

Using of Event-Driven Molecular Dynamics Method at the Computer Simulation of Atomic Structures of Amorphous Metals

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Abstract. The article highlights some lesser known issues related to the study of the atomic structure of liquid and amorphous metals, semiconductors, alloys and with the processes occurring in them at the atomic level at the thermal and stress effects. Features of implementation of event-driven molecular dynamics algorithm in sequential and parallel variants for study the atomic structure of amorphous metals are presented. The stages and the basic problems of computer simulation of atomic structure of metals, as well as an analysis of the results of computational experiments to study the atomic structure of amorphous aluminum at different speeds its superfast cooling liquid melt are discussed.

Keywords: computer simulation, event-driven molecular dynamics method, atomic structure, amorphous metal, calculable block, unit cell, interaction potential function

1 Introduction

Great contribution to science of metals has made the discovery of amorphous metals with unusual properties: they are very strong and at the same time have plastic properties. They have soft magnetic material properties, corrosion resistance, which leads to broad prospects of their application in industry. The basic method of producing amorphous metal is extremely fast cooling of the liquid melt. In this way obtained amorphous alloys named as metallic glass (cooling rate is very high and is in the range 10^{10} – 10^{13} K/s). Microstructure of amorphous metals is a metastable state of structure with local atomic order and this structure is not a polycrystalline structure. There are several models to explain the nature of such a structural organization in amorphous metals: crystal, the dislocation model, model of random close packing of hard spheres and cluster model.

Currently not fully resolved issues related to the study of the atomic structure of liquid and amorphous metals, semiconductors, alloys and with the processes occurring in them at the atomic level at the thermal and stress effects. These issues, for example, include correctness and the limits of applicability of different structural models of amorphous metals. For example, in various amorphous structures for the cluster model, you need to figure out the dimensions, stability

and conditions of cluster formation of an ordered structure (of conjugate tetrahedra or Frank-Kasper polyhedra). Also of interest is the question concerning the structure in the interface of the clusters, as well as the mechanisms of their transformation at the thermal and stress effects. Insufficiently explored is the process of crystallization of amorphous metals. Limited possibilities of direct experimental methods due to the specific properties of the studied medium, in particular, the lack of long-range order in the arrangement of atoms, for example, when trying to create a structural model of liquid, including molten metal. In liquids the kinetic energy of atoms comparable to their potential energy, so in relation to such medium is impossible to find an effective small parameter.

To solve these issues the most effective computer simulation method is a method of molecular dynamics, in particular, its kind – event-driven molecular dynamics method [1], which allows with sufficient accuracy in the model take into consideration and control the parameters of the phenomenon under investigation, to study the dynamics of the processes flowing on the atomic level using a variety of realistic visualizers of structure.

2 Event-Driven Molecular Dynamics Method and Its Parallelization

In classical method of molecular dynamics system is represented as a set of particles with interaction, which is described by the interaction potential function, and the evolution of the system is simulated by numerical integration of the equations of motion using a time step [2].

For a closed system the force acting on the i -th atom:

$$\mathbf{F}_i = - \sum_{j \neq i}^N \frac{d\phi_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)}{d(|\mathbf{r}_i - \mathbf{r}_j|)} , \quad (1)$$

where $\phi_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)$ – the interaction potential function between i -th and j -th atoms; $\mathbf{r}_i, \mathbf{r}_j$ – radius-vectors of atoms. Equations of motion are

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i , \quad m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i , \quad (2)$$

where m_i and \mathbf{v}_i – mass and velocity vector of i -th atom; t – temporary variable.

Positions and velocities of all N atoms of calculable system characterized by $2 \cdot J \cdot N$ coordinates (J – dimension of the calculable system): the coordinates $x_{j,i}(t)$ describe a position in space (j – number of coordinate axis), values $v_{j,i}(t) = \dot{x}_{j,i}(t)$ describe a j -component of velocity vector of i -th atom. To solve (2) can apply a numerical method for the integration of differential equations, for example, the Runge-Kutta method of 4th order accuracy or commonly known half-step Euler method:

$$\begin{aligned} v_{j,i}(t + \Delta t/2) &= v_{j,i}(t - \Delta t/2) + \Delta t \cdot F_{j,i}(t) / m_i , \\ x_{j,i}(t + \Delta t) &= x_{j,i}(t) + \Delta t \cdot v_{j,i}(t + \Delta t/2) , \end{aligned} \quad (3)$$

where Δt - integration step (time step), which is chosen by criterion: the fluctuations of total energy of the system must not exceed the fluctuations of the potential energy. Step Δt should be less than 1/4 of the smallest period of atomic vibrations (about 10^{-13} – 10^{-15} s). Otherwise the vibrations of the atoms become aperiodic (increasing energy of the system). Temperature of calculable system of atoms is given by means of set of initial velocities of atoms the according to the Maxwell distribution (the velocities have identical modulus but have random directions). The total kinetic energy must correspond to the desired temperature, and the total momentum must equal zero [2]:

$$|\mathbf{v}_i| = \sqrt{2}v_{\text{sq}} = \sqrt{2JkT/m_i}, \quad \sum_{i=1}^N m_i \mathbf{v}_i = 0, \quad T = 2E/(J \cdot N \cdot k), \quad (4)$$

where k - Boltzmann constant, T - temperature of calculable system at each iteration of the numerical experiment, v_{sq} - root-mean-square (rms) velocity of the atom, E - kinetic energy of calculable atom system.

Integration of the equations of motion, which requires a sufficiently high accuracy by using non-smooth potentials, compel to significantly reduce the global time step. Since this affects on the performance of computing, into modeling algorithm requires to include effective analysis of the need the estimation of various atom interactions. Idea of the algorithm based on the sequential control of events [1], ranked by time, is that in the time of the next event is processed only one pair of interacting atoms for which this event (collision between them) immediately comes. After all processing of all remaining pairwise interactions between atoms is delayed until the following time points, but in each successive time again handled the interaction of only one relevant to this event a pair of atoms [1]. Using of this event-driven dynamics algorithm allowed effectively take into account non-smooth potentials and accurately satisfy the modeling constraints [3]. I.e., between the events in accordance with the known analytical formulas the changes in position of the atoms are taken into account as motions of atoms under the influence of force, which is constant on the time step. So is achieved the considerable savings of calculations volume and acceleration of calculations. An additional effect of accelerating the calculations can be achieved through parallelization because in the sequence of events satisfied the condition of their independence. The following is an informal description of the event-driven molecular dynamics algorithm in serial form (non-parallel algorithm):

1. Calculation of interaction forces between the atoms
2. Initialization of current time t in the interval $(0, T)$: $t = 0$
3. Definition and addition to the queue of events for all atoms
4. Determining the next i -th event with the minimum time t_i
5. If t_i is greater than T (end time of simulation interval), then:
 - (a) Setting the current time t to the end of the interval: $t = T$
 - (b) Go to step 11
6. Setting the current time t to the time of event: $t = t_i$

7. Changing of states of participants of the event in accordance with the changed time
8. Processing of event, directly corresponding to the moment t_i
9. Defining and adding to the queue new events with the participants from processed event
10. Go to step 4
11. Changing of states of all atoms in accordance with the current time t
12. Go to step 1

In the described algorithmic diagram the end of the action interval constant interaction force can be considered as another kind of regular event, in which take part all atoms. It allows you to simulate the presence in the system of different potentials, integrating them with various steps.

Taking between the sufficiently remote atoms the interaction strength equal to zero, a high computational efficiency is achieved by calculating the interaction forces only for atoms in the same block or in adjacent blocks (by means of the coordinate space decomposition on the parallelepiped elements). I.e., using the limitedness of the interaction radius between the atoms, we can achieve almost complete parallelization of processes occurring in contiguous blocks and significant acceleration of calculations. Take into account the interaction of the atom with the other atoms in the same cell and cell entourage of 26 cells (cell block with size $3 \times 3 \times 3$ contains 27 cells). Due to the symmetry of the commonly used potentials the amount of computation is reduced 2-fold. Then for each cell having at the average n atoms, the number of verifiable interactions will be defined as $n(n-1)/2 + 13n^2$.

For event-driven molecular dynamics algorithm the global queue of events makes it difficult to parallelize, but keeping of the local time for each atom creates the possibility of a controlled parallel processing of spatially distant events. Namely, processing can last as long as the time elapsed in the absolute frame of reference, is not suitable to the nearest event in the bordering cells. After processing this event the parallel processes exchange messages [4]. If at the time of detection of the new event on the border two cells one process has already moved to the processing of later events, appear the probability of error (the lost interaction), which corrects by the recovery procedure, using a reverse pass in turn saved processed events. However, despite the cost of calculations in the case of detecting inconsistencies-errors, the possibility of acceleration of parallelization is largely preserved, since the number of events in the boundary layer is considerably lower than in cells. Since event management algorithm is applied only within a certain time step, the parallelization of periodic operations (such as the calculation of the interaction forces) can be performed with relatively high efficiency.

3 Basic Problems of Computer Simulation

Molecular dynamic experiment comprises the following stages. Primarily built the initial structure of calculable system (calculable block): are given the block

size (10^3 – 10^6 atoms) and the initial coordinates of the atoms. At this stage the temperature is usually defined by setting appropriate initial velocities by (4) or atomic displacements. The next main stage is to calculate the trajectories of each atom in the calculable block. For this are calculated the displacements of atoms from (3), using the short time step (10^{-13} – 10^{-15} s – integration step). To determine the velocity and displacement of atoms, it is necessary to know the force of interaction between them. Forces are defined by (1) using the model selected for the potential functions of the interatomic interaction. When calculating the interactions of atoms at the borders of the block it is necessary to define different, depending on the task, the boundary conditions (periodic, rigid, flexible, highly viscous or free). In the computer simulation process is performed monitoring of different characteristics (temperature, free volume, the coefficient of diffusion, pressure, etc.), as well as when it is required to explore the dynamics of atomic structure, at certain intervals of time the structures of calculable block are memorized. Study using different sub-modules of a computer program, responsible for structure visualization, charting, calculating the required parameters can be attributed to the third stage of the molecular dynamics simulation.

At the quest for a more reliable study using molecular dynamics simulations have to deal with problems that can be reduced to four basic: adequacy of interatomic interaction potential, the count rate (the speed of the experiment performance on the computer), the calculation errors, the variety of visualizers to display the structure of calculable block [5].

The correct description of the interatomic interaction is achieved by selecting an adequate potential function of interaction between atoms. There are theoretical methods based on the approximate solution of the quantum-mechanical problem of calculating the energy of the crystal: the empirical and semi-empirical methods, in which the potential is given as a function (Born-Mayer, Lennard-Jones, Morse, Mi-Gruneisen various power functions, etc.) with a set of parameters, which is chosen according to the reference values for given material. There are also a combination of first-principles (*ab initio*) and of potential (density functional method) approaches, or many-body potentials of Finnis-Sinclair type and the potentials obtained by embedded atom method (EAM). Accuracy of potential usually associated with its complexity and with execution speed of the computer experiment. Therefore, the question of finding an optimal potential function remains opened, the select of potential type in each case depends on the method of computer simulation and task. In applying the semiempirical potentials using their fitting by a three types of empirical parameters (structural parameter – lattice period, energy parameters – energy of sublimation and the energy of defect formation and etc., power parameters – elastic modules) can be investigated with high accuracy the structural and power changes occurring in the material. Should be used cautiously the energy parameters, take into account in the computer experiment only their relative changes in the study of structural-phase transitions, especially in the case of nanocrystals and low-dimensional systems.

Another major problem of molecular dynamics simulation is the count rate on the computer. High count rate allows to execute the longer experiments, increase the size of the calculable block, use a more complex and realistic interatomic potentials. Count rate indirectly affects the accuracy of computer experiments. There are several ways to increase the count rate:

1. Decrease of size of calculable block (effect – decreased reality of model, increases error at calculation of various structural-energy characteristics)
2. increase of time step of integration (effect – significantly increases the calculation error of trajectories of atoms)
3. Simplification of the potential function, tabulation of potential function, the introduction of so-called "cutoff radius" of potential (effect – strength of the interaction decreases rapidly with the distance between the atoms, so the interaction with remote atoms must be null)
4. Optimization of code – getting rid of extra functions in the main loop of a computer program (looping through all the atoms in the calculation of their interactions and displacements)
5. In the case of pair potentials calculation of force between two atoms occurs only once (the forces between atoms equal in magnitude and opposite in direction)
6. Partition of calculable block on the cells with assigning them numbers – in the calculation of interaction forces it is sufficient to consider only the atoms in neighboring cells and in compliance with "cutoff radius"
7. Acceleration of processing by means multiprocessor parallel calculations

The third problem of molecular dynamics simulation – errors that arise in calculating of the trajectories of motion of the atoms during the experiment – calculation errors, relating to the numerical method used to solve the equations of motion, or to the fact that the variables are rounded in the computer program. Errors, relating to the digitization step of the grid schemes in the solving process of the motion equations, can be reduced by using numerical methods of higher order than the Euler method, for example, the Runge-Kutta method. Furthermore, errors can be reduced by reducing the integration time step, but this leads to an increase in the duration of computer simulations, amount of experiments, or size of calculable block.

Another problem is the realistic visualization for the study of the atomic structure dynamics of the calculable block – you need a diverse set of visualizers for display of structures. There are three main types of visualization:

1. Using charts and graphs that reflect structurally dependent parameters (radial distribution diagrams, phase composition diagrams, crystallographic orientation diagrams, the intensity distribution of diffusion, etc.)
2. Two-dimensional sections of three-dimensional models, the visualizers of two-dimensional structure (areas of tensile and compression, the potential energy distribution, the phase distribution, the pattern of high-packed atomic series, trajectories and displacements of atoms in two-dimensional models, etc.)

3. Three-dimensional visualizations (atomic displacements, visualization of defect regions, fill of areas of particular phase composition, etc.)

Molecular dynamics method allows us to consider the block comprising about a billion atoms. Thus, almost any nanostructures can be modeled with a high degree of accuracy on multiprocessor computers.

4 Analysis of the Results of Computer Simulation of the Atomic Structure of Amorphous Aluminum by Event-Driven Molecular Dynamics Method

To study the structure of some metals, obtained by ultrafast cooling of the melt, in computer simulations it is necessary to change the speed of quenching. Process of simulation, in this case, comprises two stages:

1. Melting of the initial crystalline block
2. Quenching of the melt at a given rate

For example, to simulate the liquid Al structure, the temperature of initial block in crystalline state was set to 4400 K and sustainment was performed for 10^{-11} s (no more than 0.5% of all atoms evaporated - compensation wasn't been made for these atoms). Phase transition from solid to liquid state was determined by radial distribution functions, angular distribution functions, an abrupt change in the specific volume (expansion of metal) or decrease in the temperature of simulation block. The initial temperature and sustainment time were selected to minimize the time of complete destruction of the crystal structure and to prevent the evaporation of particles from simulation block, as the initial temperature is higher than the condensation temperature of aluminum (2792 K).

Simulation of amorphous aluminum by ultrafast cooling of liquid Al, obtained in the first stage, was performed in the second stage by lowering the temperature with linear decrease in velocities of atoms (it is closer to the real picture). Atoms' initial directions of velocity were assigned randomly, so the results of repeated computer experiments differed from each other. Simulation block comprised a different number of atoms (up to 20000) and represents a portion of a thin film. The interaction of atoms at a distance r was described by a paired Morse potential

$$U(r) = D \cdot (\exp(-2\alpha(r - \sigma)) - 2 \exp(-\alpha(r - \sigma))) \quad (5)$$

with parameters taken from [6]: $\alpha = 1.1646 \text{ (\AA)}^{-1}$, $\sigma = 3.253 \text{ \AA}$, $D = 0.2703 \text{ eV}$. Along two axes boundary conditions were periodic, along the third - free. The initial temperature was 4400 K. Such a high temperature is chosen to minimize the time of producing the melt. The time step was $0.01 \text{ ps} = 10^{-14} \text{ s}$.

Judging from experience of calculations performed by different authors, at the start it is sufficient to place the atoms as a regular lattice of Al (fcc crystal), and choose the initial impulses of the same modulo (subject to compliance with a given temperature) with a random distribution of their directions so that the

total momentum of the simulation block was zero. Due to instability of the trajectories of individual atoms (according to Lyapunov) initially some atomic structure containing individual atoms and clusters of atoms, as well as pores, are formed randomly in the melt. The first coordination sphere of those atoms corresponds to one or another well-known ordered structure. The structural units of the melt inside the simulation block occur chaotically. The melting in this model was conducted for 10 picoseconds.

Numerical calculations show that the structural chaos in the liquid state is largely inherited in the solid amorphous state in the case of rapid cooling, as the melt viscosity becomes so large that structural units of the melt come to a stop and retain only internal degrees of freedom. The crystallization process becomes impossible, since in a very short time, the atoms do not have time to move to a distance that would allow them to form a crystal lattice. This metastable state is not the lowest energy state, and the energy of the formed amorphous metal is determined by the arisen atomic structure. These atomic structures are largely random and varied depending on the initial conditions and the cooling rate.

Content analysis of fcc, hcp phases and Frank-Kasper polyhedra was conducted. For each atom of the simulation block the positions of nearest neighbors was evaluated, and then comparison with the reference samples was performed (results in Table 1).

Table 1. Percentages of the fcc, hcp and Frank-Kasper unit cells for three different cooling rates and simulation block of 20000 atoms. Percentage – the ratio of the number of atoms that are the "center" of cells to the total number of atoms in the system

Cooling rate	Unit cells	Fcc / all unit cells	Hcp / all unit cells	F-K / all unit cells
10^{13} K/s	$48 \pm 15\%$	$59 \pm 24\%$	$21 \pm 15\%$	$37 \pm 32\%$
10^{14} K/s	$42 \pm 2\%$	$43 \pm 3\%$	$25 \pm 3\%$	$31 \pm 3\%$
10^{15} K/s	$37 \pm 2\%$	$46 \pm 3\%$	$26 \pm 3\%$	$27 \pm 3\%$

As expected from the distribution of the number of atoms in the first coordination sphere, in all cases, 16-vertex Frank-Kasper figures were not found. Among the figures of Frank-Kasper there were found more icosahedra than any others. Based on the data given in the Table 1, for cooling rate of 10^{14} and 10^{15} K/s discrepancy in the results is of only a few percent, while for the rate of 10^{13} K/s, the scatter of results is very significant (defined statistical regularity is possible in simulation blocks hardened at high speeds). Large scatter in the data for the cells obtained at the slowest cooling may be due to the random nature of solidification centers, and the fcc, hcp and Frank-Kasper elementary cells of these systems are randomly scattered in volume and do not form a conjugate ordered structures (amorphous-nanocrystalline structure is formed).

As is well known, the choice of the interaction potential of atoms plays an important role in the application of molecular dynamics method [7]. If with this results change qualitatively, then the collection of atoms considered under con-

ditions of cooling to be regarded as structurally unstable system (according to Pontryagin), that is more likely in the neighborhood of the critical cooling rate. Complete theoretical analysis of the structural stability of systems of molecular dynamics is currently appear to be difficult to implement. However, the qualitative picture of the structural stability can be obtained by numerical analysis with the variation of empirical constants in the interparticle interaction potential [8].

5 Conclusions

Thus, it is necessary to use the concepts and methods of the modern theory of nonlinear dynamical systems in the study of atomic structure of liquids and amorphous metals. In addition, our calculations using molecular dynamics suggest that a particular atomic structure of amorphous metal is fundamentally unpredictable and irreproducible at the level of the model, as well as in a real experiment.

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