Hardness of a Crystal Lattice as Consequence of Quantum "Freezing" of Atomic Degrees of Freedom

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It has been shown that in the classical computer model the "matter of a crystal" has the kinetic and mechanical properties of a dense gas or a simple liquid at any temperature, including the area near the absolute zero. Agreement with the experiment and a stable hard crystal structure with high enough real activation energy (for instance $E \approx 40RT_\mathrm{m}$) can be obtained if quantum effects and especially quantum "freezing" of atomic degrees of freedom are introduced in the model.

Key words: Quantum "Freezing"; Lattice Stability; Solidification; Atomic Quantum Effects; Computer Simulation.

1. Introduction

In the classical computer model the "matter of a crystal" has the kinetic and mechanical properties of a dense gas or a simple liquid at any temperature, including the area near the absolute zero. In the context of such a theory a solid cannot exist and therefore there is no solidification of a liquid. If we consider the classical motion of atoms and the usual interactions, the atomic system is not stable enough against rearrangements of the atoms that correspond to plastic or viscous flow, diffusion, ionic transport etc. Always only fluid structure is obtained. The energy barriers E in the model, which are surmounted at regrouping of atoms, are not large compared with the heat energy RT_m, where T_m is the temperature of melting. Agreement with the experiment and a stable hard crystal structure with high enough real activation energy (for instance $E \approx 40RT_\mathrm{m}$) can be obtained if quantum effects and especially quantum "freezing" of atomic degrees of freedom are introduced in the model.

2. State of the Art

Many results of computer experiments on simulation of crystals and crystallization have been collected in the literature by now. But researchers usually do not determine those characteristics of a "crystal" that allow to distinguish a crystal from a liquid and show that it is a crystal indeed. It has not been found out whether a structure has mechanical strength or high enough viscosity typical for a solid. It has not been clarified whether diffusion coefficients, ionic conductivity and other kinetic coefficients of a "crystal" in the model correspond to reality or not. Stiffness of the structure, i. e. the activation energy E_A, has not been considered, and it has not been found out whether the phase in the model has the same strict long-range order and sharp phase transitions as a real crystal, and whether these transformations occur over narrow temperature intervals or not.

Only those properties which are qualitatively the same for a liquid and a crystal, for example the energy of the structure, specific heat, compressibility and elastic modulus, are under determination. Doubtless formation of a "crystal" is considered to be obvious if an ideally regular structure and a temperature below the melting point were present at the beginning of the calculation.

The coefficients of viscosity, diffusion etc. are sometimes determined for overheated simple liquids, where the model provides wholly satisfactory agreement with the reality, but not for lower temperatures, for example for a glass or a crystal. In these cases, the discrepancies between the model and reality reach really catastrophic values, e. g. 15 – 20 orders of magnitude for viscosity. If, nevertheless, the listed distinguishing properties of the "crystal phase" are sometimes determined in computer experiments (perhaps, "by an oversight"), they turn out to be "liquid-like". In this way according to computer determinations by Tanaka [1, 2], crystalline rubidium at the temperature of about absolute zero appears to be more liquid than sunflower seed oil ($\eta = 10^0$ Pa · s). As is shown in [3], diffusion coefficients in solid glasses have "liquid-like" values. The duration of different transformations in the model of a solid (phase transitions, sintering, crystallization etc.) does not exceed 10^{-9} s, which also corresponds to the consistence of a substance not more viscous than sunflower seed oil [3 – 6]. (Such examples are considered below in more detail.) In real solids such transitions are slower, sometimes they take years and their direct simulation is impossible because the computer experiment corresponds to not more than 10^{-9} lifetimes of the system.

If in a computer experiment, that is during $\sim 10^{-9}$ s, the processes are successfully carried out, that is a proof itself that they have a characteristic time typical for "liquid-like" processes, and their duration is by 10 – 20 orders of magnitude smaller than that of real processes in a solid.

If disagreements between the results of computer experiments and reality are recognized well, they are often explained by a small number of particles in the system, short lifetime of the system, and insufficiently high operating speed of the computer. In particular, such explanations are given by Belashchenko [3]. But modern computers have a higher (for example, by 3 orders of magnitude) operating speed compared with the computers of the seventies, when the initial determinations were performed. Application of supercomputers allows to increase the amount of calculations by some orders of magnitude, but the calculated values of kinetic coefficients remain practically the same.

If in the classical system an elementary act of a process is simulated, for example a jump of an atom from its lattice point to a neighbouring vacancy, then the jump parameters will mainly depend on the nearest surroundings of this atom. The activation energy of the jump does not depend much on whether only 100 particles surround the selected atom or 100000 particles.

The simulation results do not change essentially when the number of particles in the system is varied over a wide range. The results also do not change qualitatively with the transition to periodical boundary conditions when, for instance, the crystal in the main cell was replaced with an infinite medium, consisting of the same repeated cells.

It is frequently assumed that crystals are simulated very well, better than liquids and glasses. Indeed, it is easier to program the ideal crystal lattice than a more complicated structure of a liquid or a glass.

Such a peculiar state of affairs concerning simulation is due to some historical reasons, and so it is expedient to look into the history of the question.

Mechanical and kinetic properties of the liquid and the solid and also the problem of solidification were studied in the past by a lot of outstanding scientists. It is enough to mention the Newtonian viscosity of a liquid, relaxation time of mechanical stress by Maxwell ($t = \eta/G$, where G is the shear modulus), Kelvin's viscoelastic body, the formula of Stokes-Einstein, $D = kT/6\pi r\eta$, for the relationship between the coefficient of viscosity (η) and diffusion constant (D).

The general idea that solidification at crystallizing of a liquid is related to the definite densification and ordering of the atomic structure and to approaching a dense spherical packing established itself long ago. The same ordering under compression of the system can be applied to "jars on a shelf". Hardness is associated with similarity of a crystal to "a crowd which is tightly compressed within enclosed space[1]". Such theories, for instance, were put forward in the 18th century by M. V. Lomonosov and P. Boshkovich.

By now these notions have become widely spread, and any doubts are perceived as a violation of the existing ideology. Such a violation is psychologically very complicated to perform (see e. g. [7]). It is well known that the facts which are contrary to the prevailing ideology are frequently dissembled, and "startling blindness" appears towards them [7, 8]. The facts are confusing, and this is the main difficulty of the issue. The sizes of atoms and regularities of their interacting became certain at the beginning of the 20th century. It allowed turning to quantitative calculations of strength or viscosity and of activation energies (E_{A}). However,

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[1] However, it is clear now that the cores of atoms, which are impenetrable at the energy kT_{m} occupy only about half of the volume of a system even with the densest packing. The fraction of such occupied volume in crystals with weak bonds (hydrogen, helium, neon, etc.) is about 10%. The free volume in a crystal is large, and it shows no resemblance to a tightly compressed crowd, and rearrangements of atoms are difficult due to other reasons.

it was soon found that it is impossible to perform step by step calculations of real values of E_A and of real (but not "theoretical") strength from interatomic interactions without powerful or artificial assumptions [9]. Since glass has strength without long-range order, and liquid crystals have long-range order without strength, there were difficulties concerning the interpretation of the strength of a crystal as a consequence of long-range order. These difficulties were overcome with the help of additional assumptions. Now, when computer simulation has allowed to get over the computational complications, the above-mentioned difficulties and uncertainties of the theory have turned already into obvious "catastrophes".

Already at the beginning of the 20th century the interest in these problems dropped considerably because of the difficulties that had arisen. Currently the theory of a solid and the theory of a liquid deal very little with their initial properties, that is, with "hardness" and "fluidity" of a substance, respectively. Crystallization/solidification is often considered now as an order-disorder transition, but not as a jump of kinetic and mechanical characteristics.

Until now it has not been made clear if it is correct to speak about viscosity of a solid and about a jump of viscosity at crystallization[2]. According to [8, 10], at real solidification (both crystallization and glass transition) viscosity increases by approximately 15 orders of magnitude, activation energies of the viscous flow (E_v) and diffusion (E_D) increase from insignificant values to $E_\mathrm{v} \approx 40RT_\mathrm{m}$ and $E_\mathrm{D} \approx (15-20)\cdot RT_\mathrm{m}$, respectively, and the mechanical strength appears to be about 10^7 Pa.

Specialists in simulations frequently do not correlate their results with the real consistence of the substance. The "liquid" values of the kinematic properties of a "crystal phase" in the model do not arouse any surprise.

In viscosimetry processes of gelling and solidification are frequently divided into the following steps:

1) From the state of a simple liquid which is characterized by insignificant E and has a typical order of magnitude for viscosity of 10^{-4} Pa · s up to the viscosity of water ($\eta = 10^{-3}$ Pa · s).
2) From the viscosity of water up to the consistency of glycerin or sunflower seed oil.
3) Next up to the state of thick honey (10^4) or up to the "weakening point".
4) Up to the consistency of pit asphalt (10^7) or up to "softening point".
5) From the state of pit asphalt up to the "glass transition point" (T_g) with a viscosity of $\eta = 10^{12}$ Pa · s. The latter is considered to be the boundary line between liquid and solid states; activation energies are here as large as those typical of a solid.
6) Further from T_g up to the state of a "perfectly rigid" or "perfectly brittle" solid body which comes upon reaching the viscosity of 10^{19} Pa · s. This value is often reached at temperatures near $T = T_\mathrm{g}/2$, and it is a threshold for the possibility of viscosity measurement. It is not possible to observe any viscous flow or any relaxation of mechanical stress in a solid body at lower temperatures and moderate loadings. Here the Maxwell relaxation time ($t = \eta/G$) exceeds at least a year or 10^8 s.

There are practically no atomic processes in such a condition of an inert "perfectly rigid (brittle)" body arising at temperatures about either $T_\mathrm{g}/2$ or $T_\mathrm{m}/4$. Their characteristic time exceeds a year and is not measurable. However, the durations of mechanical stress relaxation and of other atomic processes (phase transitions, sintering, crystallization etc.) in the computer model are of the same order of magnitude as the period of atomic oscillations, i. e. 10^{-12} s like in a simple liquid, both at the temperature $T_\mathrm{m}/4$ and even nearby absolute zero (for example, at $T = 0.01T_\mathrm{m}$). That is why it is possible to simulate such processes in a computer experiment which corresponds to the lifetime of a system that does not exceed 10^{-9} s. The difference between the classical computer model and reality concerning the time of relaxation of mechanical stress in the given condition of an inert "perfectly rigid" body is over 20 orders of magnitude (10^8 s/10^{-12} s = 10^{20}).

Since crystallization is a point process, some of the above-mentioned intermediate states do not manifest themselves.

The behaviour of the kinetic properties of crystals below the melting point and of vitrified liquids below T_g does not have any distinctions.

Our computer experiments did not have any essential differences from the experiments of other authors.

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[2] In principle, it is possible not to apply the term "viscosity" ($\eta = P/v$) to a crystal or glass and to operate only with values of mechanical pressure (P) and rate of deformation (flow velocity, v). However, tables of viscosity (η) in the literature contain extensive experimental material on mechanical properties of solids.

Table 1. The results of the kinetic coefficients of viscosity, η, diffusion, D, and electrical conductivity, χ, determination by the molecular dynamic method and the parameters velocity, ν, and field intensity, ε, of the processes under simulation.

Nr.	Substance	Potential	T/T_{m}	$\eta \cdot 10^3$, Pa · s	$D \cdot 10^5$, cm^2/s	χ, S/cm	Process under simulation	ν, 1/s	ε, V/cm
1	Ar	6 – 12	0.24	5.3	0.53	–	Viscous flow	$4.9 \cdot 10^7$	–
2	Ar	6 – 12	0.24	4.2	0.46	–	Viscous flow	$4.9 \cdot 10^8$	–
3	Ar	6 – 12	1.20	0.35	0.57	–	Viscous flow	$6.9 \cdot 10^9$	–
4	Ar	4 – 8	0.12	0.13	0.10	–	Viscous flow	$6.9 \cdot 10^9$	–
5	NaCl	1 – 10	0.42	9.40	–	–	Viscous flow	$4.0 \cdot 10^9$	–
6	Pb	Oscillating	0.40	8.60	4.20	–	Viscous flow	$4.0 \cdot 10^8$	–
7	Fe	Oscillating	0.40	7.40	3.40	–	Viscous flow	$4.0 \cdot 10^8$	–
8	Oxide	Ion-covalent	0.40	5.00	–	–	Viscous flow	$4.0 \cdot 10^8$	–
9	Ar	6 – 12	0.24	6.00	–	–	Flow at $P = 1.373 \cdot 10^8$ Pa	–	–
10	Ar	6 – 12	1.40	0.32	–	–	Flow at $P = 1.373 \cdot 10^8$ Pa	–	–
11	Ar	4 – 8	0.24	0.10	–	–	Flow at $1.373 \cdot 10^8$ Pa, the attraction is “turned off”	–	–
12	Ar	Hard sphere	0.24	0.15	–	–	Flow at $1.373 \cdot 10^8$ Pa, hard sphere potential	–	–
13	Ar	6 – 12	0.24	3.40	0.39	–	Stress relaxation	–	–
14	Ar	6 – 12	0.80	2.40	0.73	–	Stress relaxation	–	–
15	Ar	6 – 12	0.24	3.70	0.67	–	Shape relaxation	–	–
16	NaCl	1 – 10	0.23	–	15.00	0.80	Electricity transport	–	$6.2 \cdot 10^6$
17	NaCl	1 – 10	0.23	–	8.00	1.40	Electricity transport	–	$6.2 \cdot 10^7$
18	NaCl	1 – 10	0.60	–	–	3.00	Electricity transport	–	$6.2 \cdot 10^7$
19	NaCl	1 – 10	0.60	–	–	0.20	Electricity transport	–	$2.0 \cdot 10^9$
20	Oxide	Ion-covalent	0.40	–	6.00	2.40	Electricity transport	–	$6.2 \cdot 10^6$
21	Oxide	1 – 10	0.60	–	2.00	0.23	A plane, electricity transport	–	$6.2 \cdot 10^7$
22	Oxide	6 – 12	0.24	1.40	–	–	A plane, viscous flow	$3.0 \cdot 10^{10}$	

The programs and techniques of the molecular dynamic simulation were similar and our results agree closely with the results of other authors when the properties of the liquid state were under simulation. The main difference of some of our experiments was in the direction:

1) Our main aim was to simulate the distinctive features of the solid state [8], which other authors usually do not determine. Each time we carefully ascertained whether “the crystal phase” in the computer model really has the properties of a crystal and not of a liquid.
2) The calculated values of viscosity, diffusion, conductivity coefficients, their activation energies, characteristic time of processes etc. were thoroughly compared with the real values of crystals. The calculated values of the kinetic properties were compared with the consistence of the substance.

3. Results of Simulations

We have performed more than one hundred computer experiments, using various techniques to make sure that “the substance” in the traditional molecular model has the kinetic properties of a simple liquid at all temperatures, and that, indeed, the real solidification mentioned above does not take place. The results are published in several dozens of papers (e. g. [11 – 13]).

The commonly accepted potentials of the interatomic interaction, for instance Lennard-Jones potential (6-12) for dispersion interaction, Born-Mayer potential (1-12) for ionic interactions, oscillated potentials for metallic bond, were used. More complicated potentials were used for ion-covalent coupling.

Direct simulation of viscous or plastic flow, of ionic electrotransmission, of mechanical stress relaxation, of system shape relaxation, of ordering (crystallization) and of other processes was carried out. Vibration spectra of atomic systems were determined and “soft modes” indicative of reduced (or negative) stability of the structure were revealed. Usually it was evident that the results did not change essentially with the variation of the number of particles, calculation steps and boundary conditions or with certain variation of potential parameters. The systematized tables of results are given in initial publications and later in monographs [8, 10]. Certain results are listed in Tables 1 and 2 and illustrated by Figs. 1 – 3. The molecular mechanism of

Table 2. The viscosity and diffusion coefficients at the simulation of plane and three-dimensional (T-D) systems (98 and 108 particles); $T = 0$.

Nr.	System	ε, 1/s	$\varepsilon_{\max}$	T/T_m	η_{ordered}, Pa · s	$\eta_{\text{aver.}}$, Pa · s	$D_{\text{ordered}} \cdot 10^5$, cm^2/s	$D_{\text{aver.}} \cdot 10^5$, cm^2/s	$\tau_{\max}/G$	$\tau_{\max}/G$	$U_{\text{inter.}}/U^0_{\text{inter.}}$
1	Plane	$2.5 \cdot 10^{10}$	2	0	0.2	–	4	110	0.12	0.04	–
2	Plane	$3.1 \cdot 10^9$	0.65	0	0.14	0.02	6	30	0.07	0.025	0.74
3	Plane	$5.8 \cdot 10^8$	0.13	0	0.11	0.06	6	8	0.02	0.015	0.91
4	Plane	$3.1 \cdot 10^9$	0.05	0	0	–	5	–	−0.006	−0.003	0.79
5	T-D	$4.1 \cdot 10^9$	0.35	0	–	0.012	–	20	0.016	0.011	0.86
6	T-D	$4.1 \cdot 10^8$	0.05	0	0.11	0.06	–	16	0.009	0.005	0.96
7	T-D	$4.3 \cdot 10^7$	0.007	0	–	–	7	–	$2 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	1.0
8	Plane	$6 \cdot 10^8$	0.07	0	–	0.023	–	9	–	0.008	–
9	Plane	$4 \cdot 10^{10}$	1.0	0.5	0	–	–	100	$3 \cdot 10^{-3}$	–	–
10	Plane	$4 \cdot 10^{10}$	0.6	0.5	0	–	–	200	0.01	0.06	–
11	T-D	$4 \cdot 10^{10}$	1.0	0.25	0.004	0.001	–	250	0.032	0.015	–

the process is most clear in the plane system and with little number of atoms; see the systems in Figs. 1 – 3.

The principal conclusion is the following. All computer estimations demonstrate a lack of hardness and give "liquid-like" values of kinetic coefficients. For example, the viscosity (η) lies between 10^{-4} and 10^0 Pa · s, diffusion constants are approximately equal to 10^{-4} – 10^{-8} cm^2/s, the ionic conductivity has an order of magnitude of about $10^0\ \Omega^{-1} \cdot \text{cm}^{-1}$, the characteristic time of all the studied atomic processes does not exceed 10^{-8} s even in the region of solid state. These values differ very much (that is by 5 – 20 and more orders of magnitude) from the real kinetic properties of solid bodies. Therefore, there is no possibility to treat the obtained "liquid-like" values as "solid state" ones. Both the highest values of the viscosity ($\eta = 10^0$ Pa · s) and the stress relaxation time ($t = \eta/G = 10^{-8}$ s) and the lowest values of the diffusion constants (10^{-8} cm^2/s) or the ionic conductivity ($10^{-2}\ \Omega^{-1} \cdot \text{cm}^{-1}$), resulting from the simulation, correspond to that consistence of the substance which is known in viscosimetry as the consistence of glycerin or of sunflower seed oil. As far as we know, no author has succeeded in getting higher values of the viscosity and the life of the process as well as lower values of the diffusion constants and the ionic conductivity by direct simulation. In other words, no computer experiment has given "solidification" or "thickening" of a liquid even up to the consistence of sunflower seed oil.

Now, after numerous computer experiments and discussions, this conclusion is quite clear and does not provoke any objections of the investigators that are familiar with the corresponding materials. It was discussed, in particular, at all 11 conferences on the structure and properties of metallurgical melts covering a period of over 20 years.

The simulation of sintering provides especially significant results. Real sintering is a strong joining of two samples of a solid body. Sintering differs from other simulated processes because of its very fast, almost instant accomplishment, which is quite obvious even without computer simulation. When two samples of a solid body are pressed to each other by a compressing machine, the atoms on the two sintered surfaces are brought together by external pressure. It is clear without simulation that these atoms should immediately enter into of some kind interaction (dispersion, ionic, metal etc. one), but according to present-day ideas, the formation of chemical bonds across an interface is sintering. Of course, all the computer experiments give practically instant sintering taking, for example, about 10^{-9} s. But actually, compression of two samples of a solid at moderate temperatures by no means results in their sintering even when the compacting force reaches the ultimate strength of the material, and many, if not all, surface asperities should be crushed and diffusion resistance of the process is insignificant. In conventional processes of powder metallurgy of iron at temperatures of about 1000 °C real sintering is hindered, slow and lasts, for example, for several hours even in the absence of "transport" difficulties, surface films and adsorbed layers. The time of real sintering grows rapidly with the temperature dropping, and sintering is accompanied by overcoming high energy barriers, i. e. $E = 30RT_m$. This process during sintering/caking of minerals in the earth's crust can take a whole geological epoch (for example, one million years). Here the contradiction between the model and the reality is quite obvious. We tried to simulate a friction of two small crystals but also got practically immediate sintering (coalescence) of samples and then liquid vis-

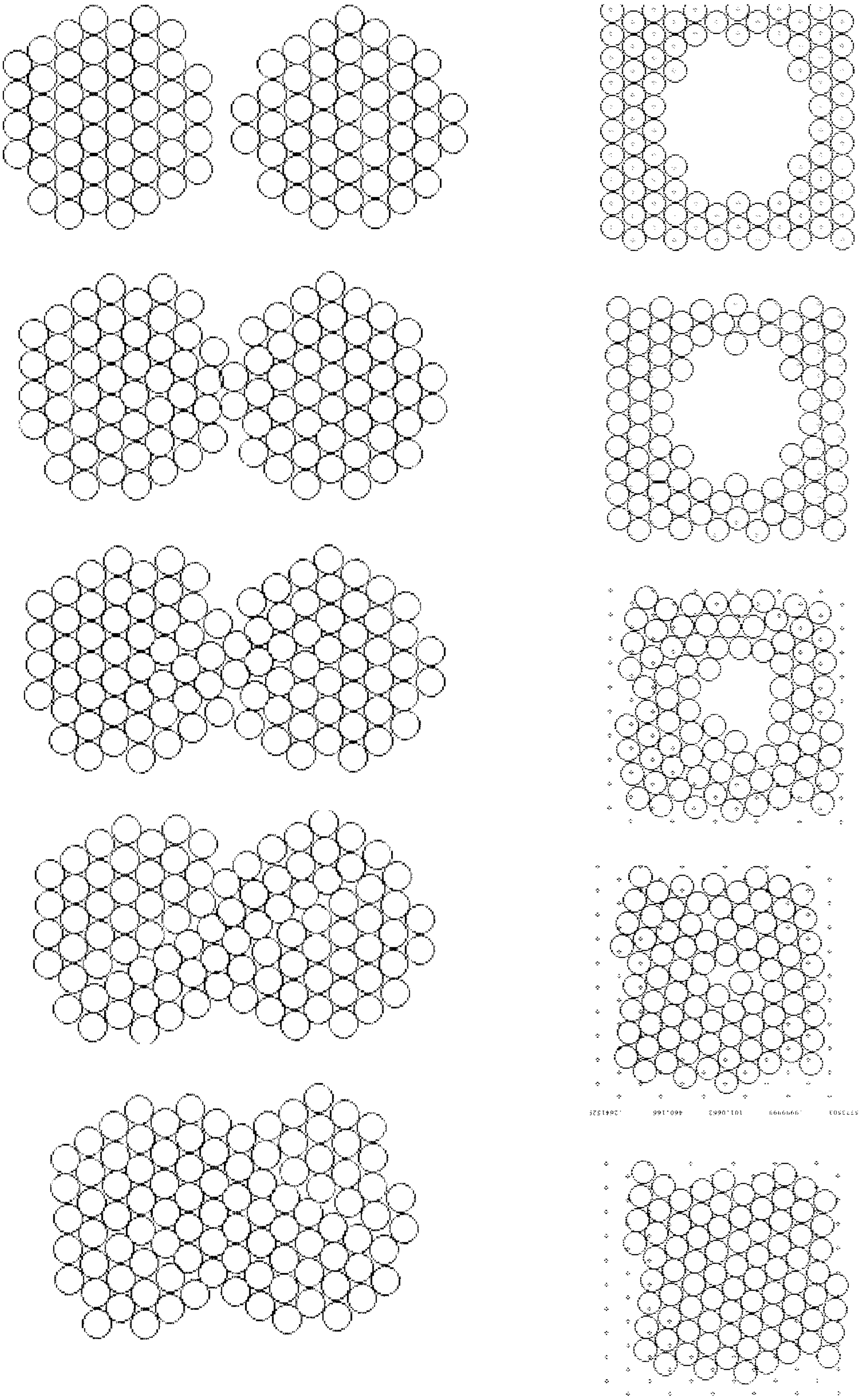

Fig. 1. The sintering of particles of powder and flowing (closing) of a pore in a crystal at $T \cong 0$, Lennard-Jones potential. The processes duration in the model is 10^{-9} s, whereas real time exceeds one year and is immeasurable.

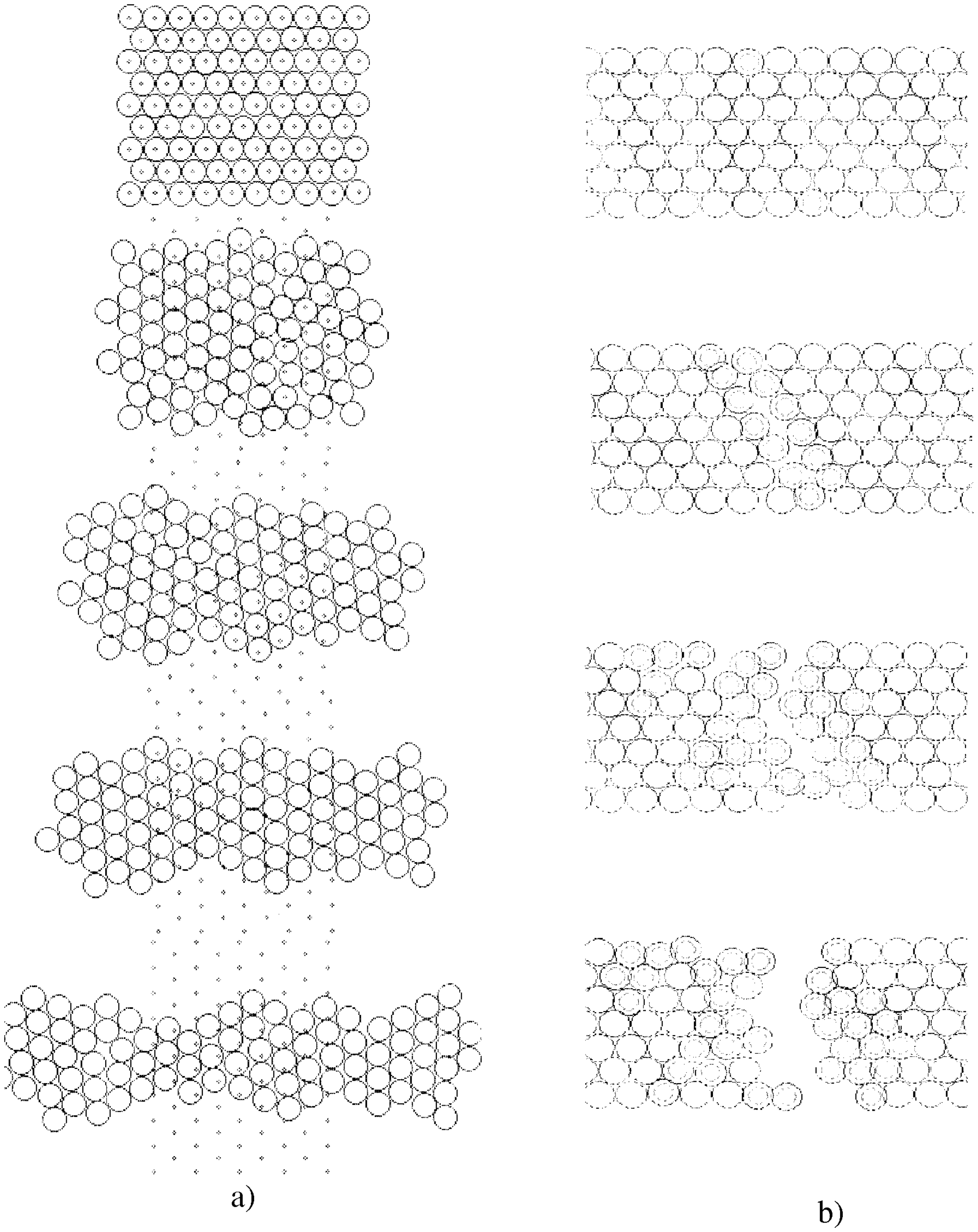

Fig. 2. A rod stretching at $T \cong 0$. (a) Within the classical system the structure is fluid and has no brittle failure. (b) Introduction into the model of the quantum freezing result in a more real process.

cous flow of the combined mass in the model instead of friction.

Simulation of a brittle fracture, which is a process inverse to sintering, is not possible either, even for $T = 0.01T_\mathrm{m}$. At stretching a "rod" we, like other authors, observed only a flow, which is similar to the extension of a liquid stream, instead of the formation of a brittle crack and disintegration of the sample into two pieces, since the model has no stiffness of atomic structure (see Fig. 2a). If the "freezing" of the quantum free-

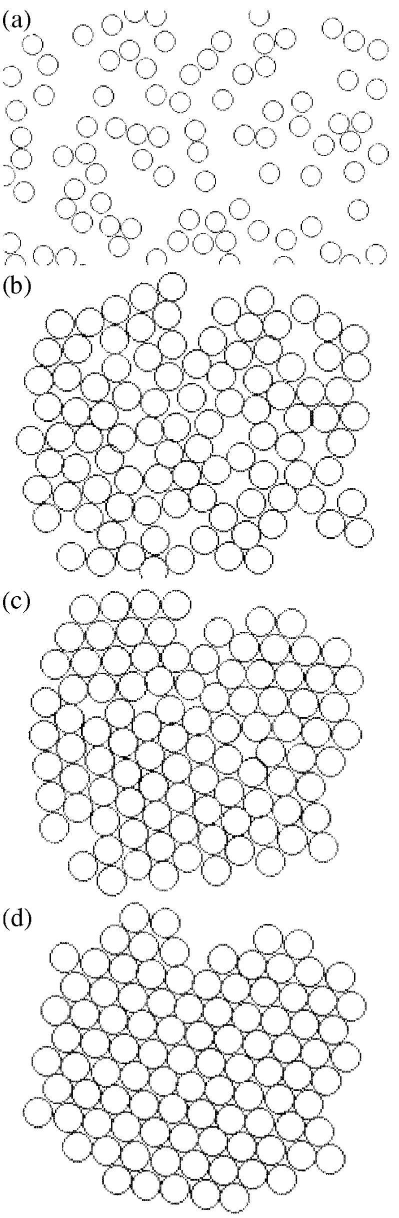

Fig. 3. Ordering crystallization at $T = 0$, Lennard-Jones potential. Stage (a) corresponds to the dense gas, (b) to liquid, (c) to "polycrystal", (d) to monocrystal. The processes duration in the model is 10^{-9} s, in reality it exceeds one year.

dom degrees is loaded into the simulation program, the structure of the solid becomes hard enough and capable of a brittle fracture, crack extension (Fig. 2b).

It should be pointed out that a lot of results on molecular dynamic simulation of kinetic properties in the area of solid state are already accumulated in the literature. Already in Tanaka's early works [1,2] "liquid-like" values of self-diffusion and viscosity of crystalline rubidium were obtained at 5 K and nearly at the melting point. In the latter case crystalline rubidium turned out to be more liquid than ··· water ($\eta = 0.5 \cdot 10^{-3}$ Pa · s)! In [14] "fluid" values of self-diffusion coefficients were obtained during the simulation of solid vitreous (or amorphous) aluminum. The crystallization time near absolute zero, calculated by Hsu and Rahman [6], amounts to 10^{-9} s, whereas the real time of crystallization at these temperatures exceeds one year. The data on fast ordering ("crystallization"), obtained according to the model, are summarized in the reviews [4,5,15]. The ordering time does not exceed 10^{-8} s.

Too high diffusion coefficients, *D*, in the model are also established in the detailed review [3]. Direct calculations of D of solid glasses result in values of $\sim 10^{-8}$ cm^2/s [3] (i. e. sunflower seed oil consistence). Even at multifold decrease of temperature (for instance from $T = 1.5T_\mathrm{m}$ to $0.1T_\mathrm{m}$) the D value in the model decreases by $1-2$ orders from $D = 10^{-5}$ cm^2/s (simple overheated liquid) to $10^{-6} - 10^{-7}$ cm^2/s. Whereas the real D value frequently decreases by 13 orders of magnitude to 10^{-18} cm^2/s at the vitrification temperature and goes beyond the possibilities of measurement, computer determinations for KCl give $D = 10^{-6}$ cm^2/s at $T = T_\mathrm{m}$. In the case of Lennard-Jones (dispersion) interactions corresponding to noble gases $D > 10^{-7}$ cm^2/s was obtained according to the model even at $T = 0.1T_\mathrm{m}$ [13].

In our computer experiments the effect of further temperature decreasing (e. g. to $0.01T_\mathrm{m}$) on such unordered systems was considered. The relaxation procedure was also used, that is, the velocities of the particles were nulled at the end of each step (it corresponds to $T = 0$ [8]). In such a model of glass the ordering (crystallization) occurs in a short time interval (of about 10^{-9} s). The mobility of the particles and coefficients D and $1/\eta$ decrease little and sometimes even increase at "cooling". During the relaxation procedure heat vibrations of the particles disappear completely and only directed movements, which agree with ordering, remain. Structural reordering at $T = 0$ testifies that $E_\mathrm{A} = 0$ (null activation energy of the process).

It should be pointed out that some researchers denote the same facts very mildly, for example "reduced stability" of the glasses or "overestimated diffusion coefficients" ($D > 10^{-8}$ instead of 10^{-18} cm^2/s) [3].

The activation energy of viscous flow, diffusion, crystallization and other processes in the model can be calculated according to computer experiments of different authors using the temperature dependence of these processes. For example, the activation energy of viscous flow is

$$E_\eta = R\frac{\ln\left(\dfrac{\eta_1}{\eta_2}\right)}{\dfrac{1}{T_1}-\dfrac{1}{T_2}}. \qquad (1)$$

At low temperature the activation energy in the model usually is of the order of RT_m or $0.1RT_\mathrm{m}$ and even less, whereas real $E_\eta \sim 40RT_\mathrm{m}$. In spite of the fact that the regular crystal lattice corresponds to the minimum of energy, this minimum is very shallow and the system finds a way out of the minimum surmounting the small energy barrier of height $E_\mathrm{V} < RT_\mathrm{m}$.

In the classical computer model the rates and durations of the processes depend little on the temperature (let that be iron and the temperature range from $T \approx 0$ and up to $T \sim 20000$ K). But in reality, only at crystallization (1808 K) or at vitrification (near 900 K) the viscosity (η) and stress relaxation time (t_r) increase by about 15 orders of magnitude. In the model, the duration of the processes also depends little on the pressure, even if the pressure is high enough to lead in reality to solidification, and η and t_r increase by 15 orders too.

It should be emphasized that at present our computer experiments are not necessary to make the main conclusion. Our main conclusion is that there is no solidification within the traditional model, and the same idea follows clearly from the results of other authors.

4. Simulation of a Crystal with "Frozen" Freedom Degrees

There is no hope of obtaining real properties of a crystal just by the modification of the potentials. It is necessary to introduce in the model the effects which will be qualitatively new as compared with the usual interactions. For instance, if agreement with the experiment on diffusion coefficients is achieved by fitting the potentials, then a catastrophic discrepancy on viscosity appears, and vice versa [8]. There is no hope of obtaining in the model real effects of long-range action, for example the real change of stiffness of the crystal structure due to the interface influence at the distance of 10 μm or 10^4 interatomic spacing [8]. The real properties of a crystal are possible to obtain by even simplified introduction of the quantum "freezing" of atomic movement freedom degrees.

Almost all practically important crystal substances consist mainly of atom-bosons, i. e. atoms with an even sum of protons and neutrons.

According to Einstein's theory of the heat capacity the fraction of atoms on the n-th energy level in a crystal is equal to

$$\alpha_n = \frac{1}{b\cdot\exp\left(\dfrac{n\cdot\Theta}{T}\right)-1}. \qquad (2)$$

Here $\Theta = h\nu/k$ is the characteristic temperature (according to Einstein or Debye), b is the normalization factor, and α_0 (at $n = 0$) is a part of "frozen" atoms (more exactly, the part of freedom degrees or oscillators at zero level $n = 0$).

In Einstein's (or Debye's) theory of the heat capacity α_0 is easily expressed by a formula or found in tables and depends on experimental values of the frequency (ν), temperatures (Θ), and also of the heat capacity (C) or entropy (S) of the substance.

It is known that a lattice has stiffness and high strength if the artificial condition that atoms are permanently located in the lattice points (or their displacements are little) is imposed. This condition makes any flow in the structure under discussion impossible. The fact that the location of atoms in their lattice points is permanent is postulated in calculations of many crystal properties [9]. In particular, this assumption provides a reasonable value of the activation energy (E_D) of the jump of an atom from its point to a neighbouring vacancy. In this case the atom needs essential energy E_D to "squeeze" between the immovable neighbouring atoms. At the classical free movement the neighbouring atoms easily give way and the activation energy becomes insignificant. When in a computer model the shifts of the 2nd, 4th, 8th … neighbouring atoms were sequentially allowed [8], the activation energy E_D quickly decreases.

At low temperatures the fraction α_0 of frozen degrees of freedom approaches 100% according to (2). The "frozen" atoms cannot leave their points without quantum-mechanical excitation, that is, without the transition from zero ($E = 0$) to at least the first energy level $E = h\nu$. As a first approximation it is assumed that the "frozen" atoms are immovable. The fact that the quantum freezing of freedom degrees is taken into account is equivalent to the artificial condition about hard location of all atoms in their points and imparts stability and hardness to the structure.

In particular, the diffusion jump of an atom to a neighbouring vacancy, when some of (α_0) neighbouring atoms (= freedom degrees) are frozen, was simulated. The α_0 value was selected by a random-number generator (RNG). We got reasonable estimation of the activation energy E_D of the order $15RT_m$, while in the classical model E_D remains insignificant. In the systems with "frozen" freedom degrees the computer experiments also give reasonable values of the order of $E_V = 40RT_m$ of plastic deformation or viscous flow (for more details see [8]).

It is frequently assumed that near the melting point T_m the atomic quantum effects are unessential, and α_0 is insignificant; quantum crystals make the only exception. The minimal values of α_0 were found to belong to heavy elements – tungsten ($T_m = 3650$ K) and molybdenum ($T_m = 2890$ K). However, even for such systems $\alpha_0 \sim 10\%$, that is enough to preserve the stability of the structure. In such a dense packing if 10% of the atoms are "frozen" and fixed in lattice points, the other atoms also lose mobility. For other substances the typical values of α_0 near the melting point or vitrification are about 50%, sometimes up to 90%. Thus, the direct calculation of α_0 does not confirm the opinion that quantum atomic effects are negligible near solidification temperatures.

5. Summary

The computer experiments were carried out within the framework of the usual methods of molecular dynamics and the only differences were 1) focus on distinctive features of crystal state and 2) careful juxtaposition of the results with the real properties of crystal matter. The results clearly demonstrated that within the framework of the classical model the computer model of a crystal has the properties of a liquid without any evidence of solidification. Real hardness of the structure and real values of energy barriers E can be obtained by introducing into the program the quantum prohibition of the movement of atoms located on zero energy level, $E = 0$, in other words, for atoms with frozen freedom degrees. Permanent location of atoms in a lattice point was postulated earlier to reach a rigid structure, which had no quantum mechanical foundation.

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