

Study of viscosity of aluminum melt during glass transition by molecular dynamics and Green–Kubo formula

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Abstract. Molecular dynamics study of shear viscosity behavior of liquid aluminum is performed. The embedded atom method potential is used at the simulation of isobaric cooling. The viscosity is calculated using the Green–Kubo formula. The stress autocorrelation functions are obtained in the range 300–1200 K. The calculated kinematic viscosity is in agreement with the experimental data for the temperatures above melting temperature. The steep change of the shear viscosity is found below 650 K which we associate with the glass transition and is in a good agreement with the temperature which is obtained using the calorimetric criterion Kolotova *et al* (2015 *J. Non-Cryst. Solids* **429** 98). The viscosity coefficient can not be calculated using the direct atomistic simulations below that temperature.

1. Introduction

Glass is an amorphous solid with unique isotropic properties. The liquid-glass transition is one of the most interesting questions of the physics of amorphous state.

Glass transition occurs when the liquid is cooled at the rate higher than some critical cooling rate. From a practical point of view, the transition into a solid is characterized by a steep change of the viscosity coefficient to 10^{12} Pa.s. However, the direct experimental measurement of viscosity during the dynamic cooling (at the rates more than 10 K/min) is not always convenient or even possible, that is why different indirect criteria are used. There are structural, dynamic and calorimetric criteria for the glass transition. The first one is splitting of the second peak of the pair correlation function, i.e., the emergence of two local maxima and one minimum in the second coordination sphere. The second one is the formation of clusters in the one-component systems. Another important criterion is the change in the activation energy of self-diffusion of atoms. Changes in heat capacity during cooling or heating is the most convenient criterion for determining the glass transition in the experiments [1].

The problem is that the glass transition temperature depends on what criterion is used to define it. It has been shown in molecular dynamics (MD) simulations for silicate [2] and aluminum [3] melts. To obtain the temperature of viscosity jump and to understand the way it relates to the other temperatures is the main motivation for writing this article.



The information about the other criteria for the glass transition can be found in the article [3]. The comparison of the structural, dynamic and calorimetric criteria is also considered.

In this paper, the behavior of the shear viscosity during the glass transition is studied. There are two basic techniques for calculating the transport coefficient from equilibrium molecular dynamics simulations.

The first one is based on the Einstein–Helfand equations [4, 5]. In the Einstein–Helfand theory, the coefficient is obtained by using the slope of the Helfand moment versus time. The second one is based on the Green–Kubo relations [6]. Green and Kubo proved that the coefficients describing the transport properties of the system can be represented as integrals of autocorrelation functions. In the article [7], both approaches are shown to give consistent result for the case of simple Lennard-Jones liquid. The Helfand approach to calculate viscosity, however, suffers from the sensitivity of the results to the system size and the presence of boundaries [5]. The Green–Kubo relation-based approach is free from this drawback. Therefore, we choose the Green–Kubo method in this work to study the viscosity.

Alternatively, one may calculate the viscosity from nonequilibrium MD simulations. Such approach involves creating the Couette flow in liquid and finding the proportionality coefficient between momentum flux and the velocity gradient [8]. We do not use this approach in this work because it imposes high shear stresses which may destroy the microstructure of glass.

The current paper is composed as follows. The molecular dynamic model, the initial configuration and the calculation technique are described in section 2. The calculation technique and simulation details are given in section 3. Section 4 is devoted to the dependence of shear viscosity on temperature. Also, the obtained glass transition temperature is described. The comparison with the theoretical and experimental data is considered. Section 5 contains our conclusions.

2. Molecular dynamics model

Aluminium melt is taken as an example of the system with a many-body interatomic interaction potential. Molecular dynamics method [6, 9] is used to study the aluminum melt cooling. The embedded atom method potential [10] is used in the simulation. The expression for the potential is

$$U = \sum_{i<j}^N \varphi(r_{ij}) + \sum_{j=1}^N F(\bar{\rho}_j), \quad \bar{\rho}_j = \sum_{i \neq j}^N \rho(r_{ij}). \quad (1)$$

The first term is a sum of pair potentials φ over all atom pairs in the system, r_{ij} is the distance between atoms i and j . A non-linear embedding function $F(\bar{\rho}_j)$ introduces many-body effects, ρ_j is an effective electron density that is induced by the neighbouring atoms at the given atom. The parametrizations of the functions φ , ρ , F for aluminum are taken from [11].

The state to be studied is a MD computational cell with the periodic boundary conditions. The initial configurations are prepared by the procedure used in [3]. In the initial configuration, atoms are placed at the sites of the face-centred cubic lattice with parameter $a_0 = 4.08 \text{ \AA}$ 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 . So, 32800 atoms are placed as a film, that takes a half of the volume of the simulation box (Figure 1). That is why the pressure remains near-zero as the film volume changes during the cooling process.

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. Numerical integration of the equations of motion is done using 2 fs timestep.

To investigate the glass transition, the system is rapidly cooled with a constant rate from 1500 K to 300 K. MD simulations are performed for the cooling rate $4 \times 10^{13} \text{ K/s}$.

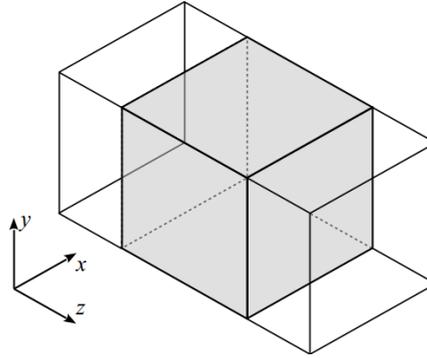


Figure 1. Molecular dynamics model. The initial configuration. Gray color shows the region filled with atoms.

3. Simulation

The expression for the shear viscosity coefficient η is

$$\eta = \frac{V}{k_B T} \int_0^{\infty} dt \langle P_{xy}(0) P_{xy}(t) \rangle, \quad (2)$$

where V is the volume, occupied by the melt, T is the temperature, k_B is the Boltzmann constant, $\langle \dots \rangle$ is averaging over the ensemble, P_{xy} is the microscopic shear stress, which is defined by the formula:

$$P_{xy} = \frac{1}{V} \left[\sum_{i=1}^N \frac{p_i^x p_i^y}{m_i} - \sum_{i=1}^N x_i F_i^y \right], \quad (3)$$

where p_i^α are the momentum components, m_i is the mass, x_i is the coordinate, and F_i^y is the y -component of the force acting on the i -th particle.

The equations (2)–(3) assume that V is the volume occupied by atoms. Because we simulate a film which may change its thickness, this value is ill-defined. But we can unambiguously calculate the value PV which includes only the per-atom sum (see equation (4)). So, we can calculate the kinematic viscosity ν , which is defined by the expression:

$$\nu = \frac{\eta}{\rho} = \frac{V}{M} \eta = \frac{V}{M} \frac{V}{k_B T} \int_0^{\infty} dt \frac{\langle (P_{xy}V)(0)(P_{xy}V)(t) \rangle}{V^2} = \frac{1}{M k_B T} \int_0^{\infty} dt \langle (P_{xy}V)(0)(P_{xy}V)(t) \rangle, \quad (4)$$

where ρ is the density, M is the total mass of all atoms in the system.

The rightmost part of equation (4) has under the sign of integral the expression which is exactly defined by the instantaneous positions and velocities of atoms. So, in this paper the dependence of the kinematic viscosity on the temperature is obtained.

There have been some problems in calculating viscosity coefficient via the Green–Kubo formula. If the integrand in equation (4) is smooth and convergent, then the integral to the infinity can be substituted by the integral over a large finite time. In the case of slowly decaying SACF (stress autocorrelation function) the tail can be approximated by a power function and integrated analytically.

To reduce statistical uncertainties and eliminate the dependence on a particular choice of the initial configuration, it is important to use ensemble averaging along with time averaging. So, the results are averaged over 23 MD trajectories that differ in the choice of initial velocity

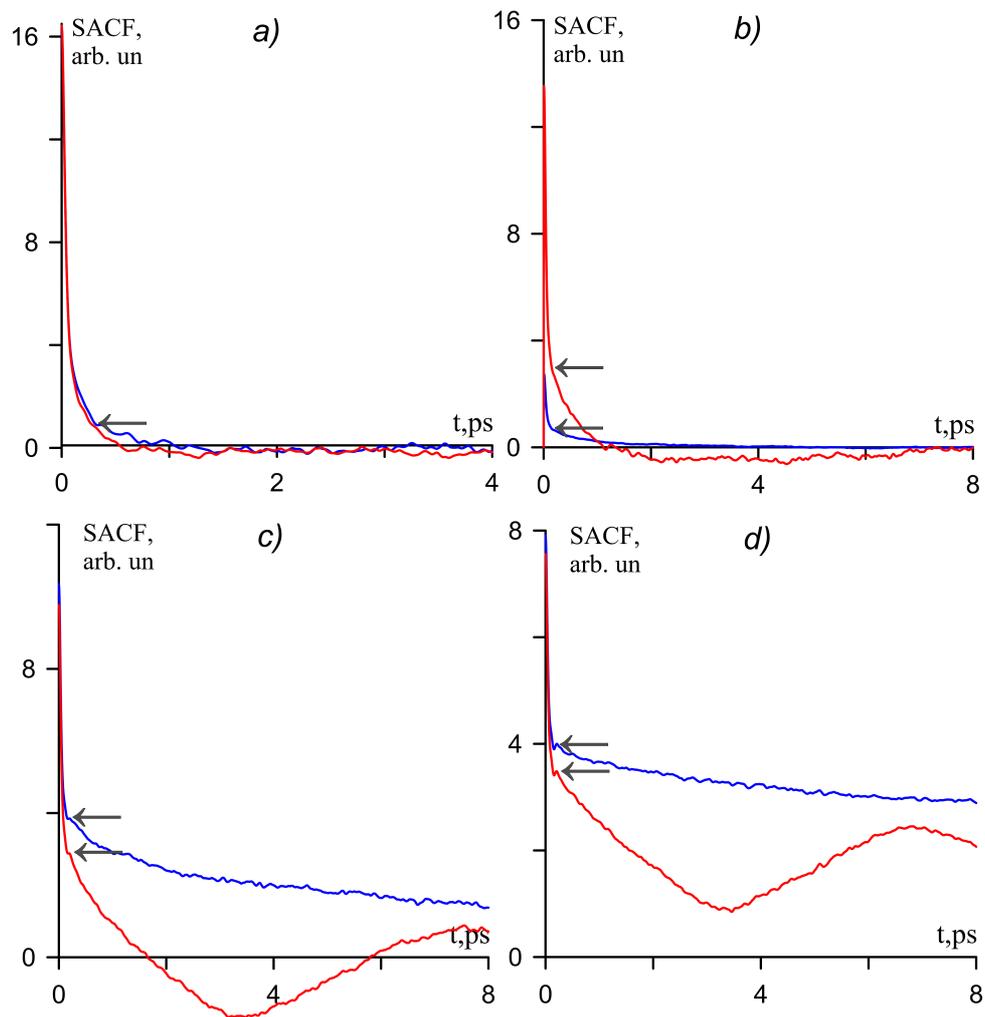


Figure 2. The SACF for 900 K (a), 700 K (b), 500 K (c) and 300 K (d). The blue line is for P_{xy} , the red line is the averaged between P_{xz} and P_{yz} . The break of a slope is indicated with an arrow.

distribution. The difference in the initial conditions leads to the divergence of the microscopic trajectories after the first few picoseconds [12] for this type of many-particle interatomic interaction potential, thus producing a set of independent microstates.

To obtain the dependence of the viscosity coefficient on temperature, we prepare the initial configurations by saving the intermediate configurations during cooling every 50 K. Then, we run NVE simulations from these states for 1.2 ns to calculate the SACFs.

The code, based on LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator), is used to get the dependence of the viscosity coefficient on temperature.

4. Results and discussion

At the study of shear viscosity during the glass transition, SACFs are obtained in the temperature range 1200–350 K. Figure 2 shows, that both SACFs (one contains the components along the z direction, the other is in the xy plane) change their behavior.

The stress autocorrelation function with components along the z direction begins showing weakly damped oscillations at 600–700 K. The half-period of the SACF approximately equals

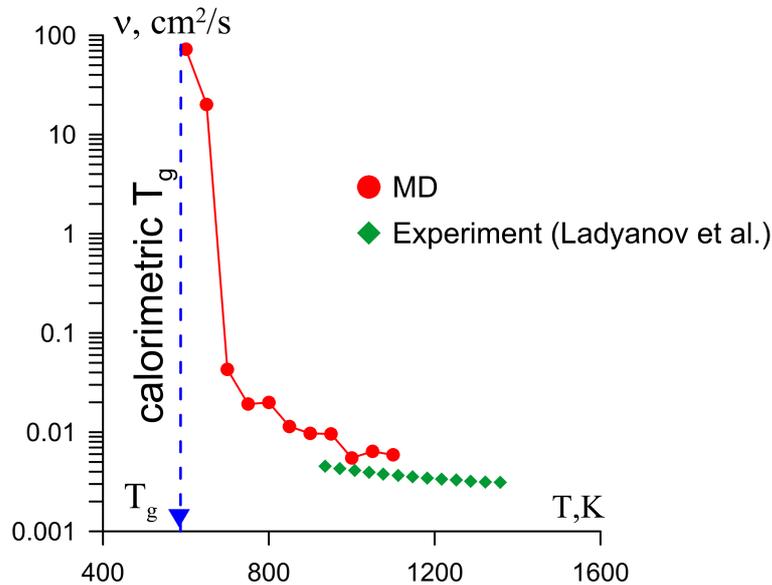


Figure 3. The dependence of the kinematic viscosity coefficient on temperature for $|dT/dt| = 4 \times 10^{13}$ K/s. MD simulation results are depicted by circles, the experimental data [13] are depicted by diamonds. The temperature, which is obtained using the calorimetric criterion, is indicated by the dashed vertical line. As the viscosity is calculated every 50 K, the viscosities are not shown for the temperatures below 650 K since the integral of the SACF diverges (see text).

$L/2c_s$, where L is the size of a computational cell, c_s is the speed of sound in aluminum. This can be interpreted as the oscillation of a solid film.

The autocorrelation function of shear stress in the plane of the film demonstrates very slow decay in the same temperature range. The tail of the autocorrelation function is approximated by a power function to calculate the integral of the SACF analytically. For the temperatures below 650 K, the tail decays slower than t^{-1} . It means that the integral is divergent and the viscosity coefficient is formally infinite.

On small values of time, the functions show the break of a slope of the curves. It is clearly seen in the graph for 300 K (Figure 2d). The time is the same for P_{xy} and the averaged between P_{xz} and P_{yz} . It can be interpreted as the change of the relaxation mode.

The dependence of the viscosity coefficient on temperature is presented in figure 3. The temperature range of the glass transition is found around 650 K, where a step change of the shear viscosity takes place. It is in a good agreement with the glass transition region, that was found for liquid aluminium, using the calorimetric criterion, where T_g equals 637 K [3] for the cooling rate used in the present work. Also the kinematic viscosity is compared with the experimental data, for the temperatures above the melting temperature [13,14].

5. Conclusions

Molecular dynamics simulation is applied to study the shear viscosity coefficient of supercooled aluminum melt. The Green–Kubo relation is used.

The dependence of the viscosity on temperature at rapid cooling is obtained. At the temperatures above the melting temperature the calculated viscosities agree with the available experimental data. The step change of the shear viscosity coefficient is found at 650 K. Such an increase of viscosity is interpreted as the glass transition.

It is shown that for the temperatures below 650 K, the integral of the SACF is divergent. So, the viscosity coefficient is formally infinite. It is considered as the behavior of a rigid body. The obtained temperature is compared with experimental and is in a good agreement with the temperature which is obtained using the calorimetric criterion. Further investigation of interplay between melt microstructure and viscosity is planned for the future work.

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