Collective effects and liquid–glass transition in supercooled melts of binary alloys

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Abstract. A possibility of a transition into a glassy state of binary alloys based on aluminum, nickel, and copper after ultrafast cooling has been investigated using the method of molecular dynamics. It was demonstrated that some 4-point correlators changed their behavior and depended on the parameters of the metastable alloy state. By analyzing the complex dynamics of particle motion in overcooled liquids some certain conditions for the formation of the glass for aluminum–nickel melt was founded.

1. Introduction

The processes of the development and the abilities to create new technological equipment very depend on the perspective structural materials. Metallurgy proposes thousands of special alloys for every engineering request. But sometimes thousands of types of compounds are not enough to create the better machinery. The fundamental science can offer a new interesting type of structural materials. So, the goal is to find areas of possible using of metastable states of usual compounds, named metal glasses. Let us begin by considering the advantages of using the glass state of some alloys.

Using the non-crystalline form of an alloy gives a good combination of characteristics, which results from its inner disordered structure. Commonly, a detail without defects in the crystal structure is much durable. So, amorphous metallic alloys, or metal glasses, are more useful than polycrystalline billet of a compound [1]. Some alloys, after conversion into the glass, become exceptionally corrosion resistant, other become to behave as soft magnetic materials etc [2]. The most reliable way to make conversion into the glass state is an ultrafast supercooling of the glass-forming liquid. If the process occurs with sufficient speed, the liquid will be overcooled lower its melting point. After reaching the special temperature, so-called glass transition temperature, the supercooled liquid will become very viscous. The metallic glasses, obtained by this procedure, differ by high strength combined with good bending ductility [3, 4]. It must be emphasized that amorphous materials lose their high fracture tensile strength and ductility, et cetera, upon crystallization. That is the reason to use them only under well-known phase conditions to avoid an unwanted crystallization. It is very important to establish borders of the glass phase state, the obtained temperature of glassy transition will determine boundaries of the application of new
materials. As well, the technology of manufacturing the structure with new useful properties is also limited by this parameter.

Nowadays, there are many different, inconsistent theories of the transition from liquid phase to the glass [5, 6]. Some theories 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. The fact is that complex dynamics of glass-forming liquids can have a significant influence on the crystallization process. This dynamic affects the related markers of the internal structure, such as its scattering function. 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 [7]. Note that the RDF is not one of the correlation functions that can describe the dynamics or the structure of matter.

The method of molecular dynamics (MD) can produce all dynamic properties of the system under investigation, so it will be used to carry out a detailed study of glass-forming liquids and obtain various characteristics of this process [8–14]. Thus, it will be possible to obtain not only the RDF, which is commonly used in MD for analyzing the amorphous structure and determining the vitrification. Other correlation functions can also be good tools and allow us to investigate spatial and time behavior of quasi-equilibrium systems in details. 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 preceded vitrification could be responsible for the stretched exponential decay of the density–density autocorrelation function.

The goal of this paper is to study the collective motion of the glass-forming binary alloys on base Al–Cu–Ni in a vicinity of their phase transition point. In a number of works was introduced [15–17] and applied [18, 19] the method of thermal-hydrodynamic fluctuations in liquids. These papers discuss the motion of the system particles in detailed descriptions. We are interested in the part that affects the collective motion of groups of particles. Particularly, it is expected to find changes in the character of the collective motion after transition into the supercooled liquid like it was shown here [20] in the case of pure metal melt (after abrupt cooling below the phase transition point). This approach will be used as a way to refine the temperature of the phase transition in the overcooled matter. The expected discrepancies in the 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 modeled supercooled binary alloys for the first time.

2. Model

The simulation was performed using the LAMMPS software package for liquid binary alloys Al$_{30}$Cu$_{70}$ and Al$_{30}$Ni$_{70}$(index means weight percent of the elements). The canonical ensemble of atoms of Al–Cu–Ni, containing 13 824 atoms was melted and equilibrated at 3000 K for 100 ps and then cooled down to 600–2200 K by the method of velocity rescaling at different cooling rates. However, all further data corresponds to a cooling rate of 10$^{14}$ K/s due to an insignificant difference in the behavior of the system with cooling in the range (5–50)$\times$10$^{13}$ K/s. This range of temperatures was chosen to cover the dynamics of alloys above the liquidus line and below the eutectic line of investigated compounds. From the experimental works [21] was founded that for Al$_{30}$Cu$_{70}$ eutectic temperature $T_{eut1} = 821.4$ K, liquidus line lay nearby 1090 K and for Al$_{30}$Ni$_{70}$ alloy $T_{eut2} = 913.1$ K. But the liquidus line in this alloy is located in the vicinity of eutectoid point $T_{eut2} = 1911$ K of Al$_1$Ni$_1$ phase, therefore characterized by higher than expected transition temperature 1910 K.

To create the initial configuration of Al–Cu and Al–Ni atomic structure, atoms were placed at the sites of the primitive cubic lattice with parameters $a_1 = 2.519$ Å and $a_2 = 2.475$ Å correspondingly. These parameters correspond to the densities of alloys in liquid state $\rho_1 = 4.71$ g/cm$^3$ and $\rho_2 = 4.69$ g/cm$^3$, which were taken from experimental data [22–24]. After
Figure 1. Mean-square change in the vector connecting two atoms \( i \) and \( k \) \( V^2(t) \) at \( R_0 = 3 \text{ Å} \). Picture (a) corresponds to Al\(_{30}\)Cu\(_{70}\), (b) to Al\(_{30}\)Ni\(_{70}\). The curves (from top to bottom) correspond to the temperatures from 1300 (a), 2200 (b) to 600 K (a, b). \( V^2(t) = V^2(t)/[1 \text{ Å}] \); \( t^* = t/[1 \text{ ps}] \).

supercooling, density was increased to 5.2 g/cm\(^3\) to prevent gaps in the liquid, and this value also converges with the experimental data at low temperatures. The simulation box with sizes \( 24a_i \times 24a_i \times 24a_i \) along the axes \( x, y, z \) and periodic boundary conditions on all axes was used. Liquid Al–Ni, Al–Cu describes by the many-body embedded atom method (EAM) potential [25, 26]. This approach is based on the ideas of the density-functional theory (and amenable to MD-simulation modeling). 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 \( \Phi_{ik} \) is a pair potential. The embedding energy term \( F(n_i) \) is supposed to describe complex many-atom interactions.

3. Calculation and results

In the previous work [20] was shown that some correlators reflect the collective processes in a vicinity of the phase transition point. They are not trivial functions and must be dependent on at least 4 phase points of the observed system. Therefore, the investigation of the dynamic inhomogeneities in the amorphous binary material must use the 4-point correlation functions. Below it will be described which behavior of these functions will be considered proper for prediction of glassy transition.

At first, let us describe definitions: \( \mathbf{r}_i(t) \) is a radius-vector of the atom \( i \) at time \( t \); \( r_i(t) \) 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 \( R_0 \pm \Delta \) between particles.

In order to obtain an approximate idea of the dynamics of the particles in melts over a wide range of temperatures lower and above than liquidus line, two-particle modification of the well-known RDF (radial distribution function) was calculated. The time dependence of the
Figure 2. Correlator CC(t). Picture (a) corresponds to Al$_{30}$Cu$_{70}$, (b) to Al$_{30}$Ni$_{70}$. The curves (from top to bottom) correspond to the initial distance between the pair of molecules $R_0$. The solid curves correspond to 1300 (a) and 2200 K (b), dotted to the 900 K for both.

mean-square displacement of the particles in our notations looks like $R^2(t) \equiv \langle [r_i(t) - r_i(0)]^2 \rangle$, and considered two-particle function is $V^2(t) \equiv \langle [r_{ik}(t) - r_{ik}(0)]^2 \rangle_{R_0}$. The square of the change in the vector connecting a pair of atoms $i$ and $k$ with initial distance $R_0$ $V^2(t)$, shown in figure 1, should be like $2R^2(t)$ in case if there no connections in particle movements, especially at long observation times. If the system is modeling by random walk model, this difference is practically absent, which was shown in the paper [18]. As it was seen before in [20], these functions differ from each other over a long period, since using molecular dynamics we can model the inhomogeneities and thus allowing us to confirm the presence of the group motions. Also looking on its dependence on temperature, there is nothing unusual except strange behavior for Al$_{30}$Ni$_{70}$ at low temperatures.

Check of the differ in the values of the $V^2(t)$ function and predicted $2R^2(t)$ (diffusion asymptote value of movement of two free particle in a liquid) on long times been done by introduction of a new correlator DP(t). It has been determined like a deviation of the function $V^2(t)$ from the diffusion asymptotes $2R^2(t)$ in that unusual way, and after normalization for more obvious features detection, we will obtain the new useful correlator CC(t):

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

Such non-obvious way of determining of correlator DP(t) gives an understandable physical meaning. It is an average scalar product of the displacement vectors of two particles in the selected pair:

$$DP(t) \equiv \langle [r_i(t) - r_i(0)] \cdot [r_k(t) - r_k(0)] \rangle_{R_0}. $$

(3)

If we normalize vectors of the displacements, to see details of different scales, we obtain the correlation coefficient:

$$CC(t) \equiv \langle [\Delta r_i \cdot \Delta r_k] / || \Delta r_i || \Delta r_k || \rangle_{R_0} = \langle \cos \varphi \rangle_{R_0},$$

(4)

with physical meaning as 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 2 shows us differences between motions of Al$_{30}$Cu$_{70}$ and Al$_{30}$Ni$_{70}$ alloys in supercooled and normal liquid states. Correlator CC(t) shows almost no correlation in the movement at high temperatures for both alloys, but its plateau till 2.5–3 ns for the supercooled state means that particles move similar for some reason, losing similar dynamics over long times due to the diffusion motion.
Figure 3. Correlator CC(t). Picture (a) corresponds to Al\textsubscript{30}Cu\textsubscript{70}, (b) to Al\textsubscript{30}Ni\textsubscript{70}. The curves (from top to bottom) correspond to the temperatures from 600 (a, b) to 1300 (a) or 2200 K (b). Radius $R_0 = 3$ Å for all curves.

Figure 4. Correlator CC(τ, T). The curves (from top to bottom) correspond to the initial distance between the pair of molecules $R_0$. Dotted curves correspond to Al\textsubscript{30}Cu\textsubscript{70} alloy (a, b); solid—Al\textsubscript{30}Ni\textsubscript{70} (b); characteristic time $\tau = 1.0$ ns.

If we expand the analysis of CC(t) for different temperatures, like represented in figure 3, we can see that the correlation coefficient undergoes changes of the time behavior from a linearly decreasing function to an exponential sharp drop. This behavior of CC(t) is interrupted by the appearance of the foregoing plateau in the region of 800–950 K, and it can be seen for Al\textsubscript{30}Ni\textsubscript{70} it can turn into a constant value, which indicates the vitrification during the life of the system.

It is interesting to analyze this correlator in time region before the melt reaches the glassy state since, for different temperatures, this phenomenon can occur not fast. We should analyze values of correlation coefficient curves at low observation times ($\tau \ll T_{\text{obs}}$) for various liquid temperatures and interpret the changes if we find that they strongly differ.

As it can be seen in figure 4, the correlation between particles in both alloys does not reach zero values even for high temperatures during taken characteristic time. On the contrary, curves for both alloys reach a certain plateau. The value of the function on the plateau is related to the initial distance between the melt atoms $R_0$ but the difference is small for hot melts. The closer atoms were at the initial time, the more correlated their motion. Presented graphs plotted for the characteristic time $\tau = 1.0$ ns, but they are similar in the range 800–1500 ps.
Note that curves of \( CC(\tau, T) \) decrease rapidly for \( Al_{30}Ni_{70} \) alloy near \( T_{\text{glas}} = 975 \) K, and for higher temperatures curves of values of correlation show linear behavior for both alloys. This decreasing is absent in the case \( Al_{30}Cu_{70} \), means that \( Al-Cu \) alloy has no transition at this cooling rate since the particles in the melt, as expected, gradually reduce their mobility with decreasing of the temperature of the system. Thus, taking into account the absence of crystallites in the melt by analysis on \( V2(t) \) and constant average temperature in the calculations of the ensembles, 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 glassy state.

4. Conclusions
As a result of performed modeling and analysis of systems of metal melts in different conditions, we can make next conclusions:

(i) Complex 4-point temporal correlation functions reveal differences in the behavior of clusters of liquid particles of different sizes in binary alloys.

(ii) The correlator for cluster dynamics with a size \( (R_0 \leq 7 \text{ Å}) \) differs in its behavior, exhibiting a temperature dependence in the metastable region.

(iii) This change in the behavior of the correlator \( CC(t) \) gives us temperature of transition for \( Al_{30}Ni_{70} \) near 950 K.

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