized by high amplitude of defect displacement, which is related to the small displacement of many neighboring atoms.

All these cases are illustrated in Figure 5, taken from the monograph [49].

Further we will consider the dynamics of the chain of atoms including a set of the „structures introduced above“. For half-quality assessment of local oscillations, we will solve the problem using the known scheme, based directly on the initial simple ratios for the forces of interactions between the atoms.

Actually we consider a unidimensional crystal with periodically arranged vacancies (Figure 6). We are interested in oscillations along the reaction path, i. e. longitudinal oscillations along axis x. Such unidimensional problem, naturally, will not fully reflect the oscillations of a 3D crystal with vacancies.

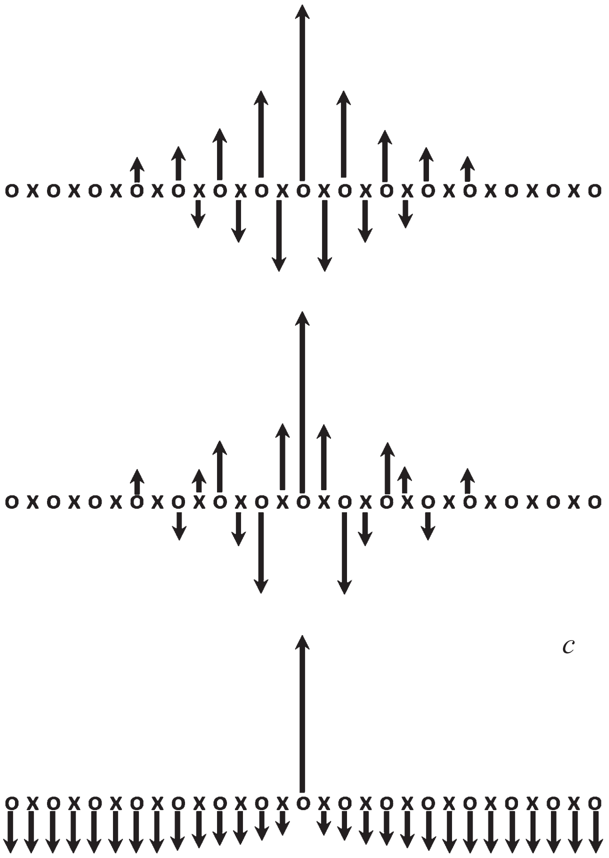

Figure 5. Comparison of phases and amplitudes of local oscillations at zero defect and long-wavelength oscillations of other atoms of a unidimensional crystal with diatomic basis [50].

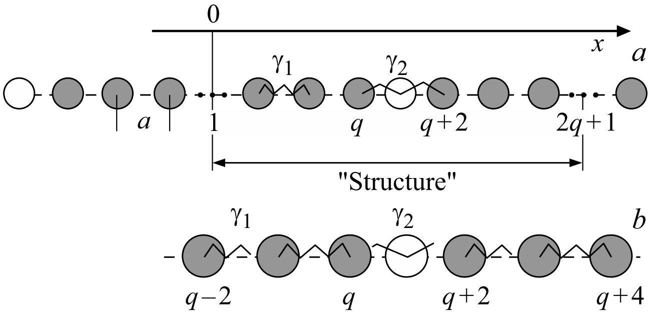

Figure 6. *a*) Model of atomic chain comprising „structures“; *b*)area of local oscillations.

For convenience of the calculation, we will place the vacancy in the middle of the „structure“ and will assume m an odd number ($m = 2q$), which is quite permissible at huge value m. We will number atoms in the structure from 1 to $(2q + 1)$, having assigned number $(q + 1)$ to the vacancy. The first atom in „the structure“ will be placed in the origin of coordinates. The distance between neighboring atoms of the main lattice will be designated as a, the distance between atoms near the vacancy with numbers q and $(q + 2)$ will be designated as b.

We use harmonic approximation. In contrast to model [50], we will consider not the formal elasticity of the

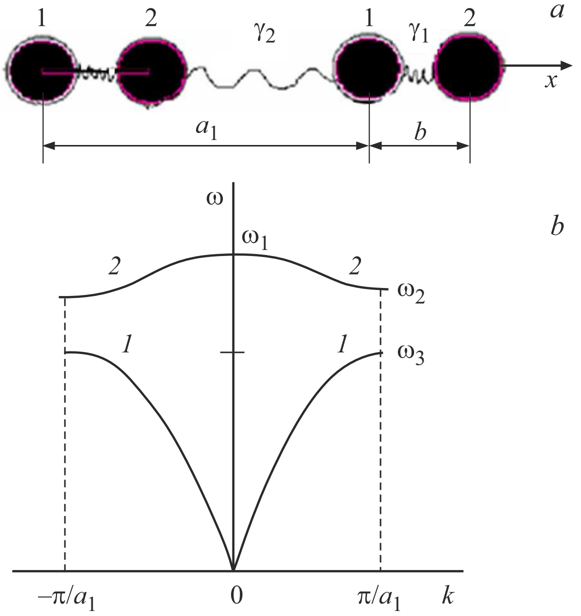

Figure 7. *a*) Unidimensional crystal (complex lattice); *b*) acoustic (*1*) and optic (*2*) branches of disperson law in the first Brillouin zone.

bond between the vacancy with the zero mass and its closest atom, but the elasticity of the bond between the atoms separated by the vacancy, i. e. with numbers q and $(q + 2)$.

Our problem is close to the problem of unidimensional crystal dynamics with a complex lattice, where atoms are same, but two values of interatomic bond elasticity alternate: γ_1 and $\gamma_2 < \gamma_1$ (Figure 7, *a*).

In this case the analysis of longitudinal oscillations along axis x leads to two branches of the dispersion law: acoustic and optic, with the prohibited area between them (Figure 7, *b*). If you designate A_1 and A_2 amplitudes of oscillation with frequency ω in atoms of type 1 and 2 in Figure 7, *a*, then at wave vector $k \ll \pi/a_1$, where a_1 — vector of elementary transmission of a unidimensional crystal, $A_1 = -A_2$. This means that in long-wavelength oscillations, i. e. practically at the same phase, atoms 1 and oscillate towards each other relative to the common center of gravity as in the case of the intramolecular oscillations. And the frequency is maximum (Figure 7, *b*) and is equal to $\omega_1 = [2(\gamma_1 + \gamma_2)/M]^{1/2}$.

In the considered case, in contrast to the problem given above, between the sections with „weak" bond (with the vacancy) there are many normally interacting atoms.

We assume that for atoms from No. 1 to No. $(q-2)$ and from No. $(q + 4)$ to No. $(2q + 1)$, which in the approximation of close-range interaction „sense no" presence of the vacancy, the dispersion law is met for a unidimensional simple lattice

$$\omega_L = 2(\gamma_1/M)^{1/2}\,|\sin(ka/2)|. \qquad (12)$$

Maximum frequency value is $2(\gamma_1/M)^{1/2}$.

Long-wavelength oscillations of the main lattice, with the wavelength of substantially lárger size than its distortions around the vacancy (i. e. several constants of the lattice), will „not sense the presence of vacancies". It is known that local oscillations decrease exponentially with the distance from the defect. Therefore, inside our „structure" we will identify a defect including the vacancy itself and two nearest atoms on the right and on the left (Figure 6, *b*). We are interested in the oscillations of this „substructure". The calculation is done with the assumption on the centrality of the action of interatomic forces in harmonic approximation and in the close-range interaction approximation.

Let us designate via U and U' amplitudes of normal oscillations with frequency ω for atoms with numbers $(q-1)$ and $(q + 3)$, U_1 and U_2 — for atoms near the vacancy with numbers q and $(q + 2)$. We assume the oscillations of atoms number $(q-2)$ and $(q + 4)$ the same as oscillations of atoms of the main lattice, and we will designate their amplitude as U_0.

For the force acting at q the atom, at frequency ω the following may be recorded (taking into account the fact that the first atom is located in the origin of coordinates):

$$\begin{aligned} F = M\ddot{u}_q &= -M\omega^2 U_1 \exp[i(\omega t + ka(q-1)] \\ &= \gamma_1\{U \exp[i(\omega t + ka(q-2)] \\ &\quad - U_1 \exp[i(\omega t + ka(q-1)]\} \\ &\quad + \gamma_2\{U_2 \exp[i(\omega t + ka(q-1) + kb] \\ &\quad - U_1 \exp[i(\omega t + ka(q-1)]\}, \end{aligned}$$

which after the cancellations and transition to cosines provides

$$U_1[M\omega^2 - (\gamma_1 + \gamma_2)] + U_2\gamma_2\cos(kb) + U\gamma_1\cos(ka) = 0. \qquad (13)$$

Similarly for $(q + 2)$th atom we get

$$U_2[M\omega^2 - (\gamma_1 + \gamma_2)] + U_1\gamma_2\cos(kb) + U'\gamma_1\cos(ka) = 0. \qquad (14)$$

For atoms number $(q-1)$ and $(q + 3)$ the formulae are the following:

$$U[M\omega^2 - 2\gamma_1] + U_1\gamma_1\cos(ka) + U_0\gamma_1\cos(ka) = 0, \quad (15)$$

$$U'[M\omega^2 - 2\gamma_1] + U_2\gamma_1\cos(ka) + U_0\gamma_1\cos(ka) = 0. \quad (16)$$

Assuming that atom oscillation amplitudes are unknown, we obtained 4 equations with 5 variables. Further, based on the symmetry assumptions, we may assume that either $U_1 = U_2$, or $U_1 = -U_2$, as in the case of atoms of type 1 and type 2 in Figure 7, *a*.

In the first case the equation $U_1 = U_2$ and formulae (13) and (14) lead to equation $U = U'$, the number of variables reduces down to three (U, U_1, U_0), and the number of independent formulae — to two. $U = U_0$ may be accepted as approximation, thus reducing the area of deformations

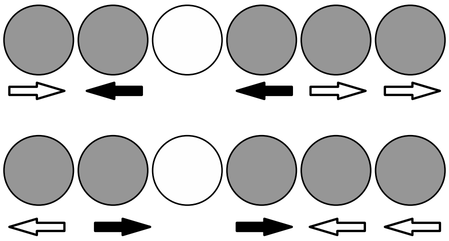

Figure 8. Directions of oscillations of unidimensional crystal atoms around vacancy at $k = 0$ and $\omega_2 = (2\gamma_1/M)^{1/2}$.

around the vacancy. Then we obtain a system of two equations with two variables:

$$\begin{cases} U_1[M\omega^2 - (\gamma_1 + \gamma_2) + \gamma_2 \cos(kb)] + U\gamma_1 \cos(ka) = 0, \\ U[M\omega^2 - 2\gamma_1 + \gamma_1 \cos(ka)] + U_1\gamma_1 \cos(ka) = 0. \end{cases} \tag{17}$$

We exclude a trivial solution $U_1 = U = 0$. In this case the system determinant is equal to zero, from where for $x = M\omega^2$ we obtain a square equation (similarly to the above problem).

For $k = 0$ (long-wavelength oscillations) we have two solutions:

$$\omega_1 = 0; \quad \omega_2 = (2\gamma_1/M)^{1/2}. \tag{18}$$

When we substitute these frequency values in one of equations (17), we get accordingly:

- at ω_1 $U_1/U = 1$, atoms at the sides of the vacancy oscillate in phase;
- at ω_2 $U_1/U = -1$, which means that atoms around the vacancy oscillate in opposition to their neighbors (Figure 8), similarly to the oscillations in the optical branch Figure 7 at $k = 0$.

Both frequencies are within the energy zone of acoustic oscillations (resonant oscillations).

In the second case the assumption that $U_1 = -U_2$ and equations (13) and (14) led to equation $U = -U'$. (15) and (16) lead to $U_0 = 0$. We get two independent equations relative to U and U_1, the standard calculation provides two positive frequencies, which depend on γ_1 and γ_2. The ratio sign U/U_1, i.e. symbasis or asymmetry of atom oscillations around the vacancy is determined at the same time by the sign of value $(\gamma_1 - 2\gamma_2)$.

Therefore, the important feature of local oscillations at the vacancy is their antisymmetry, noted already in paper [49], which promotes atom transition into a vacancy in case of long-wavelength oscillations.

Further analysis may include review of various values of the parameter b. From the calculations by some authors it follows that the vacancy size must be noticeably smaller than the interatomic distance. A variation of elastic constants is also of interest, which takes into account the specific potential of interatomic interaction. In the papers of recent years (*e.g.,* [54–57]), using more accurate theoretical methods, mainly when applicable to 3D ion crystals, semiconductors and metals, the important role is played by selection of model potential of interatomic interaction, including with long-range action. The nature of interatomic interaction will also determine the ratio of elasticities in bonds γ_1 and γ_2.

The most advanced models make it possible to numerically model phase transitions, to determine material characteristics of the medium [58–61].

In the above papers [54–57] the attention is mostly paid to real 3D lattices, including with long-range action and at high concentration of impurities. For our problem of frictional flow in the vitrification area, the conclusions are substantial on the availability of certain criteria on characteristics of zero-dimensional defect, when local oscillations appear, and also the critical concentration of defects, starting from which local oscillations start interacting. These conclusions may be qualitatively related to the size of the vacancy in the „structure“ and temperature dependence of the structure length.

5. Conclusions

1. A difference is specified in two types of models describing the role of free volume in the process of frictional flow. In the first case (Frenkel–Eyring model) the free volume means vacancies, colliding with which, the kinetic units may transition to another equilibrium position due to thermal fluctuations. The vacated place (vacancy) remains and is available for transition of the next neighboring kinetic unit. In the second case the vacancy is created by the atom itself in the process of its thermal oscillating motion. An atom in this case may or may not have time to go to the vacancy it created, i.e. change the equilibrium position. The vacancy disappears and appears in another place in the structure.

2. It was proposed to confirm the classical structural model of frictional flow according to Eyring, which considered every elementary shear not as a single act of transition of a single atom over a barrier, but as a cooperative process of subsequent transitions in the group of atoms („of the structure“). The process is similar to the motion of unidimensional dislocations, but occurs at the expense of the thermofluctuational transition through a potential barrier. Such approach is also applicable to the models of the second type, but parameter m acquires the double statistical meaning (spatial and temporary).

3. The model confirmation results in inverse relationship of the Newtonian viscosity coefficient with the vacancy concentration (relative free volume).

4. As the temperature decreases, the vacancy concentration decreases, and the length of the „structure“ we introduced increases. The cooperative nature of all disturbances in the condensed medium in reality makes a single shear „of the structure“ basically a cooperative process. In this case its elongation is equivalent to the increase of the effective size of the kinetic unit. In opinion of some

researchers, the increase in the size of the kinetic unit may lead to increase of the potential barrier U_0 and additional acceleration of the vitrification process. This also correlates to the representations of Adams and Gibbs on the decrease of configuration entropy nearing the Kozman temperature at the expense of increasing the number of molecules within a kinetic unit.

5. The frequency of oscillations of kinetic units that determine viscosity and vitrification process should be the frequency of antisymmetric local oscillations at vacancies.

Acknowledgments

The authors express their sincere gratitude to Ya.M. Beltyukov for the spoken assumptions and fruitful discussion of the model.

Funding

The study was performed under the state assignment of the Ministry of Education of the Russian Federation „Physics of Nanostructured Materials and High-Sensitivity Sensorics: Synthesis, Fundamental Research and Applications in Photonics, Life Sciences, Quantum and Nano-Technology" (subject No. 124031100005-5).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by M.Verenikina