



Original Article

Study of Dynamic Properties in MgSiO_3 Liquid under Compression by Mean of Molecular Dynamics Simulation

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Abstract: In this work, the dynamic properties of MgSiO_3 liquid are investigated by mean of molecular dynamics (MD) simulation. Our model showed that the total radial distribution function is a good agreement with the experimental and other simulation data. We found that the SiO_x - SiO_x and MgO_y - MgO_y linked pairs have a tendency to forming clusters with the structural heterogeneity. The dynamic properties in these models have been investigated through the self-diffusion and electrical conductivity. Moreover, we have presented evidence about the relationship between structure and dynamic heterogeneity in the model.

Keywords: MgSiO_3 liquid, structural heterogeneity, self-diffusion, electrical conductivity.

1. Introduction

Magnesium silicate (MgSiO_3) liquid is a main component of most natural minerals and Earth's mantle. Therefore, the information on the dynamics properties of MgSiO_3 liquid is important for many applications in industry and materials science [1-4]. The structure, thermodynamic properties and transport properties of MgSiO_3 melts were investigated [5-10]. By using ab initio molecular dynamics simulation, Justin et al., [5] revealed that properties obtained from some alternative models show large relative errors compared to experiment, with viscosity. Besides, San et al., and Gao et al., [4, 6] studied the structural, electronic and mechanical properties of two MgSiO_3 polymorphs under pressure. The network structure of MgSiO_3 liquid consists of SiO_x ($x = 4-6$) and MgO_y ($y = 3-9$) units.

Diffusivity and electrical conductivity are the two most important transport properties of dynamic behavior in MgSiO_3 liquid [11-18]. Diffusion coefficients of Si and O are similar, while Mg atoms

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diffuse the fastest under compression, but at high pressures this difference is not significant [12, 15]. Therefore, the electrical conductivity of MgSiO₃ liquid increases/decreases with pressure at low/high SiO₂ content respectively. Besides, the self-diffusion and electrical conductivity of MgSiO₃ liquid are computed as a function of temperature. The self-diffusivities and electrical conductivity of all Mg, O and Si increase with increasing temperature.

Although the characteristic of the MgSiO₃ liquid was studied in many works, however useful information on this liquid has still limited. In this work, we use MD simulations to investigate the dynamic properties of MgSiO₃ liquid at 3,000 K with the range pressure of 0-30 GPa. The result of self-diffusion and electrical conductivity showed a good agreement with the experimental data. The diffusion mechanism of Mg, Si and O was also analyzed by technical visualization to clarify at atomic level.

2. Computational Method

MD simulation is built on MgSiO₃ models containing 1,000 Si, 3,000 O and 1,000 Mg atoms. The pairwise potentials and the periodic boundary conditions are used to construct the models. We use the Oganov potentials to construct MgSiO₃ models at 3,000 K, in the range 0-30 GPa [17, 18]. This potential has the following form:

$$V_{ij}(r_{ij}) = k \frac{q_i q_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where $k = 8.987551 \times 10^9 \text{ N.m}^2.\text{C}^{-1}$ is Coulomb constant, r_{ij} is the distance between i^{th} and j^{th} atoms. The potential parameters A_{ij} , B_{ij} and C_{ij} are listed in Table 1.

Table 1. The parameters of Oganov potential [17, 18]

i	j	$A_{ij}(\text{eV})$	$B_{ij}(\text{\AA})$	$B_{ij}(\text{\AA}^6)$	q
Mg	Mg	0	0	0	$q_{\text{Si}}=2.9043$
Mg	Si	0	0	0	$q_{\text{Mg}}=1.9104$
Mg	O	1041.43266	3.48918	0	$q_{\text{O}}=-1.6049$
Si	Si	0	0	0	-
Si	O	1137.02499	3.53732	0	-
O	O	2023.79522	3.73972	3.30544	-

We used the Verlet algorithm with a time step of 0.47 fs. The initial configuration of the model is generated by placing all atoms randomly in a basic cube and heating it up to 6,000 K to remove possible memory effects. Next, this model is cooled down to 4,500 and finally to 3,000 K. The model 3,000 K is relaxed for a long time (2×10^5 time step) in ensemble constant temperature and pressure to produce a model at 3,000 K and 0 GPa. The different models at 3,000 K and 5, 10, 15, 20, 25 and 30 GPa are produced by compressing model 0 GPa to corresponding pressures. Each pressure is relaxed for a long time (3×10^5 time step). To calculate bonds, coordination number, we chose the cutoff distance of 2.2 Å (the minimum position after the first peak of the pair radial distribution function).

The self-diffusion coefficients of different atoms were calculated from the slope of the mean square displacement and follow equation Einstein below:

$$D_X = \lim_{t \rightarrow \infty} \frac{\sum_{i=1}^{N_X} \langle [r_{Xi}(t) - r_{Xi}(0)]^2 \rangle}{6N_X t} \quad (2)$$

where $r_{Xi}(0)$ and $r_{Xi}(t)$ is the position of atoms of type X at time $t = 0$ and t respectively, N_X the number of atoms of type X.

The electrical conductivity of $MgSiO_3$ liquid is calculated from diffusion (D) and they are related through the Eyring equation

$$\sigma_X = D_X \frac{N_X q_X^2}{k_B T} \quad (3)$$

where, $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant, T is the temperature, q_X is charge atom of type X.

3. Results and Discussion

Figure 1 shows the total radial distribution functions (RDFs) of $MgSiO_3$ liquid at 0 GPa and 3,000 K by X-ray and simulation method. The result indicated that the simulated total RDFs are in good agreement with the experimental and other simulation data reported in [3, 4] in terms of shape and peak position. The results obtained in the current work show that our model is reliable and can be widely used.

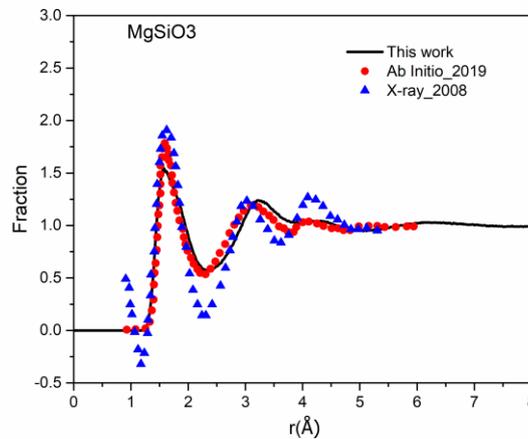


Figure 1. The total RDFs $g(r)$ of $MgSiO_3$ at 0 GPa and 3000 K is compared with experimental and simulation data [3, 4].

Figure 2 displays the pair RDF $g_{Si-O}(r)$ and $g_{Mg-O}(r)$ at 3,000 K and different pressures. As seen, for the $g_{Si-O}(r)$, the position of the first peak significantly increases as seen in the inset plot of Figure 2; meanwhile, the height significantly decreases with increasing pressure. For the $g_{Mg-O}(r)$, the first peak and the height is almost unchanged as the pressure increases. The significant change of the $g_{Si-O}(r)$ indicates that the structure of $MgSiO_3$ liquid strongly depends on the compression process. At ambient pressure, the first peaks of the $g_{Si-O}(r)$ and $g_{Mg-O}(r)$ are 1.66 and 1.98 Å, respectively.

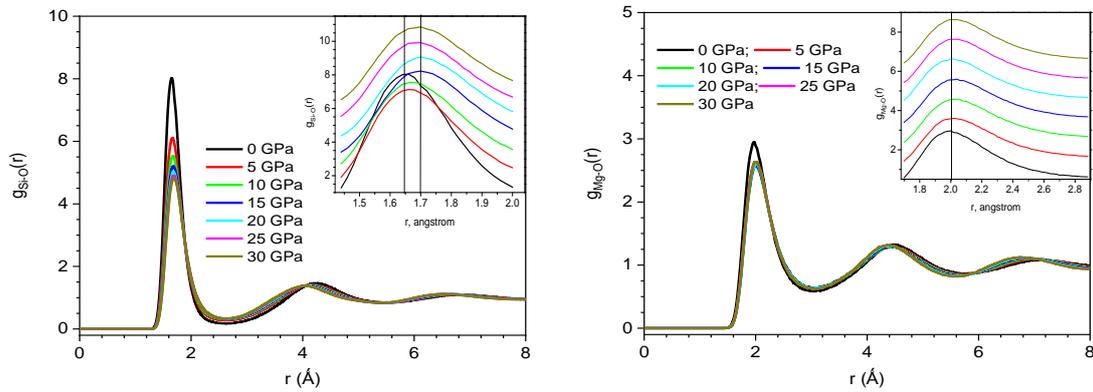


Figure 2. The pair RDFs of Si–O and Mg–O pairs in MgSiO₃ at different pressures, the *inset* plot clearly shows change of peaks of PRDF under compression.

Yen et al., [19] showed the spatial distribution of corner-, edge-, and face-sharing bonds at different pressures. As seen, the distribution of corner-, edge- and face-sharing bonds is not uniform, but instead they have a tendency to forming clusters of corner-, edge- and face-sharing bonds. This again shows the structural heterogeneity of MgSiO₃ liquid. It is also seen that edge- and face-sharing bonds are mainly between TO₅ and TO₆ units. It means that the clusters of edge- and face-sharing bonds form high-density regions. This also demonstrates that there exists structural heterogeneity in MgSiO₃ liquid.

Dynamics properties were investigated by the behavior of the mean square displacement (MSD) of all atoms that is also the reason for dynamic process such as self-diffusion and electrical conductivity in the MgSiO₃ liquid. Using Eq. (2), we have calculated the self-diffusion coefficients of Si, O and Mg atoms. Figure 3 shows the self-diffusion coefficients of Si, O and Mg atoms in MgSiO₃ liquid. It can be seen that self-diffusion of Si, Mg atoms anomalous behavior, when pressure increases initial self-diffusion of Si and Mg slightly increase then decrease.

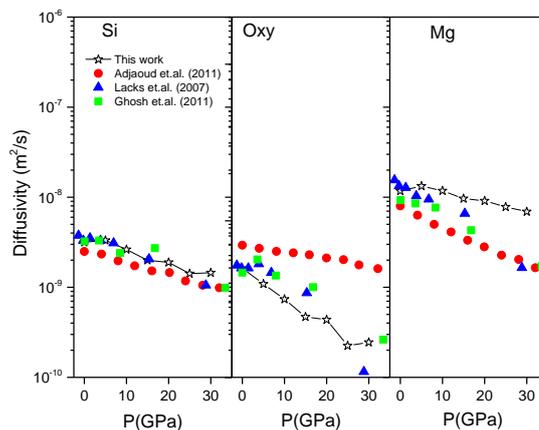


Figure 3. Pressure dependence of self-diffusivity for O, Si, and Mg in MgSiO₃ liquid, Lacks (2007) at 3000 K [5], Ghosh (2011) at 3000 K [6], Adjaoud (2011) 3200 K [7].

The self-diffusion of Si atoms reaches the peak value at 10 GPa (4.228×10^{-9}), while the peak value of Mg atoms at 5 GPa (1.641×10^{-8} m²/s). With oxy atom, self-diffusion decreases with pressure. At ambient pressure, self-diffusion of Si, Mg and O are 4.581×10^{-9} , 1.610×10^{-8} , 6.727×10^{-9} m²/s, while this value of pressure 30 GPa are 2.259×10^{-9} , 1.129×10^{-8} and 2.790×10^{-9} m²/s respectively. In addition, it can be seen that self-diffusion of Mg is significantly larger than self-diffusion of Si and O, while self-diffusion of Si and O is similarly in range pressure 0-30 GPa. This result is related to the structure of the system when the Si-O bond is more stable than the Mg-O bond. It means that Si and O atoms move together while the Mg atom is free. All self-diffusion atoms have been compared to another result indicating there is good agreement between us and other works [11-13].

Figure 4 and 5 display the SiO_x units, Mg atoms distribution and three channels for a typical spatial distribution of the atoms at 10 GPa and 3,000 K. Figure 5 shows that the Mg atoms are mainly localized beyond the cluster of SiO_x-SiO_x. It means that Mg atoms are more mobile than Si and O atoms. It can be shown in Figure 5, several channels (cross-sections) where all atoms are shown, and the Mg atoms near each other are highlighted in red. It is noted that the size and location of these channels insignificantly change in time.

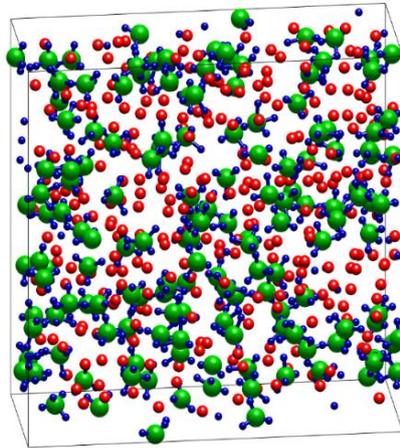


Figure 4. Snapshots of SiO_x units and Mg atoms distribution in model at 10 GPa and 3000 K. Here Si,

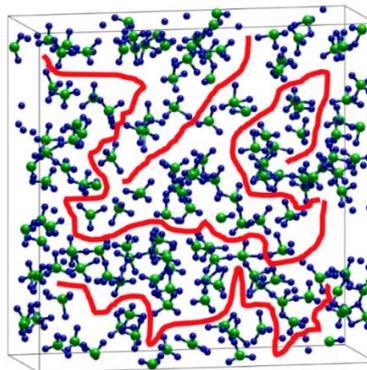


Figure 5. Snapshot of three channel for a typical spatial distribution of the atoms at 10 GPa and 3,000 K. Here, in red highlight is the Mg-rich region; Si, O and Mg are green, blue and red spheres, respectively.

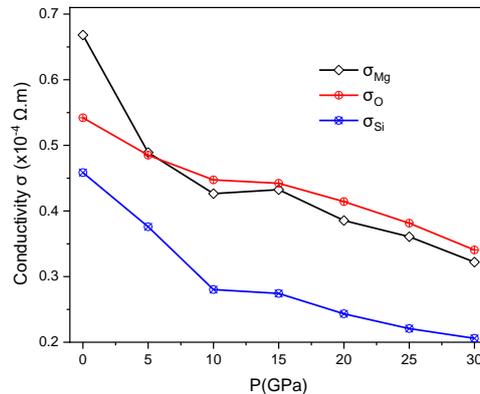


Figure 6. Electrical conductivity of Si, Mg and O atoms in MgSiO₃ liquid at different pressures.

Using Eq. (3), the electrical conductivity of Si, O and Mg atoms are calculated as can be seen on Figure 6. This figure shows that the electrical conductivity of Si, O and Mg atoms decrease under compression. This result proves that the diffusion electrical conductivity of atoms decreases when pressure increases. It means that the atoms exhibit lower dynamics under compression. At high pressure, the atoms become immobility because the self-diffusion coefficient of Mg atom is largest, so it is the most mobility, while a similar mobility found for Si and O atoms is small. This leads to the existence of different dynamics regions to create heterogeneous dynamics in the model. As above analyzed, the structural heterogeneity due to the edge- and face-sharing bonds of two neighbor structural units to create high-density regions in the model. The clusters of Mg-Mg and Si-Si bonds form the separation of Mg- and Si-rich regions. This is evidence to show a correlation between dynamic heterogeneous and structure heterogeneous. It means that the dynamic heterogeneity leads to structure heterogeneity and vice versa.

4. Conclusion

MD simulation has been used for MgSiO₃ models in a wide pressure range 0-30 GPa, at 3,000 K. The structure of MgSiO₃ liquid comprises MgO_y (y = 3, 4...9) units distributed in Si-O network structure. Mg-O, Si-O linked clusters lead to form the structural heterogeneity. Under compression, self-diffusion of O atoms decreases, meanwhile self-diffusion of Si and Mg atoms at first increased, then decreased. The electrical conductivity of atoms decreased with increasing pressure. We found that there is a relationship between structure and dynamic heterogeneity, i.e. the structure heterogeneity leads to dynamic heterogeneity and vice versa. There exist Si-rich and Mg-rich regions in the model, while the region of Si-rich is low dynamic, the region of Mg-rich is fast dynamic.

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References

- [1] A. Douy, Aqueous Syntheses of Forsterite (Mg₂SiO₄) and Enstatite (MgSiO₃), Journal of Sol-Gel Science and Technology, Vol. 24, No. 3, 2002, pp. 221-228, <https://doi.org/10.1023/A:1015332607551>.

- [2] J. Temuujin, K. Okada, K. J. D. Mackenzie, Role of Water in The Mechanochemical Reactions of MgO–SiO₂ Systems, *J. Solid State Chem*, Vol. 138, No. 1, 1998, pp. 169-177, <https://doi.org/10.1006/jssc.1998.7768>.
- [3] M. C. Wilding, C. J. Benmore, J. K. R. Weber, In Situ Diffraction Studies of Magnesium Silicate Liquids, *Journal of Materials Science*, Vol. 43, No. 14, 2008, pp. 4707-4713, <https://doi.org/10.1007/s10853-007-2356-5>.
- [4] L. T. Sam, N. V. Hong, T. Iitaka, P. K. Hung, Structural Organization, Micro-Phase Separation and Polyamorphism of Liquid MgSiO₃ under Compression, *The European Physical Journal B*, Vol. 89, No. 3, 2016, pp. 1-10, <https://doi.org/10.1140/epjb/e2016-60740-4>.
- [5] J. B. Haskins, E. C. Stern, C. W. Bauschlicher Jr, J. W. Lawson, Thermodynamic and Transport Properties of Meteor Melt Constituents from Ab Initio Simulations: MgSiO₃, SiO₂ and MgO, *Journal of Applied Physics*, Vol. 125, No. 23, 2019, pp. 235102, <https://doi.org/10.1063/1.5079418>.
- [6] J. Gao, W. Zeng, B. Tang, D. H. Fan, Q. J. Liu, X. H. Chang, M. Zhong, Effects of Pressure on Structural, Mechanical and Electronic Properties of Trigonal and Monoclinic MgSiO₃, *Solid State Sciences*, Vol. 105, 2020, pp. 106261, <https://doi.org/10.1016/j.solidstatesciences.2020.106261>.
- [7] Y. Lou, S. Stackhouse, A. M. Walker, Z. Zhang, Thermoelastic Properties of MgSiO₃-Majorite at High Temperatures and Pressures: A First Principles Study, *Physics of The Earth and Planetary Interiors*, Vol. 303, 2020, pp. 106491, <https://doi.org/10.1016/j.pepi.2020.106491>.
- [8] T. T. Nguyen, T. T. Nguyen, H. T. Dinh, V. V. Le, Molecular Dynamics Simulations of Structural and Mechanical Properties in MgSiO₃ Glass, *Physica Status Solidi (B)*, Vol. 256, No. 11, 2019, pp. 1900215, <https://doi.org/10.1002/pssb.201900215>.
- [9] P. S. Salmon, G. S. Moody, Y. Ishii, K. J. Pizzey, A. Polidori, M. Salanne, S. G. Macleod, Pressure Induced Structural Transformations in Amorphous MgSiO₃ and CaSiO₃, *Journal of Non-Crystalline Solids: X*, Vol. 3, 2019, pp. 100024, <https://doi.org/10.1016/j.nocx.2019.100024>.
- [10] X. Liu, Y. Qi, D. Zheng, C. Zhou, L. He, F. Huang, Diffusion Coefficients of Mg Isotopes in MgSiO₃ and Mg₂SiO₄ Melts Calculated by First-Principles Molecular Dynamics Simulations, *Geochimica et Cosmochimica Acta*, Vol. 223, 2018, pp. 364-376, <https://doi.org/10.1016/j.gca.2017.12.007>.
- [11] D. J. Lacks, D. B. Rear, J. A. V. Orman, Molecular Dynamics Investigation of Viscosity, Chemical Diffusivities and Partial Molar Volumes of Liquids Along the MgO–SiO₂ Join as Functions of Pressure, *Geochimica et Cosmochimica Acta*, Vol. 71, No. 5, 2007, pp. 1312-1323, <https://doi.org/10.1016/j.gca.2006.11.030>.
- [12] O. Adjaoud, G. S. Neumann, S. Jahn, Transport Properties of Mg₂SiO₄ Liquid at High Pressure: Physical State of a Magma Ocean. *Earth and Planetary Science Letters*, Vol. 312, No. 3-4, 2011, pp. 463-470, <https://doi.org/10.1016/j.epsl.2011.10.025>.
- [13] D. B. Ghosh, B. B. Karki. Diffusion and Viscosity of Mg₂SiO₄ Liquid at High Pressure from First-Principles Simulations. *Geochimica et Cosmochimica Acta*, Vol. 75, No. 16, 2011, pp. 4591-4600, <https://doi.org/10.1016/j.gca.2011.05.030>.
- [14] O. Adjaoud, G. S. Neumann, S. Jahn, Mg₂SiO₄ Liquid under High Pressure from Molecular Dynamics. *Chemical Geology*, Vol. 256, No. 3, 2008, pp. 185-192, <https://doi.org/10.1016/j.chemgeo.2008.06.031>.
- [15] G. B. Martin, F. J. Spera, M. S. Ghiorso, D. Nevins, Structure, Thermodynamic, and Transport Properties of Molten Mg₂SiO₄: Molecular Dynamics Simulations and Model EOS, *American Mineralogist*, Vol. 94, No. 5-6, 2009, pp. 693-703, <https://doi.org/10.2138/am.2009.3087>.
- [16] B. B. Karki, L. Stixrude, Viscosity of MgSiO₃ Liquid at Mantle Conditions: Implications for Early Magma Ocean. *Science*, Vol. 328, No. 5979, 2010, pp. 740-742, <https://doi.org/10.1126/science.1188327>.
- [17] D. Nevins, F. J. Spera, M. S. Ghiorso, Shear Viscosity and Diffusion in Liquid MgSiO₃: Transport Properties and Implications for Terrestrial Planet Magma Oceans, *American Mineralogist*, Vol. 94, No. 7, 2009, pp. 975-980, <https://doi.org/10.2138/am.2009.3092>.
- [18] A. R. Oganov, J. P. Brodholt, G. D. Price, Comparative Study of Quasiharmonic Lattice Dynamics, Molecular Dynamics and Debye Model Applied to MgSiO₃ Perovskite, *Physics of The Earth and Planetary Interiors*, Vol. 122, No. 3-4, 2000, pp. 277-288, [https://doi.org/10.1016/S0031-9201\(00\)00197-7](https://doi.org/10.1016/S0031-9201(00)00197-7).
- [19] N. V. Yen, E. L. Plan, P. H. Kien, A. T. Nguyen, N. V. Hong, H. Phan, Topological Structural Analysis and Dynamical Properties in MgSiO₃ Liquid under Compression, *The European Physical Journal B*, Vol. 95, No. 4, 2022, pp. 1-11, <https://doi.org/10.1140/epjb/s10051-022-00313-0>.