Molecular dynamics simulation of viscosity of selected pure oxide melts

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ABSTRACT

Viscosity of oxide melts is one of the fundamental physicochemical properties that plays a crucial role in important technological and natural processes like slag flow, slag/metal separation, volcano eruptions etc. However, many oxides melt at extremely high temperatures and are highly corrosive in the liquid state, which makes experimental measurement of melt viscosity by traditional experimental techniques a difficult and expensive, if not unachievable, task. In this case it might be useful to employ other methods of viscosity determination such as modelling or simulation. In the present paper the shear viscosity coefficients of selected pure refractory oxides (CaO, MgO, Al_2O_3 and others) have been simulated at temperatures above their melting points via the classical molecular dynamics and compared to the available viscosity data (e.g. experimental viscosities, other model predictions) collected by the authors. The simulation has been carried out using the non-commercial molecular dynamics simulation package LAMMPS and the Born-Mayer-Huggins potential, which parameters for the selected oxides were taken from the literature. Several viscosity calculation techniques (the Stokes-Einstein & Green-Kubo equations, the so called Einstein relations, and the non-equilibrium molecular dynamics methods) have been applied to ensure a more reliable viscosity calculation. It has been demonstrated that the simulated viscosity of the selected melts agrees with the available experimental data. It has also been shown that the simulated viscosity of a number of the oxide melts investigated is close to that calculated by phenomenological viscosity models, which supports viscosity extrapolation from the corresponding binaries and ternaries, if no experimental data is present for unary systems. In general, it has been demonstrated that the molecular dynamics simulation could provide a reasonable estimation of viscosity if no other viscosity data is available

INTRODUCTION

The extreme melting temperatures and/or extreme reactivity in the molten state of many pure oxides preclude experimental investigation of important melt properties such as viscosity, density, etc. A number of practical, phenomenological models have been developed to calculate viscosity of oxide melts (or slags) as a function of temperature and chemical composition; in the present study four such models are used to compare with MD results: the FactSage (Grundy 2008), GTT (Wu 2015), Kondratiev-Jak (Forsbacka 2007) and Starodub (Starodub 2019) models. However, all these models are usually based on known viscosities of the pure oxides that are used then to calculate viscosity of binary, ternary and high-order melts. If viscosity of a pure oxide is not experimentally measured, it can be estimated *vice versa* from corresponding binary or ternary oxide systems. Typically, such estimation is not very reliable and can produce significant uncertainty in calculation of viscosity of multicomponent oxide melts. Therefore, it is necessary to obtain a more reliable estimation for viscosity of pure oxide melt. Among other methods, classical molecular dynamics (MD) simulation appears to be a reliable and powerful tool for evaluation of physical properties of molten pure oxides including viscosity.

A number of different techniques have been developed to evaluate the shear viscosity coefficient from MD simulation. These techniques include the equilibrium MD methods (Einstein, Green-Kubo) and non-equilibrium MD methods (periodic perturbation, SLLOD and Muller-Plathe). Compared to a phenomenological approach to viscosity modelling the approach based on MD simulation can provide more reliable and physically rigorous viscosity values.

In this study four different MD methods were used to calculate the shear viscosity of selected pure oxide melts (CaO, MgO, and Al_2O_3), and the Born-Mayer-Huggins potential was used to describe interatomic interactions for MD simulations. As no experimental data exists for liquid CaO, the shear viscosity of the pure CaO melt calculated in the present work for the first time is compared to viscosities predicted by the different practical models. Viscosities of other oxides calculated by MD simulation are also compared to the available data, which is discussed below.

COMPUTATIONAL METHODS

Viscosity calculation methods depend on the MD simulation, which is based on the interatomic potential, boundary conditions, number of atoms per simulation. The LAMMPS non-commercial package (CERN, Switzerland) was employed to carry out classical MD simulations. The details of calculations are provided below.

Viscosity calculation

The shear viscosity can be obtained from an equilibrium MD simulation via the stress tensor autocorrelation function (Allen and Tildesley 2017) by the Green-Kubo formula:

$$\eta = \frac{1}{3} \frac{V}{k_B T} \sum_{\alpha,\beta} \int_0^\infty \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle \, dt \qquad (1)$$

Following (Nevins and Spera, 2007), two independent stress tensor components ($P_{xx} - P_{yy}$ and $P_{yy} - P_{zz}$) were included to estimate the shear viscosity. The standard deviation of the calculated shear viscosity 'components' represents the error of estimation:

$$\Delta\eta = \sqrt{\frac{\left(\eta_{xy} - \eta_{av}\right)^2 + (\eta_{xz} - \eta_{av})^2 + \left(\eta_{yz} - \eta_{av}\right)^2 + \left(\eta_{xxyy} - \eta_{av}\right)^2 + \left(\eta_{yyzz} - \eta_{av}\right)^2}{5}}, \qquad (2)$$

where η_{av} is the arithmetic mean of the five independently determined shear viscosity components η_{xy}, η_{xz}, η_{yz}, η_{xxyy} and η_{yyzz}.

The shear viscosity can also be determined via the following Einstein relation (Hess, 2002):

$$\eta = \lim_{t\to\infty} \frac{1}{6} \frac{V}{k_B T} \sum_{\alpha,\beta} \frac{d}{dt} \left\langle \left(\int_{t_0}^{t_0+t} P_{\alpha\beta}(t') dt' \right)^2 \right\rangle \Bigg|_{t_0}, \qquad (3)$$

where V is the system volume, k_B is Boltzmann's constant, T is the absolute temperature, t is the time and $P_{\alpha\beta}$ is the off-diagonal pressure tensor component, α, β refer to x, y, z and α≠β.

Alternatively, the shear viscosity can be obtained from a non-equilibrium MD simulation by applying an external perturbation to the system. The shear viscosity relates the maximum shear rate s (equal to the gradient of x-component of the fluid velocity regarding z-direction) with the flux of transverse linear momentum $j_z(p_x)$ (Todd 2017):

$$\eta = \frac{-1}{s} j_z(p_x), \qquad (4)$$

where $s = \left(\frac{\partial v_x}{\partial z}\right)$. It is important to use a high shear rate to obtain reliable statistics, but not so high that the system moves too far from its equilibrium. The system will be able to relax when the inverse shear rate is longer than the relaxation time.

The SLLOD method (Hess 2002) is used to simulate the planar Couette flow by planar movement of the box wall. The momentum flux can be considered as an off-diagonal (e.g. xz) component of the stress tensor:

$$j_z(p_x) = \langle P_{xz} \rangle, \qquad (5)$$

where P_{xz} is the off-diagonal pressure tensor component.

The periodic simulation box is divided into slabs along the z coordinate in the Müller-Plathe method (Muller-Plathe 1999). A momentum flux (Eq. 6) and a fluid velocity gradient are generated by momentum swaps between slabs.

$$j_z(p_x) = \frac{p_x}{2tA}, \qquad (6)$$

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where p_x is the total momentum transferred in a simulation, t is the simulation time and A is the box face area.

The error bar for the shear viscosity is calculated as follows (Bordat and Müller-Plathe, 2002):

$$\Delta\eta \leq \eta\left(\frac{\Delta J}{J} + \frac{\Delta G}{G}\right), \qquad (7)$$

where J is the flux equal to the slope of the exchanged momentum with the simulation time, determined by a least squares fit, G is the slope of the linear velocity profile, also obtained by a least-squares fit, and the error bars ΔJ and ΔG were both obtained from a least squares fit.

Equations 8 and 9 can be used to obtain the shear rate and momentum flux, respectively, when a periodic external force creates a periodic force field in the periodic perturbation method (Hess 2002):

$$j_z(p_x) = \rho\frac{a}{k}, \qquad (8)$$

where ρ is the density, a is the external acceleration, and

$$s = -vk, \qquad (9)$$

where v is the velocity profile amplitude, $k = 2\pi/l_z$, l_z is the box length.

Molecular dynamics simulation

Classical MD simulations were carried out using atomic interactions in the form of the Born–Mayer–Huggins (BMH) potential, for which the potential energy of interactions between atoms is given by the following equation:

$$u(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij}\exp\left(\frac{\sigma_{ij} - r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} + \frac{D_{ij}}{r_{ij}^8}, \qquad (8)$$

with i and j being atomic species and r_{ij} being the interatomic distance between two ions of species i and j. It should be noted that only the van der Waals term was taken into account in the dipolar expansion. Parameters in Eq. (10) with the corresponding references are given in Table 1. Parameters by Alvares (2007) are used for simulation of the CaO melt, while parameters by Arkhipin (2024) are used for simulation of the MgO and Al2O3 melts. Parameters from Gutierrez (2000) are given for comparison.

TABLE 1 – Parameters of the Born-Mayer-Huggins potential

Atom / interaction	q	A_{ij}(eV)	ρ_{ij}(Å)	σ_{ij}(Å)	C_{ij}(eV Å^6)	Reference
Ca	1.2					Alvares 2007
Mg	1.2					
Al	1.8					
O	-1.2					
Ca−Ca		0.0035	0.0800	2.3440	20.9856	
Ca−O		0.0077	0.1780	2.9935	42.2556	
O −O		0.0120	0.2630	3.6430	85.0840	
Mg−Mg		38868.5	0.2066	0.0	43.773	Arkhipin 2024

Mg−O		12655.4	0.2089	0.0	36.798	
Al− Al		0.00290	0.0680	1.5704	14.0498	
Al −O		0.0075	0.1689	2.6067	20.7448	
O −O		0.01015	0.2140	3.2678	5.0840	
Al	1.4175					
O	-0.9450					
Al− Al		0.00295	0.068	1.5704	14.0524	Gutierrez 2000
Al −O		0.00746	0.172	2.6067	34.5814	
O −O		0.0120	0.276	3.643	85.1011	

Using this empirical potential, classical molecular dynamic simulations were performed with the LAMMPS code. At the first stage simulations were performed in the isobaric–isothermal ensemble (NPT) using a Nosé–Hoover thermostat coupled with an isotropic barostat (Martyna 1994) to determine the mean volume of system over a period of 100 ps. The system volume was adjusted to the mean value, and equilibration in the canonical (NVT) ensemble with coupling constant 0.1 ps was carried out for 100 ps. Periodic boundary conditions were applied in the three directions of space, and the long-range Coulomb interactions were treated within the Ewald summation method. Equations of motion were solved numerically by the Verlet algorithm in the velocity form using the time step of 1 fs. The simulation box contains different numbers of atoms in the initial crystalline configuration dependent on the MD method used for viscosity calculation. For example, the cubic box containing 729 Ca or Mg atoms and 729 O atoms for CaO or MgO and 600 Al atoms and 900 O atoms for Al_2O_3 was used for the Green-Kubo and Einstein viscosity calculations. The equilibration stage of non-equilibrium MD simulations by the SLLOD and Müller-Plathe algorithms lasts for 100 ps followed by the production stage lasting 100 ps. The orthorhombic box (LxLx3L) with 1029 Ca or Mg atoms and 1029 O atoms for CaO or MgO and 768 Al atoms and 1152 O atoms for Al2O3 was used for the Müller-Plathe method. The temperature ranges were 3200-4000 K, 3100-4000 K, and 2300-3200 K for CaO, MgO and Al_2O_3, respectively.

RESULTS AND DISCUSSION

Selected examples of the MD simulation and viscosity calculation results obtained for three oxides (CaO, MgO and Al2O3) are presented here. Some MD simulations are still to be carried out; only the preliminary results are published in the paper.

General MD results

During the production stage of MD simulations used further for the Green-Kubo and Einstein calculations, the off-diagonal components of the stress tensor and the corresponding stress autocorrelation functions (SACF) were written into a file every 5 timesteps. Figures 1(a-c) demonstrate the normalised SACFs obtained for CaO, MgO and Al_2O_3 at temperatures of 3500, 3600 and 2800 K, respectively. The autocorrelation functions for CaO and MgO decay significantly after 0.5 ps, while for Al_2O_3 it decays after 1 ps. The autocorrelation functions obtained at other temperatures exhibit the same behaviour. The shear viscosity was calculated by integrating the SACF using Equation (1) and the trapezoidal integration method.

During MD simulations used for the Müller-Plathe method, the orthorhombic simulation box is divided into 20 slabs in the z direction, which is the direction of the momentum flux exchange. Momentum exchange periods (w) were chosen at intervals of 1, 10, 20 and 40 timesteps. During the production stage velocity profile, temperature profile, density profile and transferred momentum were written into a file every 100 timesteps. The duration of the production stage was 500 ps for a temperature interval of 3400–4000 K and 1 ns for a temperature interval of 3100–3300 K for MgO. The momentum when the system reached a steady state was controlled by a dependence of cumulative shear viscosity upon time (Figure 2). The viscosity calculation was based solely on data obtained in a steady state.
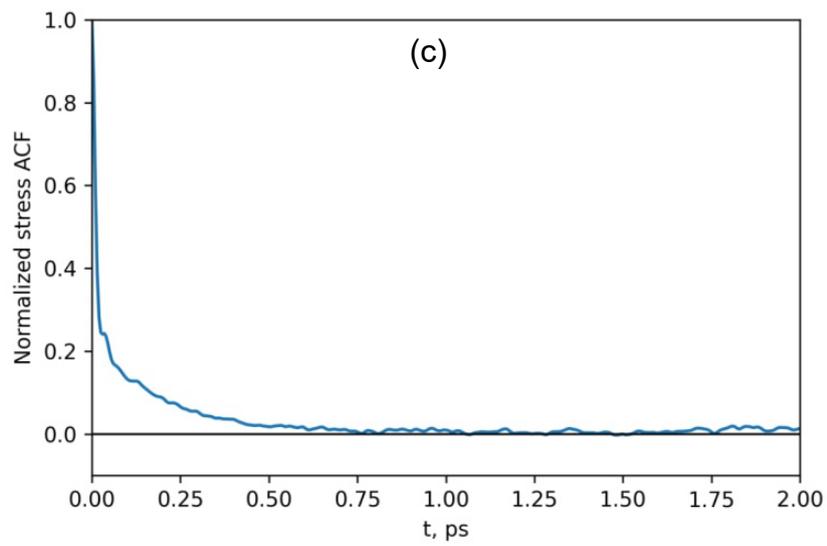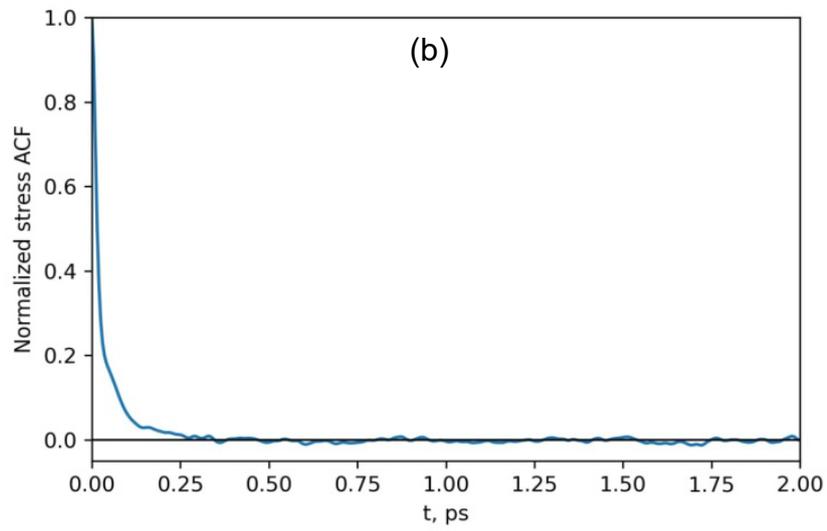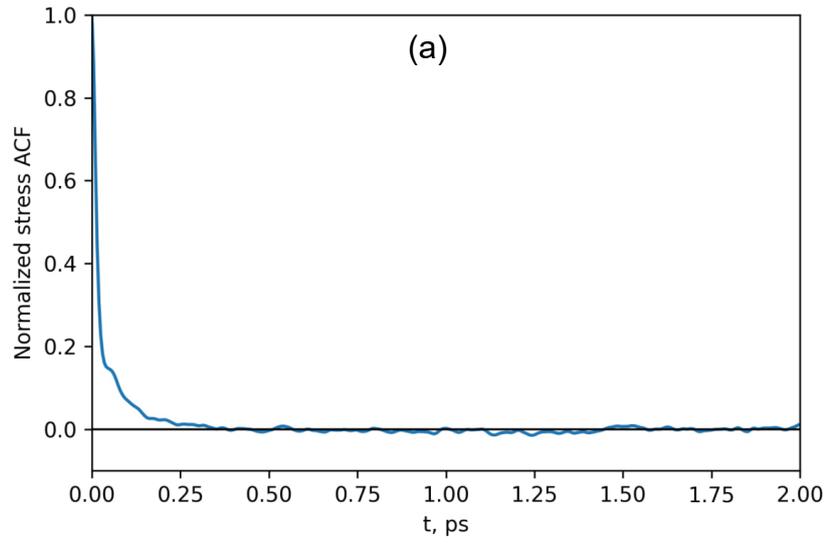
FIG 1 – Normalized stress autocorrelation functions for (a) CaO at 3500 K, (b) MgO at 3600 K, (c) Al_2O_3 at 2800 K.
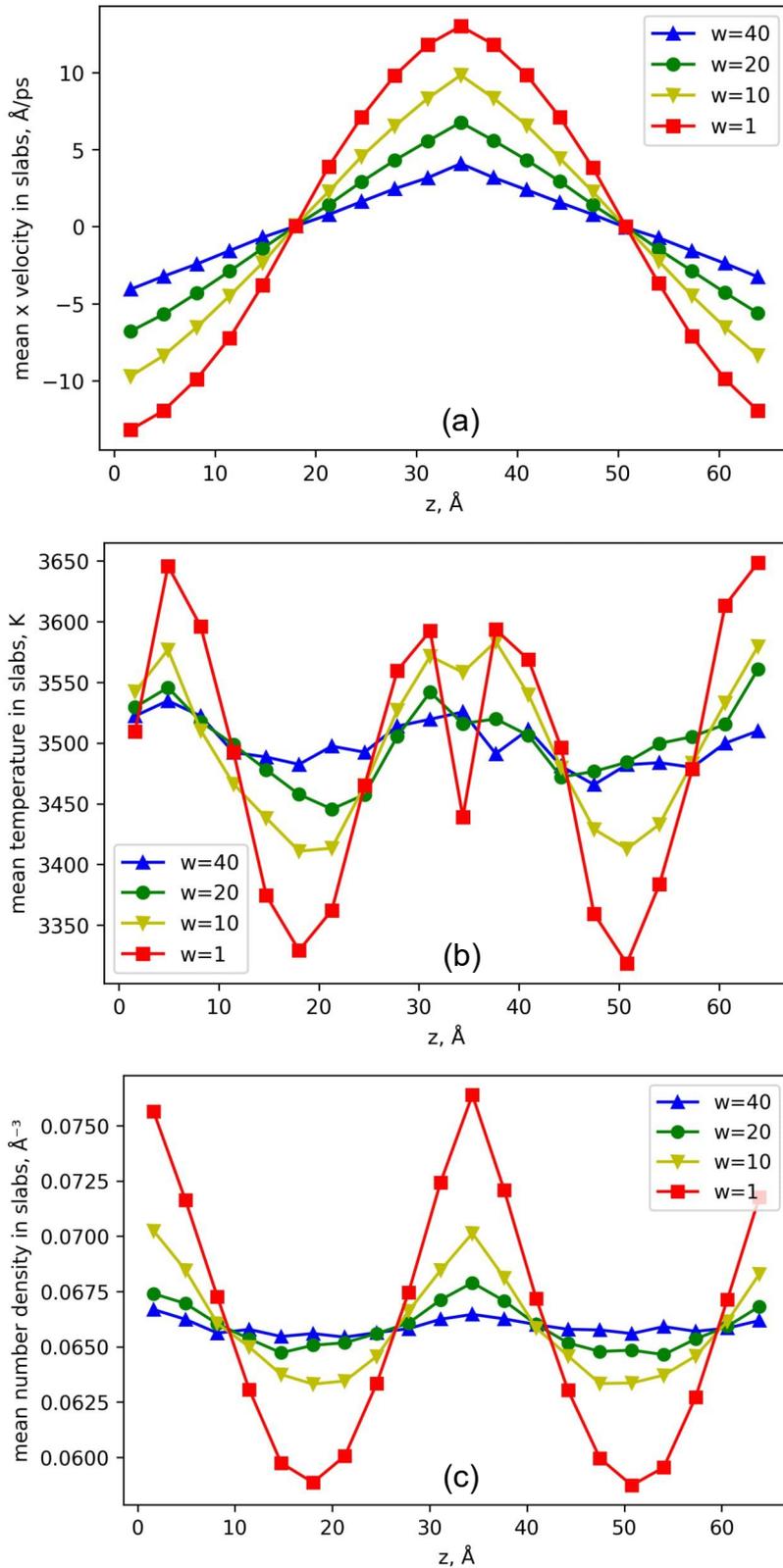
FIG 2 – The MD results for MgO at 3500K: (a) velocity, (b) temperature, (c) density profiles.

Viscosity of the CaO melt

Figure 3 demonstrates viscosity of the CaO melt calculated by four different MD (Green-Kubo, periodic perturbation, SLLOD and Muller-Plathe) methods at different temperatures. Additionally shown a viscosity value at 3200K calculated via the MD simulated oxygen diffusion coefficient and Stokes-Einstein equation. It can be seen that all the MD methods provide very close results, although one method uses equilibrium MD simulation and three use non-equilibrium MD simulation. It can

also be seen that the viscosity value calculated via the oxygen diffusion coefficient is lower than that calculated by the Green-Kubo equation by an order of magnitude. The viscosity of pure CaO liquid is evaluated in the present work for the time, and it should be noted that the MD results usually underestimate measured viscosity values (e.g. Kondratiev et al. 2024).
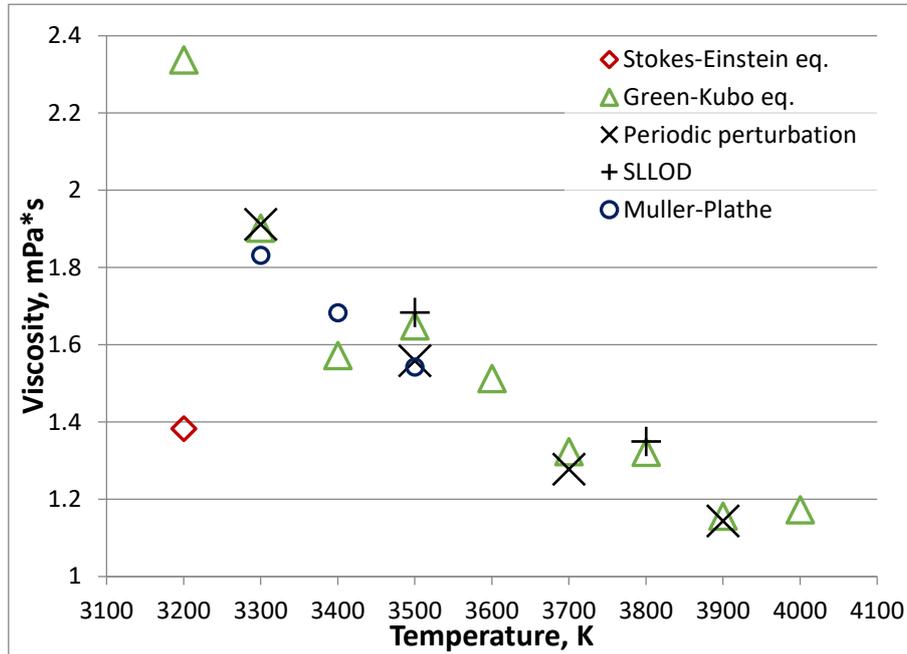
FIG 3 – Viscosity of the CaO melt calculated by four different MD methods.

The average Arrhenius dependence (logarithm of viscosity as a function of the reciprocal temperature) was obtained for the four MD calculations by fitting the classical Arrhenius equation to the MD results. Figure 4 shows comparison between viscosities calculated by four different (FactSage, Kondratiev-Jak, Starodub and GTT) viscosity models and the average MD dependence. It can be seen that the FactSage, GTT and Kondratiev-Jak models underestimate viscosity of the pure CaO melt, as these model curves lie substantially below the MD average curve. It demonstrates that extrapolation from the corresponding binary and ternary systems does not always provide a correct estimation of viscosity of pure oxides.
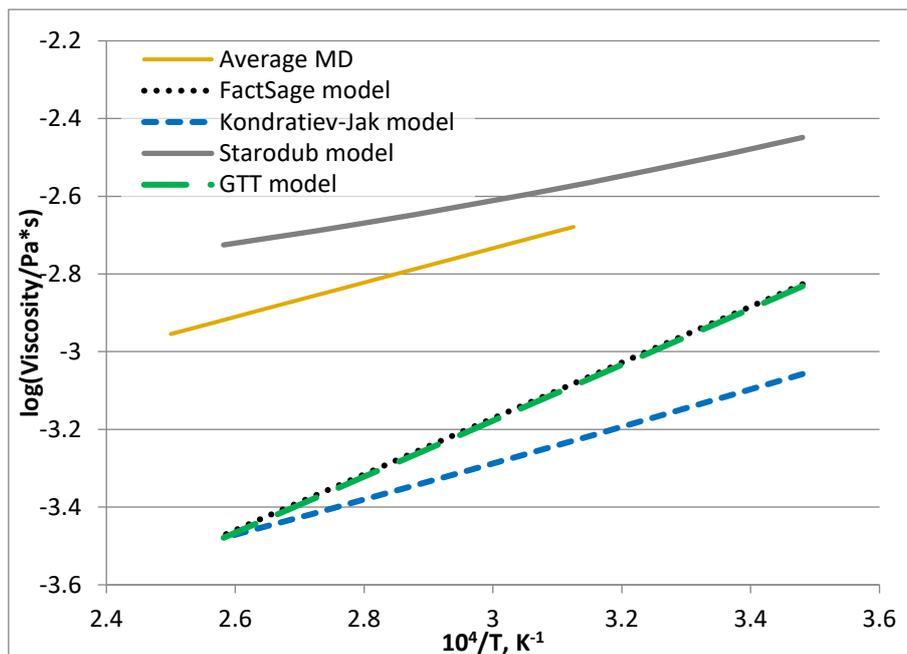
FIG 4 – Comparison of the CaO viscosity calculated via MD simulation and by different viscosity models.

Viscosity of the MgO melt

Figure 5 shows viscosities of the MgO melt calculated in this work by two equilibrium MD methods (Eqs. 1 & 3), in the study of Karki et al. (2013) using the ab-initio MD simulation, and by Leu et al. (1975) using the significant structures theory. It can be seen that the MD results by Karki (2013) are very close to the MD results obtained in the present work.
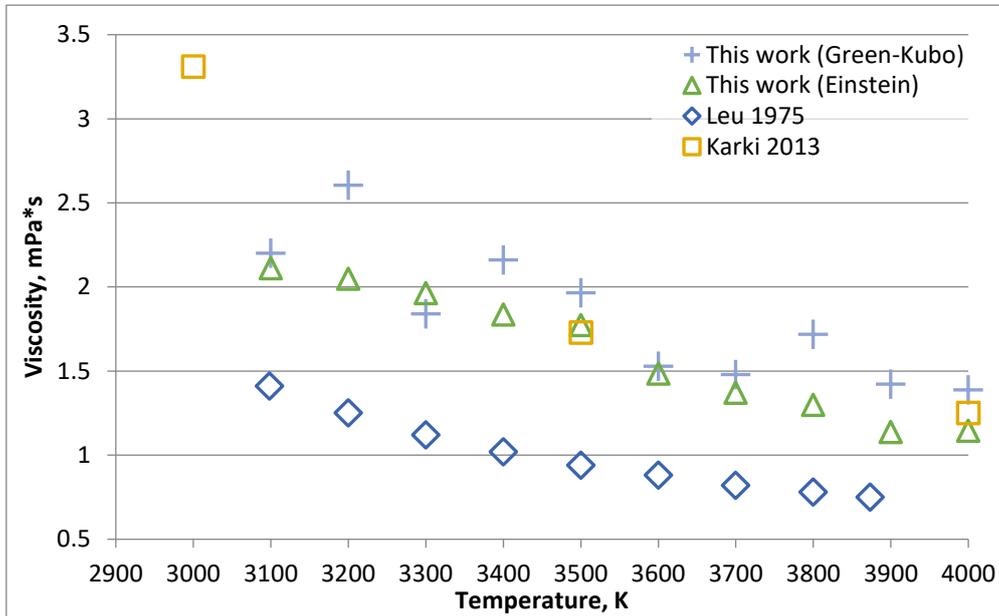
FIG 5 – Viscosity of the MgO melt calculated in different works.

Figure 6 shows the average Arrhenius viscosity for two MD methods used and calculations by different viscosity models in logarithmic format as a function of the reciprocal temperature. It can be seen that the GTT model might underestimate viscosity of pure MgO, while the viscosity curve by the Kondratiev-Jak model provides more realistic estimation of the MgO melt viscosity.
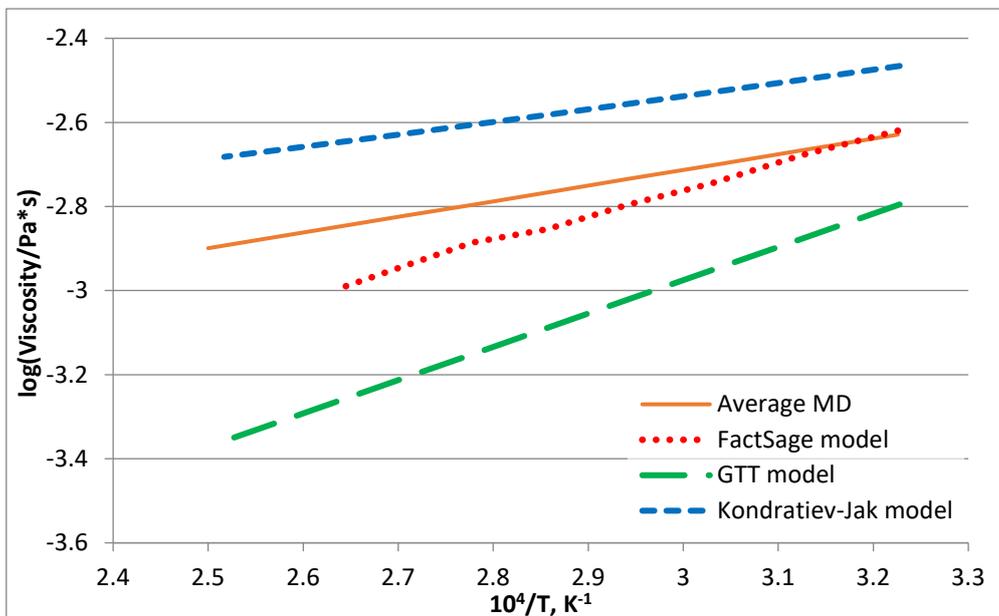
FIG 6 – Comparison of the MgO viscosity calculated via MD simulation and by different viscosity models.

Viscosity of the Al₂O₃ melt

Viscosity of the Al_2O_3 melt was calculated by two different methods: Green-Kubo (equilibrium MD) and Muller-Plathe (non-equilibrium MD). Only preliminary MD results are presented here. The available experimental data for Al_2O_3 can roughly be divided into two large groups dependent on a

method used to determine viscosity: those obtained via conventional viscometry methods (e.g. rotational cylinder technique, oscillation technique) and those measured indirectly by levitation methods. Figure 7 demonstrates agreement of MD simulation results obtained in this work with the Al_2O_3 experimental data and other MD simulation by Jahn (2007, 2008). The classical MD simulation with the BHM potential and the Green-Kubo formula (Eq. 1) was used in the present work to estimate viscosity of pure Al_2O_3, while Jahn (2007, 2008) employed an aspherical ion model potential with more complex interactions. It can be seen that viscosity calculated by the Green-Kubo equation is much lower than the most of the experimental points, while the Muller-Plathe method provides slightly higher values. In total, the viscosity calculation results obtained in the present work indicate that MD simulation with a simple interatomic potential can provide a lower estimation of viscosity.
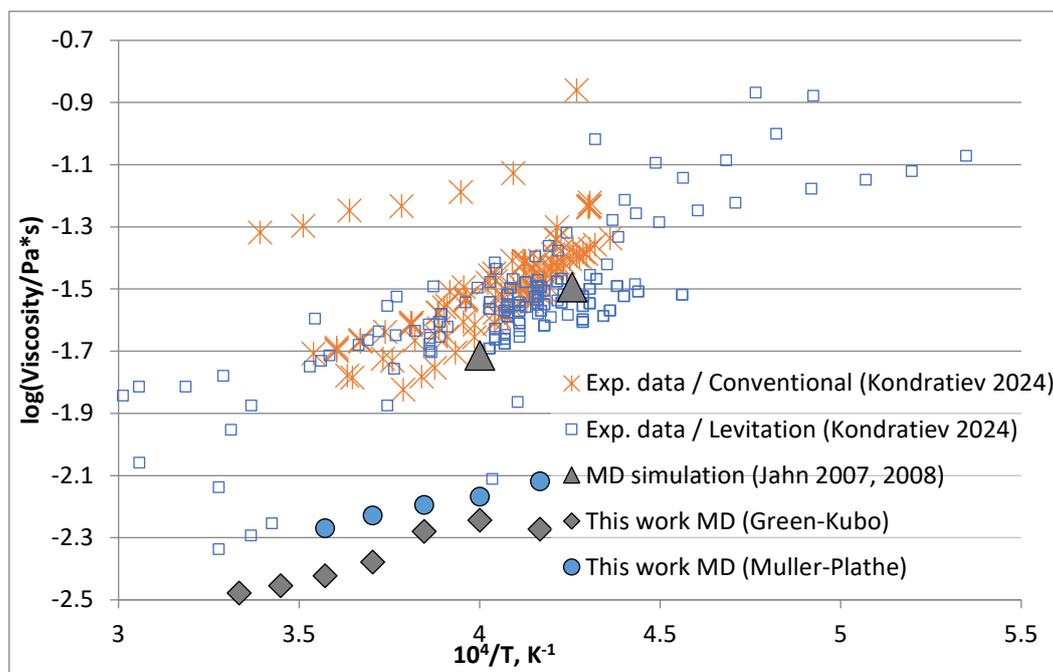
FIG 7 – Comparison of the calculated (MD) and experimental viscosity for the Al2O3 melt.

CONCLUSIONS

Equilibrium and non-equilibrium molecular dynamics simulation coupled with viscosity calculation was carried for the CaO, MgO, and Al2O3 melts using the Born-Mayer-Huggins interatomic potential. Parameters of the BHM potential were taken from the literature.

Viscosity of the pure CaO melt was evaluated by MD simulation for the first time and compared to predictions of the selected viscosity models. It was shown that the MD results are higher than most of the model predictions and can now be used as a more reasonable estimation for CaO viscosity.

Viscosity of the pure MgO melt evaluated by MD simulation was compared to other theoretical calculations and showed a reasonable agreement with other MD simulation.

Viscosity of the pure Al2O3 melt evaluated by MD simulation was compared to the available experimental data, and the comparison demonstrated that MD simulation with a simple interatomic potential (like BHM) can provide a lower estimation of viscosity in relation to the experimental points.

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