

Dependence of self diffusivity on P and T in molten NaAlSi₂O₆: Comparison of laboratory and molecular dynamics experiments

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Abstract. We have used molecular dynamics (MD) simulation to investigate ionic self-diffusivity in NaAlSi₂O₆ melts and glasses at pressures of 3 – 58 GPa and temperatures of 2500 - 5000 K, to evaluate the effectiveness of a two-body potential in reproducing pressure and temperature dependence of tracer self-diffusivities. For each species, self-diffusivity increased with increasing temperature; with increasing pressure up to ~15 GPa, the self-diffusivity of O, Si, and Al increased, while mobility of Na decreased. An Arrhenian fit to self-diffusivity data collected from simulations at temperatures above the kinetic glass transition (up to 15 GPa) gives:

Species	E_a (kJ/mol)	V_a ($\times 10^6$ m ³ /mol)	log D*
Na	81 ± 14	3.5 ± 0.5	-6.8 ± 0.17
Al	306 ± 31	-5.6 ± 1.1	-6.5 ± 0.35
Si	294 ± 23	-6.1 ± 0.9	-6.9 ± 0.26
O	302 ± 23	-5.9 ± 0.8	-6.6 ± 0.26

for activation energy (E_a) and activation volume (V_a). The MD-derived $E_{a,O}$ and $V_{a,O}$ agree with laboratory results of 275 ± 10 kJ/mol and -6.2 ± 0.6 cm³/mol for $E_{a,O}$ and $V_{a,O}$ respectively [Shimizu and Kushiro, 1984] measured in experiments at 1673 to 1923 K and 0.5 to 2 GPa. Agreement with the pre-exponential factor (D*) is poorer, with MD result of $\sim 10^{-6.6}$ for O and laboratory value $\sim 10^{-4.7}$. From ~15 GPa - 25 GPa, V_a is ~ 0 m³/mol for O, Si, and Al; these species have a positive V_a for pressures above 25 GPa ($V_{a,O}$ is $\sim +1$ cm³/mol). For pressures ~ 15 GPa the majority of the network cations are in 5- or 6- fold coordination, and more than 20% of the O is in 3-fold coordination. With increasing pressure, 4-fold Si and Al decrease monotonically, while 6-fold Si and Al increase monotonically. Pentahedral Si and Al maximize at nearly the same pressure as O self-diffusivity.

Introduction

Silicate melts, play an important role in planetary differentiation and petrogenesis. Molecular dynamics (MD) simulations afford experimenters an opportunity to study the high pressure and temperature behavior of silicate melts and to explore the relationships between their properties and structure rapidly and inexpensively.

In this report, we present results of MD calculations on NaAlSi₂O₆ (Jd) melts and glasses, at pressures from 3 to 58 GPa and temperatures from 2500 - 5100 K. Specifically, we (1) test how well MD experiments, capture the laboratory-measured pressure- and temperature- dependence of ionic self-diffusivity [Shimizu and Kushiro, 1984] and (2) use the MD-

derived structures to investigate the mechanisms for pressure-induced changes in diffusivity.

Methods

MD calculations were made using a FORTRAN code previously described in Stein and Spera [1995,1996]. Accounts of both the MD technique and applications to sodium aluminosilicates can be found elsewhere [e.g., Poole *et al.*, 1995].

Molecular dynamics simulations are brute-force solutions to the classical equations of motion for a set of particles. Forces acting on particles were computed using the pairwise-additive potential:

$$U_{ij} = q_i q_j / r_{ij} + A_{ij} \exp(-B_{ij} r_{ij}) \quad (1)$$

which calculates the total energy acting on each particle (i) summed over the ensemble in terms of Coulombic interaction (with charges q_i , q_j evaluated over interparticle distance r_{ij}) and Born-Mayer repulsion terms (computed using coefficients of interparticle interaction A_{ij} , B_{ij} evaluated over interparticle distance r_{ij}). This pair-wise potential supplies a radially-symmetric potential interaction and neglects covalency and polarization effects. Several pairs of parameters have been introduced to describe the steepness of the Born-Mayer interaction in sodium aluminosilicate materials [e.g., DK - Dempsey and Kawamura, 1984; SA - Scamehorn and Angell, 1991; also see Table 1 in Stein and Spera, 1995]. All experimental Jd configurations were initially random configurations [cf. Matsui *et al.*, 1982] which were given 1 ps equilibration time at $T \sim 10^4$ K using the 'softer' SA potential during which the velocity of each particle was scaled and excess kinetic energy and momentum were removed. These configurations were then quenched, using the 'stiffer' DK potential, according to a quench rate (dT/dt) of 100 K/ps. For any changes in pressure, the configurations were subjected to pressure quench rate (dP/dt) of 1 GPa/ps.

Using these procedures, simulations were run for systems of 1200 and 1500 particles (Na + Al + Si + O) with box sizes adjusted to give $\rho \sim 2200$ kg m⁻³ at low pressure. Run durations of ~ 50 ps were used to minimize uncertainties in computed diffusivities. The transition from ergodic to non-ergodic behavior in a computer fluid occurs at a critical temperature (T_c) roughly four times higher than a laboratory fluid because MD experimental times are very short [see Bryce *et al.*, 1994; Bryce and Spera, 1995]. When a particle samples sufficient phase space during experiments, the ergodicity hypothesis, which allows for the equivalence of time-averaged and ensemble-averaged properties, is satisfied. When this hypothesis is satisfied, meaningful properties relevant to the material in a molten state can be extracted provided the potential is adequate [cf. Brawer, 1985].

Sampling errors on MD-computed properties were evaluated through comparisons of properties calculated from configura-

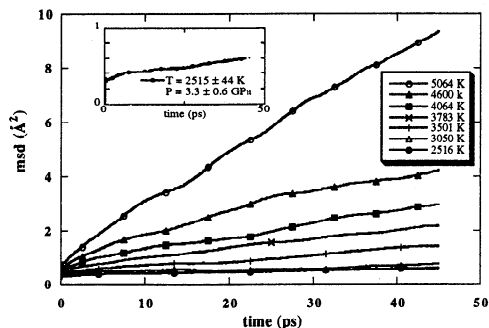


Figure 1. Mean Square Displacement (MSD) for oxygen ions in molten $\text{NaAlSi}_2\text{O}_6$. Oxygen ~ 2500 K (inset of MSD versus time) exhibits behavior typical of a thermally arrested or 'frozen' material.

tions run at similar pressure and temperature but developed from multiple quench cycles. Transport coefficients and structures were evaluated from particle positions saved over short time intervals (50 fs) during the 50 ps microcanonical (constant number, volume, and energy or NVE) experiments.

Results and Discussion

Mean square displacement (MSD) versus time fits, calculated for each species, can be used to compute self-diffusion coefficients (where D_i is the diffusion coefficient of species i) according to the Einstein relation of the limiting slope of MSD and experimental time (t):

$$D_i = \lim_{t \rightarrow \infty} \frac{\langle [r_i(t) - r_i(0)]^2 \rangle}{6t} \quad (2)$$

where the brackets imply an ensemble average [cf. *Haile*, 1992]. The numerator of (2) is the species-averaged MSD, a time-averaged square displacement for the all ions of a particular species in an experiment. MSD plots for oxygen in MD experiments ranging in temperature from ~ 2500 K to > 5000 K are shown in Figure 1. Low-temperature simulations are characterized by arrested behavior, as seen in Fig. 1 (and inset); studies using tagged particle dynamics [cf. *Stein and Spera*, 1996] find small populations of oxygen ions ($< 10\%$) exhibiting displacements greater than the diameter of an oxygen ion at temperatures below T_c . The higher temperature experiments demonstrate ionic mobility by continuous diffusive jumps by the majority of the population of ions (e.g., $> 70\%$ of the oxygen ions).¹

Tagged particle dynamics analyses as well as these polythermal MSD data illustrate an important criterion that must be satisfied for accurate calculation of transport properties of fluids in MD experiments: the importance of sufficient sampling of phase space during the experiment [*Stillinger*, 1995]. Several criteria can be used to locate the critical temperature separating computer 'liquids' and computer 'glasses'. These analyses range from the most simple involving identification of a minimum MSD (e.g., $\text{MSD} \equiv 6Dt \geq \sim 2\text{-}3 \text{ \AA}^2$) to more sophisticated approaches such as analysis of the van Hove self-correlation function or non-Gaussian statistical parameters [e.g., *Barrat and Roux*, 1991; *Odagaki and Hiwatari*, 1991]. In the low pressure MSD plots portrayed in Figure 1, the onset of

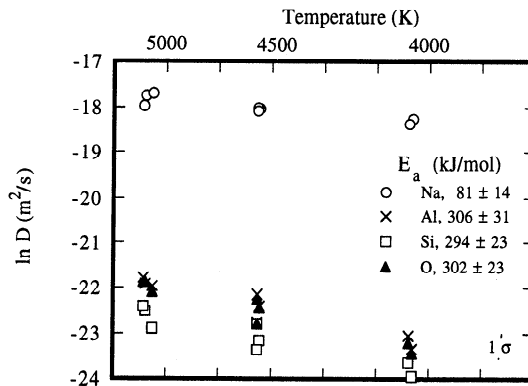


Figure 2. Diffusivity in the polythermal experiments. All determinations are based on self-diffusivity coefficients evaluated from species' MSD. Separately run configurations developed from different quench cycles are plotted to estimate the reproducibility of MD-calculated diffusion coefficients. Pressures lie in the small range $\sim 3 - 4$ GPa.

ergodic behavior is seen at ~ 4000 K, in which the majority of the oxygens exhibit sufficient squared displacements.

We have used results of simulations at temperatures $> \sim 4000$ K at ~ 3 GPa and > 3500 K at $P \sim 10$ GPa to determine the temperature dependence of ionic self-diffusivity. Computed D_i values for each atomic species are shown in Figure 2, with data extracted from simulations carried out at $P \sim 3$ GPa and $T > \sim 4000$ K. To determine the activation energies for ionic self-diffusivity, we used multiple regression to fit the data in Figure 2 as well as data collected from polythermal runs at ~ 10 GPa to the Arrhenian relation

$$\ln D_i = \ln D_* - \frac{E_a + PV_a}{RT}, \quad (3)$$

with coefficients D_* , temperature derivative E_a (activation energy), and pressure derivative V_a (activation volume). The fit parameters D_* , E_a , and V_a are constants independent of temperature and pressure within the range of applicability of the Arrhenian relation.

The E_a for oxygen self-diffusion computed by MD at temperatures $> \sim 4000$ K (302 ± 23 kJ/mol) agrees with the laboratory result of 275 ± 10 kJ/mol [*Shimizu and Kushiro*, 1984]. The activation energies for Al and Si self-diffusivity are comparable to that of oxygen ($E_{a,\text{Si}} = 295 \pm 23$ kJ/mol; $E_{a,\text{Al}} = 306 \pm 31$ kJ/mol), and agree with laboratory data (e.g., $E_{a,\text{Si}} = 307 \pm 4$ kJ/mol, *Shimizu and Kushiro*, 1991). The similarity for O, Si, and Al is consistent with a cooperative diffusion mechanism [*Leshner et al.*, 1996]. For comparison to the network-forming species, the activation energy for sodium self-diffusion is 70 ± 7 kJ/mol for the MD experiments. Our MD experiments do not reproduce laboratory $\ln D_*$ values very well. For example, oxygen, $\ln D_* = -15.2 \pm 0.6$ while experimental data provides $\ln D_* = -10.8 \pm 0.7$. This misfit may be due, in part, to the selection of the potential parameters; employment of other potential parameters [e.g., *Scamehorn and Angell*, 1991] can drastically change ionic mobility while producing little change in pressure and temperature derivatives of self-diffusivity [see discussion in *Stein and Spera*, 1995 pp. 420-421].

We also studied pressure effects on the self-diffusivity of the atomic species; results for the same set of experiments are shown in Figure 3(a,b). The network species (Si, Al, O) show

¹Supporting diffusivity data are available via anonymous FTP from kosmos.agu.org, (Username=anonymous, Password=guest) in the directory /APEND.

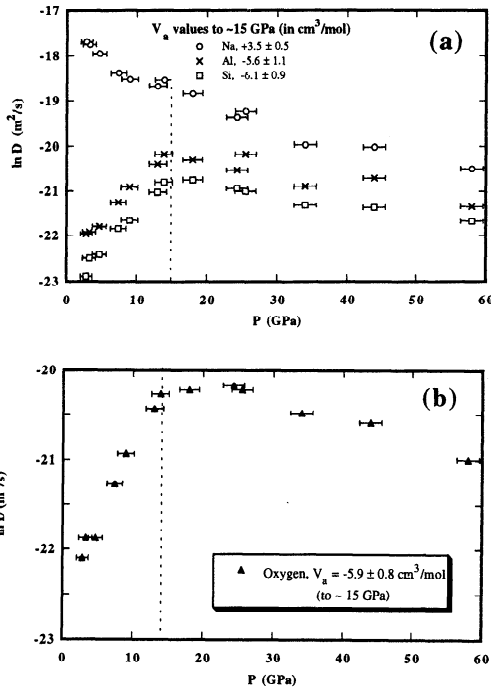


Figure 3 (a-b). Polybaric self-diffusivity measurements in MD experiments. (3a) Na, Al, and Si; (3b) O. All simulations are executed at ~ 5000 K. Note the decrease in sodium mobility with increasing pressure, corresponding to a positive V_a . MD calculations find a negative V_a for all of the network forming ions up to ~ 15 GPa, where the V_a of the network formers approaches zero. We speculate that intermediate range (3 to 7 Å) structure (i.e. ring statistics) may be greatly affected by the destruction of AlO₄ and SiO₄ tetrahedra.

increased mobility with increased pressure, consistent with trends found in laboratory studies at 0.6 - 2.0 GPa and 1673-1923 K [Shimizu and Kushiro, 1984, 1991; Kushiro, 1983]. Sodium self-diffusivity decreases with increasing pressure, consistent with previous MD studies [Angell et al., 1982; 1983]. Activation volumes are calculated for each atomic species for pressures up to ~15 GPa; these values are positive for Na ($V_a = +3.5 \pm 0.5 \text{ cm}^3/\text{mol}$), whereas Si, Al, and O have negative activation volumes, with $V_{a,O} = -5.9 \pm 0.8 \text{ cm}^3/\text{mol}$, $V_{a,Si} = -6.1 \pm 0.9 \text{ cm}^3/\text{mol}$, and $V_{a,Al} = -5.6 \pm 1.1 \text{ cm}^3/\text{mol}$. There is excellent agreement with laboratory measurements for the oxygen MD calculations (Shimizu and Kushiro, 1984: $V_{a,O} = -6.2 \pm 0.6 \text{ cm}^3/\text{mol}$), but Si agrees less well (e.g., $V_{a,Si} = -13.3 \pm 0.8 \text{ cm}^3/\text{mol}$ from Shimizu and Kushiro, 1991). As noted in Figure 3, at pressures ~15 GPa activation volume of the network-forming species approaches zero. Eventually at $P > \sim 25 \text{ GPa}$, activation volume becomes positive for all ions.

Coordination statistics were calculated for all polybaric experiments, and are shown in Figures 4(a,b,c). Other MD experiments (e.g., Stein and Spera [1996] on NaAlSi₂O₆ have shown that structures produced in runs at low pressures (2-4 GPa) agree with those observed in laboratory experiments, with the majority of the Al and Si in tetrahedral coordination (⁴Al and ⁴Si). Raman studies of the coordination of Al in jadeite melts confirms tetrahedral coordination in melts up to 4 GPa [Sharma et al., 1979]. In higher pressure MD simulations, many of the ions of these species move into higher order (five-, six-, or seven-fold) coordination. This phenomenon has been noted in both laboratory and MD experiments [cf. Yarger et al., 1995]. The change in the pressure-derivative of self-dif-

fusivity at ~15 GPa (where V_a approaches zero) is clearly correlated with increasing abundance of AlO₅, AlO₆, SiO₅, and SiO₆ polyhedra at the expense of ⁴Al and ⁴Si (see Figure 4a, inset). We speculate that these structures cause changes in the intermediate range order (i.e., ring statistics) that plays an important role in the response to pressure. Previous workers (e.g., Stebbins [1995]; Kubicki and Lasaga [1990]) have discussed the important role of 5-fold Si in explaining melt fluidity. For $P \sim 15 \text{ GPa}$, there are approximately equal populations of tetrahedral ('T': ⁴Al and ⁴Si) and non-tetrahedral ('NT': ⁵Si, ⁵Al, ⁶Si, and ⁶Al) network cations; if the system is treated as a binary one, consist-

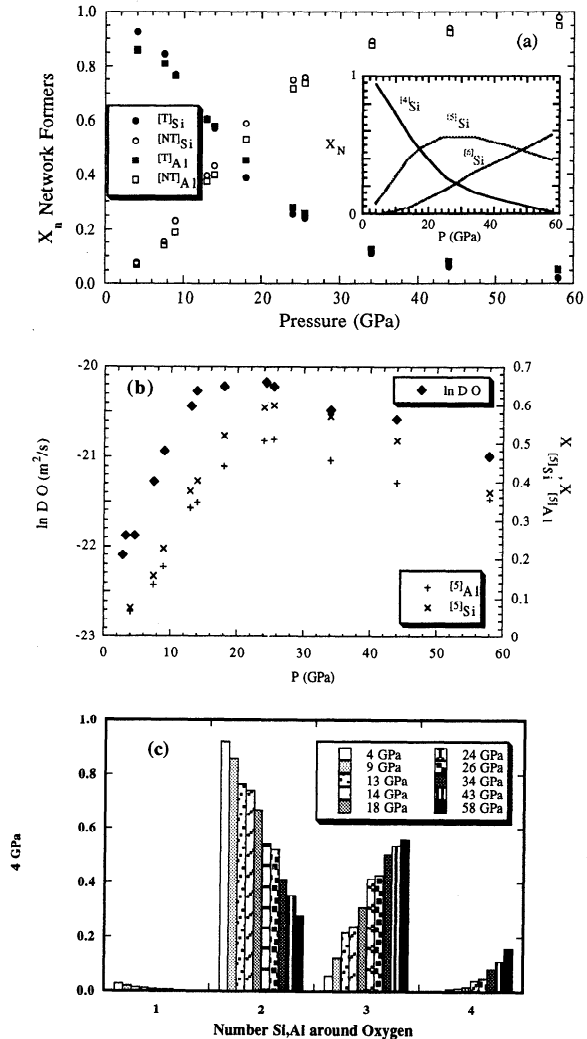


Figure 4 (a-b-c). Coordination statistics for network-forming ions in molten jadeite at ~5000K. Note the dominant effect of pressure on structural change and the emergence of anomalous structures at pressures $> \sim 15 \text{ GPa}$. (4a) Pressure effects on the network structure: comparisons of the mole fraction of Al and Si surrounded by four nearest neighbor oxygens ($X_{T,Al}$ and $X_{T,Si}$) and mole fraction of these network ions surrounded by more than four nearest neighbor oxygens ($X_{NT,Al}$ and $X_{NT,Si}$). The inset shows the coordination for silicon ions, broken down into the four-, five- and six- fold coordination components. ⁵Si reaches a maximum concentration in the 15-25 GPa pressure range. The coordination profiles of ⁴Al, ⁵Al, and ⁶Al are very similar to trends for Si (inset). (4b) Oxygen self-diffusivity and the mole fraction of ⁵Al and ⁵Si. Clearly, these two phenomena are correlated (4c) Coordination statistics for oxygen as a function of pressure.

ing of mole fractions of T and NT network-formers, the configurational entropy maximum is located where the mole fractions are equal. Interestingly, the Adam-Gibbs (AG) model [1965] predicts a viscosity minimum (and hence diffusivity maximum) at the maximum configurational entropy (S_{conf}) state. Bottinga and Richet [1995] have recently applied the AG model to rationalize the pressure-dependence of the viscosity of molten silicates treated as binary solutions of bridging (oxygen coordination number 2 or greater) and non-bridging (singly-coordinated) oxygen (BO's and NBO's). They found that the 'anomalous' pressure effect (where increased pressure makes viscosity decrease) occurs for melts consisting of < 50 mol % NBO. We propose a simple extension of the Adam-Gibbs model to explain the maxima in Si, Al, and O tracer diffusion in network fluids with low concentrations of NBO. Assuming that S_{conf} is the entropy of mixing of $^{[2]}O$ and $^{[3]}O$ on the oxygen sub-lattice, entropy is maximized when the concentrations of $^{[2]}O$ and $^{[3]}O$ are equal. This is approximately the case as noted by examination of Figure 4c. Mixing on the oxygen sub-lattice can also be viewed from the vantage of network (Si and Al) atom coordination. As noted from Figure 4a, the concentrations of $^{[4]}Si$ and $^{[5]}Si$, as well as $^{[4]}Al$ and $^{[5]}Al$, are approximately equal to each other at a pressure of ~ 15 GPa where oxygen diffusivity maximizes. Finally, as with E_a , the Al, Si, and O possess nearly the same V_a in the pressure range of the experiments: negative V_a up to ~ 15 GPa, $V_a \sim 0$ in the 15-25 GPa range, and positive V_a above ~ 25 GPa. These observations, as well as similarities in E_a , suggest cooperativity over medium-range (5 to 10 Å) length scales is involved in the mechanism for diffusion in molten silicates.

Conclusions

Molecular dynamics experiments have recovered activation volume and activation energies for oxygen and silicon self-diffusion in good agreement with laboratory measurements. Accurate capture of the temperature dependence of oxygen self-diffusion is possible by the use of long duration simulations using many particles. Simulations run at $T > T_c$ are essential for recovering accurate properties. We can identify structural change (higher coordination of the network-forming species) at pressures above ~15 GPa as the cause of the decline in V_a for the network cations, but a more quantitative description of the interplay between structural and transport properties, including the role of intermediate-range structural order (e.g., ring statistics) on transport properties, awaits further investigation.

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