Study of phase transition in the pure metal melt during ultrafast cooling by method of higher-order correlation functions

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Abstract. This paper discusses the results of the application method of spatial correlation functions on a glass-forming liquid of a pure metal melt by performing molecular dynamics simulations. We define a high-order correlation function that quantifies a spatial correlation of single-particle displacements in liquids and amorphous systems. Time dependencies of the different 4-point spatial functions for supercooled and normal melt are obtained.

1. Introduction

The development of the new materials is an important activity in the continued progress of science and technology. Aluminum alloy is one of the substances which are widely used as structural materials. However, its non-crystalline form is also interesting to use, especially due to the fact that it has an excellent combination of characteristics resulting from its disordered structure. First of all, amorphous alloy is a more durable sort of matter than polycrystalline billet without surface treatment [1]. Some of them are exceptionally corrosion resistant, behave as very soft magnetic materials [2] etc. We define such material as glass because of its structure.

Supercooled liquids can vitrify if crystallization can be avoided under appropriate conditions such as rapid refrigeration, or mixing of the melt with another coarse grained material. This is the so-called glass transition. Metal glasses possess high strength combined with good bending ductility [3, 4]. These features are natural in different alloys but sometimes they can be found in pure metallic glasses [5]. It must be emphasized that metamaterials lose their high fracture tensile strength and ductility, et cetera, upon crystallization. Thus, it is very important to establish a phase state, that depends on external parameters, to essentially avoid an unwanted crystallization. The obtained parameters of the phase transition will determine boundaries of the application of the new structure, as well as the manufacturing technology in which the structure will have new useful properties.

However, at the moment there is no generally accepted theory describing the details of the glass transition itself. Nowadays, the transition from the liquid phase to the glass has many
different criteria for estimating the establishment of the system’s equilibrium [6, 7]. Some works discuss the fact that the transition is not accompanied by a sharp change in symmetry at the molecular level as it is in the case of the transition of a liquid crystal. Complex dynamics of glassy liquids can have a significant influence on the crystallization process. Correlation functions are a tool that allows us to investigate spatial and time behavior of quasi-equilibrium systems in details. Various studies confirm that the second peak of the radial distribution function (RDF) begins to split when the viscosity of the melt undergoes drastic changes [8]. Thus, the splitting of the second peak of RDF can be used as a criterion for the glass transition. Voronoi polyhedra are also used for a more detailed study of the structure [9]. Influence of the number of different types of Voronoi polyhedra on a form of pairwise correlation functions is considered in [8].

The method of molecular dynamics (MD) can produce a detailed study of glass and phase transitions and obtain various characteristics of this process [10–15]. RDF is commonly used in MD for analyzing the amorphous structure and determining the vitrification. In the particular case of supercooled glass-forming liquid, the main question is whether there is a correlated motion of particles or not. These correlated motions could be responsible for the stretched exponential decay of the density-density autocorrelation function.

The goal of this work is to study the collective motion of a metal melt in a vicinity of a phase transition point. The method of thermal-hydrodynamic fluctuations was developed [16–18] and applied in some papers [19–22]. These papers represent a detailed description of the motion of the system in the liquid phase. We are interested in the part that affects the collective motion of groups of molecules. We expect changes in the character of the collective motion in the supercooled liquid (abrupt cooling below the phase transition point). In this case, this approach could be used as a way to refine the temperature of the phase transition in the cooled matter. The expected discrepancies in a behavior and their relationship with the phase transition will be determined from the point of view of the dynamics of atomic motions. In this paper, we will apply this approach of high-order correlation functions for a supercooled metal melt for the first time.

2. Model
The simulation was performed using the LAMMPS software package for liquid aluminum. The canonical ensemble of pure Al containing 4000 atoms is melted and equilibrated at 3000 K for 100 ps and cooled down to 800–1200 K by the method of velocity rescaling at different cooling rates. However, all further data correspond to a cooling rate of $10^{14}$ K s$^{-1}$ due to an insignificant difference in the behavior of the system with cooling in the range $(5–50) \times 10^{13}$ K s$^{-1}$. To create the initial configuration, atoms are placed at the sites of the fcc lattice with parameter $a_0 = 4.05$ Å. A simulation box $10a_0 \times 10a_0 \times 10a_0$ along the axes $x$, $y$, $z$ with the periodic boundary conditions on all axes is used. Liquid aluminum is described by the many-body embedded atom method (EAM) potential [23]. This approach is based on the ideas of the density-functional theory (and amenable to MD-simulation modelling). The total energy of the system in this approach is represented as follows:

$$E_{\text{tot}} = \sum_i F(n_i) + \frac{1}{2} \sum_{i \neq j} \Phi_{ij}[r_i - r_j],$$

where $n_i$ is an effective electron density at the site of the atom $i$ and is approximated by a superposition of atomic density tails from the other atoms. $F(n_i)$ is a nonlinear function (the embedding energy) describing an interaction of the atom $i$ with its electronic surrounding, and $\Phi_{ij}$ is a pair potential. The embedding energy term $F(n_i)$ is supposed to describe complex many-atom interactions.

When the system reached the desired temperature, we fixed the energy of the system to obtain the necessary trajectory of the microcanonical ensemble. The Nose–Hoover thermostat
was switched off only after a certain time of relaxation to avoid possible perturbations in the system after the cooling procedure. We calculated the trajectory of length 10 ns with a step of 1 fs. Configurations were recorded each 1000 steps, i.e., in 1 ps. As a result for each simulated trajectory, we obtained a set of 10,000 successive instantaneous configurations of the model, each of which is represented in our calculation by a list of wrapped and unwrapped coordinates of the aluminum atoms at any given time. To obtain smooth and well reproducible correlation functions, we averaged the results over a large number of starting configurations belonging to a segment of the simulated trajectory which length was much higher than the expected characteristic time of the required correlations. The calculation of all correlations functions was performed using only these sets of configurations. During the calculation, we compared the relative position of pairs of atoms of some selected configuration, called the starting configuration, with their position in the next configurations. The correlation functions were calculated separately for each of the selected ranges of initial distances.

Also, due to the fact that we used periodic boundary conditions, we reconstructed true trajectories from their wrapped position in the cube without breaking trajectory for a correct consideration of the displacements of molecules. We saved unwrapped and shifted positions of atoms to make this procedure unambiguous. First of all, we shift all unwrapped trajectories to their corresponding current positions of atoms in the cell. So when we start an investigation of the motion, we have a new initial position.

3. Calculation and results

Correlators that can reflect the collective processes occurring in a vicinity of the molecule have to be special functions. They must be dependent functions of at least two particles and the moments of time of observations. Therefore, the investigation of the dynamic inhomogeneities in the amorphous material must use the 4-point correlation functions. It is necessary to describe a behavior of various types of such correlators and below some of these functions will be considered.

3.1. Ordinary correlators

We will describe definitions and notations: \( \mathbf{r}_i(t) \) is a radius-vector of the atom \( i \) at time \( t \); \( \mathbf{r}_i(t) \) is a length of this vector; \( \mathbf{r}_{ik}(t) = \mathbf{r}_k(t) - \mathbf{r}_i(t) \) is a vector that connects the atom \( i \) to the atom \( k \) at time \( t \); the angular brackets \( \langle \ldots \rangle \) denote averaging over all the atoms, and the angular brackets \( \langle \ldots \rangle_{R_0} \) denote averaging over all the atoms in their pairs separately for each range of initial distances \( R_0 \).

At first, we calculate a well-known single-particle distribution function—the time dependence of the mean-square displacement of the particles, there \( R_2(t) = \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle \) is shown in figure 1. Also we consider the two-particle function \( V_2(t) = \langle |\mathbf{r}_{ik}(t) - \mathbf{r}_{ik}(0)|^2 \rangle_{R_0} \), the square of the change in the vector connecting a pair of atoms \( i \) and \( k \) with initial distance \( R_0 \) (figure 2), and \( D_2(t) = \langle |\mathbf{r}_{ik}(t)|^2 \rangle_{R_0} \), the squared length of this vector at time \( t \) (figure 3). As it can be seen, these functions depend on temperature, but there is nothing unusual in their behavior over a long period.

Later we will check whether the value of the \( V_2(t) \) function corresponds to the diffusion asymptote value on long times. To do this, we should subtract the trivial part from the \( V_2(t) \) function, thereby defining the new correlator \( DP(t) \). If we expand the functions \( V_2(t) \) and \( D_2(t) \) into terms, we will see that the trivial part of \( D_2(t) \) is a doubled single-particle function, but \( D_2(t) \) expands not only to \( R_2(t) \). We could define it as the IDP\((t) \) correlation function.

We also calculated correlation function \( C_2(t) = \langle |\mathbf{r}_{ik}(t) - \mathbf{r}_{ik}(0)|^2 \rangle_{R_0} \), which is the square of the change in the length of the vector connecting the pair of atoms \( i \) and \( k \) (figure 4).

The figures in normal scale show that all three functions considered as \( V_2(t), D_2(t) \) and \( C_2(t) \), show no singularities, but it does not follow that they reach the particle diffusion asymptotes \( 2R_2(t) \) at time 4000 ps. We cannot neglect deviations between functions in long-term behaviour,
because they can have different asymptotes at all. To make this obvious, we should analyse deviations between $2R^2(t)$ and these asymptotes by describing of new correlators introduced below. We will also consider a temporal behavior of these correlators.

### 3.2. Non-trivial correlators

For more obvious detection of deviations between functions $R^2(t)$ and $V^2(t)$ in long-term behavior, we will define some new correlators. The deviation of the function $V^2(t)$ from the diffusion asymptotes is described by the correlator $DP(t)$:

$$V^2(t) = 2R^2(t) - 2DP(t).$$

Such non-obvious way of determining of correlator $DP(t)$ on the other hand gives an understandable physical meaning. It is an average scalar product of the displacement vectors of

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**Figure 1.** Mean-square displacement $R^2(t)$ of atoms.

**Figure 2.** Mean-square change in the vector connecting two atoms $i$ and $k$ $V^2(t)$.

**Figure 3.** Mean-square distance between two atoms without subtracting the initial distance between them $D^2(t)$; $T = 800$ K.

**Figure 4.** Mean-square of the change in a distance between the atoms comprising the pair $C^2(t)$; $T = 800$ K.
two particles in the selected pair:

\[ \text{DP}(t) \equiv \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \cdot [\mathbf{r}_k(t) - \mathbf{r}_k(0)] \rangle_{R_0}. \]  

(3)

If we normalize vectors of the displacements, we will obtain the correlation coefficient

\[ \text{CC}(t) \equiv \langle \frac{[\Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_k]}{[\Delta \mathbf{r}_i] [\Delta \mathbf{r}_k]} \rangle_{R_0} = \langle \cos \varphi \rangle_{R_0}. \]  

(4)

Physical meaning of this function is the average cosine of the angle between the displacement vectors of two atoms which were distant from each other by the initial length \( R_0 \). Figure 5 shows differences between correlator \( \text{DP}(t) \) for supercooled and normal aluminum melt; correlator \( \text{CC}(t) \) is shown in figure 6.
As it can be seen from the graphs, the correction to the function $V_2(t)$ in a form of the correlator $DP(t)$ does not reach zero values, even at long observation times. On the contrary, it reaches a certain plateau at the time of 500 ps. The value of the function on the plateau is related to the initial distance between the melt atoms $R_0$. The closer atoms at the initial time, the more correlated their motion.

Its corresponding correlation coefficient $CC(t)$ decreases rapidly for a short observation time, but at times of a few hundred picoseconds, this decrease significantly slows down (in the range of 1 to 3 ns). Correlator $CC(t)$, describing the motion of closely located atoms in range $R_0 \approx 2–7$ Å in the supercooled melt, reaches a plateau. This behavior was found to be characteristic in cases of rapid cooling below the crystallization temperature of aluminum $T_{\text{crys}} = 933$ K, and it is completely absent in the case of the dynamics of ordinary aluminum liquid. Thus, it is possible to use a set of these correlators related to different temperature systems to determine the temperature of the transition point of their liquid system to a supercooled state.

To obtain reliable graphs and significant differences of the supercooled and ordinary aluminum liquid, there were provided graphs for these two temperatures in a large neighborhood of the phase transition point. In the case of using a larger system with a larger averaging capability, it is possible to trace these differences in a small area of the crystallization point. This will be investigated thoroughly in a further research.

4. Conclusions

After carrying out the MD for a sufficiently small aluminum melt system after ultra-fast cooling to different temperatures, we can conclude the following:

(i) Supercooled liquids have in general a similar dynamics of the motion of atoms. The mean-square displacement of molecules can be used to obtain the diffusion coefficients like in the related works in order to compare the results.

(ii) The dynamics of the motion of the various groups of neighboring atoms ($R_0 \lesssim 7$ Å) in the case of a supercooled liquid is more correlated than expected.

(iii) The plateau in the behavior of a certain 4-point correlation function $CC(t)$ at large times can be used as a sign of a transition to the supercooled state.

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