The glass transition criteria for aluminum–copper melt

E M Kirova\textsuperscript{1,2,3} and V V Pisarev\textsuperscript{2,3,1}

\textsuperscript{1} Moscow Institute of Physics and Technology, Institutskiy Pereulok 9, Dolgoprudny, Moscow Region 141700, Russia
\textsuperscript{2} National Research University Higher School of Economics, Myasnitskaya 20, Moscow 101000, Russia
\textsuperscript{3} Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
E-mail: kirova@phystech.edu

Abstract. In this study, the glass transition criteria based on the viscosity change and on the transverse sound propagation, that were obtained for the aluminum melt, are validated on the aluminum–copper film. Molecular dynamics method is used to study the isobaric cooling process. The glass transition temperature is estimated from the dependence of the oscillation damping upon the temperature. The obtained temperature compared with the increasing in the kinematic viscosity.

1. Introduction
The way of obtaining the temperature of the glass transition has been a point of debate for many years. There are a few glass transition criteria that have been used. In numeric simulations, the structural criteria are used: the splitting of the second peak of the pair correlation function \cite{1} and the icosahedral short-range order \cite{2, 3}. Also, there is dynamic criterion which is based on the change of diffusivity behavior \cite{4, 5}. In the experimental works, the calorimetric criterion is widely used (the decrease of the specific heat of material) \cite{6, 7}. However, the difference between the calorimetric glass transition temperature and the temperature, obtained using the structural and dynamic criteria, might reach several hundred kelvins \cite{8}.

In the previous work, the glass transition temperatures, obtained using the structural, dynamic and calorimetric criteria, are compared with the viscosity change \cite{9}. As an example, the liquid aluminum film is considered. It is shown that the calorimetric glass transition temperature agrees with the viscosity change. Also, the new glass transition criterion is proposed which is based on the transverse oscillations in the film \cite{9, 10}. The glass transition temperature is estimated from the temperature dependence of the oscillation damping of the stress autocorrelation functions (SACF). The obtained glass transition temperature agrees with the calorimetric temperature.

In this study, the new criterion is validated on a more complex system. The copper–aluminum film is taken as an example. The temperature of the viscosity increase is compared with the glass transition temperature, based on the transversal sound propagation. The viscosity values are compared with the experimental data \cite{11, 12}. The obtained glass transition temperature compared with the structural criterion \cite{13}.
The current paper is composed as follows. The molecular dynamic (MD) model, the initial configuration and the cooling process are given in section 2. The viscosity behavior during the cooling process is described in section 3. The comparison with the experimental data is considered. Section 4 is devoted to the glass transition temperature, based on the transversal sound propagation and its comparison with the structural criteria. Section 5 contains our conclusions.

2. Molecular dynamics model
Molecular dynamics method is used to study the isobaric aluminum–copper melt cooling. 32000 atoms are placed as a thin film that takes a half of the volume of the simulation box. So, the pressure remains near-zero, as the film volume changes during the cooling process. The embedded atom method potential [14] is used in the simulation. The periodic boundary conditions are used. In the initial configuration, aluminum atoms are placed at the sites of the face-centered cubic lattice with parameter $a_0 = 4.08\, \text{Å}$ in the cubic region $20a_0 \times 20a_0 \times 20a_0$. The total dimensions of simulation box are $20a_0 \times 20a_0 \times 40a_0$ along the axes $x, y, z$. Then the random aluminum atoms for a chosen fraction are replaced with the copper atoms. In this work, the fraction of the copper atoms is set to 0.5.

At the initial step, random (in magnitude and direction) velocities are given to all the atoms. Then the system is equilibrated to the liquid state at the temperature 2000 K for the first 900 ps. The final step of the initial state preparation is lowering of the temperature and thermalization at 1500 K for 5 ps.

To investigate the glass transition, the system is rapidly cooled at a constant cooling rate $4 \times 10^{13}\, \text{K/s}$ from 1500 to 300 K. During the calculation process, every 100 K the intermediate state of the system is persisted. When the temperature of the system equilibrates, the viscosity calculations are started for the next 8000 ps. Numerical integration of the equations of motion is done using 2 fs timestep.

3. The viscosity behavior during the cooling process
The method for obtaining the ensemble averaged stress correlation functions and the kinematic viscosity coefficient via Green–Kubo formula is described in the previous works [9, 15]. The averaging is performed over 20 statistically independent MD trajectories. The code which is based on LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [17] is used to get the dependence of the viscosity coefficient on temperature.

The results for the aluminum–copper melt are presented in figure 1 together with experimental data [11, 12]. The comparison with the results for the pure aluminum is also shown.

It is shown that at the temperatures above 1000 K the kinematic viscosity values of the aluminum–copper melt are larger than of the pure aluminum. The results are consistent with the experimental data. Note that the viscosity shows the Arrhenius behavior.

Then during the cooling process, the viscosity coefficient increases, and the kinematic viscosity shows super-Arrhenius behavior. It is shown that the steep change of the viscosity is at the temperature range 500–600 K for the aluminum–copper melt and 600–650 K for the pure aluminum. That means that the glass transition temperature for the pure aluminum is higher than for the aluminum–copper melt.

The viscosity is not shown for the temperatures below 500 K for the aluminum–copper melt, since the integral of the stress correlation function diverges (see [9]).

4. The transverse oscillations in a film during cooling
The stress autocorrelation functions in the direction, which is perpendicular to the film plane, are considered in figure 2 for the aluminum–copper melt. Similarly, to the previous work [15],
Figure 1. The dependence of the kinematic viscosity coefficient on temperature for \( |\frac{dT}{dt}| = 4 \times 10^{13} \) K/s: purple line—MD simulation results for the aluminum–copper melt; blue and green crosses—the experimental data [11] and [12] respectively; red line—MD results for pure aluminum [15]; diamonds—the experimental data [16].

Figure 2. The ensemble averaged SACFs along the direction perpendicular to the film plane for the aluminum–copper melt in the temperature range 300–900 K.

we obtain the solidification temperature from the dependence of the oscillation damping upon temperature.
Figure 3. The dependence of damping via equation (1) upon temperature: arrows—the glass transition temperature; the purple line—aluminum–copper melt; red line—pure aluminum.

We define the decrement of oscillation damping $\delta$ as the ratio of two consecutive extrema:

$$\delta = \frac{A(t + T/2)}{A(t)},$$

where $A(t)$ is the amplitude of the SACF, $T$ is the oscillation period.

The dependence of the decrement $\delta$ on temperature is presented in figure 3. It is shown that the for the aluminum–copper melt the transverse sound propagation is in the temperature range 600–650 K. Than during the cooling process the decrement increases in the temperature range 450–650 K and reaches plateau, indicating a stable glass. The glass transition temperature can be estimated as the temperature at which the oscillation damping is increased by half of the total change in the whole cooling process. It is shown that the glass transition temperature for the aluminum–copper melt is about 500 K.

The results for the pure aluminum are also presented (the temperature is about 600 K [15]). It is shown, that the glass transition temperature for the pure aluminum is higher than for the aluminum–copper melt. So, the decrement behavior correlates with the viscosity change during the cooling process. In the work [13], the aluminum–copper melt during cooling process with a cooling rate $4.2 \times 10^{13}$ K/s is considered. The pair correlation functions for aluminum and copper are presented. It is shown that the second peak splits at 430 K for the aluminum, and at 700 K for the copper. So, the glass transition temperature obtained using the oscillations behavior in the film agrees with the results for the structural criterion.

5. Conclusions
In this study, the glass transition criteria based on the viscosity change and on the transverse sound propagation (obtained in [9, 15]) are validated on the aluminum–copper melt. Molecular dynamics method is used to study the film cooling. It is shown that the viscosity steep change for the aluminum–copper melt is in the temperature range 500–600 K. Also, it is shown that the
temperature of the viscosity increase for the pure aluminum is higher than for the aluminum–copper melt (600–650 K).

The temperature when the stress correlation functions along the direction perpendicular to the film begin oscillating in the aluminum–copper melt is also found (about 500 K). It is shown that glass transition temperature for the pure aluminum is higher than for the aluminum–copper melt (600–650 K). So, the new criterion based on the transverse sound propagation is consistent with the viscosity behavior and with the structural criterion.

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