# Viscosity and viscosity anomalies of model silicates and magmas: A numerical investigation

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A B S T R A C T

We present results for transport properties (diffusion and viscosity) using computer simulations. Focus is made on a densified binary sodium disilicate $2SiO_2$–$Na_2O$ (NS2) liquid and on multicomponent magmatic liquids (MORB, basalt). In the NS2 liquid, results show that a certain number of anomalies appear when the system is densified: a diffusivity maxima/minima is found for the network-forming ions (Si,O) which bears some striking similarities with the well-known case of water or liquid silica, whereas the sodium atom displays three distinct régimes for diffusion. Some of these features can be correlated with the obtained viscosity anomaly under pressure, the latter being fairly well reproduced from the simulated diffusion constant. In model magmas (MORB liquid), we find a plateau followed by a continuous increase of the viscosity with pressure. Finally, having computed both diffusion and viscosity independently, we can discuss the validity of the Eyring equation for viscosity which relates diffusion and viscosity. It is shown that it can be considered as valid in melts with a high viscosity. On the overall, these results highlight the difficulty of establishing a firm relationship between dynamics, structure and thermodynamics in complex liquids.

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## 1. Introduction

Viscosity is one of the key properties influencing the overall behavior of magmatic liquids. It is a fundamental property in Earth Sciences and has therefore led after nearly five decades of intensive research to a huge body of experimental and theoretical studies and data base (Mysen and Richet, 2005; Giordano et al., 2008). Systematic investigations with composition and temperature in simple or complex silicates have been performed, and some generic trends have been identified. For instance, it has been found that numerous systems were displaying an Arrhenius behavior (Micoulaut, 2010) with temperature of the form $\eta = \eta_0 \exp[E_A/k_B T]$ where $E_A$ represents the activation energy for viscous flow. When properly rescaled with a reference temperature, $T_g$, at which the viscosity is $10^{11}$ Pa·s, two categories of liquids have been identified (Angell, 1995): those which remain Arrhenius-like in the super-cooled liquid over the entire range of temperatures implying that $E_A$ does not depend on T, and those which display a curvature in the Arrhenius representation (a semi-log plot as a function of inverse temperature) indicating that one has a temperature dependence in the activation energy for viscous flow (Wang et al., 2006). Usually, such liquids are fitted quite successfully with a Tamman–Vogel–Fulcher (TVF) law (Pathmanathan and Johari, 1990; Giordano and Dingwell, 2003a,b): $\eta = \eta_0 \exp(A/(T-T_0))$, A and $T_0$ being constants.

There has been a continuing effort to measure viscosity as function of pressure (Scarfe, 1973; Kushiro, 1976, 1978, 1986; Kushiro et al.,

1976; Brearley et al., 1986; Dunn and Scarfe, 1986; Mori et al., 2000; Suzuki et al., 2002, 2005, 2011; Reid et al., 2001, 2003; Tinker et al., 2004; Liebske et al., 2005; Ardia et al., 2008; Del Gaudio and Behrens, 2009). At constant temperature, the evolution of viscosity with pressure is complex and depends on the composition of the silicate melt, in particular on its degree of depolymerization. With highly polymerized melts (e.g. albite and dacite) the viscosity decreases continuously with pressure, though its behavior above the maximal pressure of investigation ($\simeq 7$ GPa for albite and dacite) cannot be clearly anticipated. However, it is observed that the decrease of the viscosity with pressure becomes more gradual when the temperature is raised and can lead to a plateau value at high pressure (e.g. jadeite). When the melt is less polymerized (e.g. albite–diopside system), after an initial decrease, and according to the temperature, the viscosity exhibits a plateau value or a weakly pronounced minimum with the pressure. With depolymerized melts (e.g. diopside and peridotite) a different situation occurs. The viscosity first increases with rising pressure and reaches a maximum value prior to decrease at higher pressure, but the higher the degree of depolymerization of the melt the more pronounced the viscosity maximum. Moreover, in a more general way, the pressure evolution of the viscosity has been found to be (anti-) correlated with that of the oxygen and silicon diffusion coefficients (Shimizu and Kushiro, 1991; Poe et al., 1997; Reid et al., 2001; Tinker et al., 2003), a finding which has been interpreted as the signature of a pressure-induced structural rearrangement.

In the present contribution, we have investigated by Molecular Dynamics the transport properties of two silicate melts: a sodium disilicate (NS2) and a mid-ocean ridge basalt (MORB). Focus is

made on the self-diffusion coefficient and the viscosity at ambient pressure and in densified liquids. Results show that a certain number of anomalies appear under pressure which are extensively discussed, together with the validity of the Eyring equation relating simply viscosity and diffusion. The paper is organized as follows. In Section II, we describe the model details and the way both diffusion and viscosity is computed. In Section III we present the results for both liquids. An extensive discussion is provided in Section 4. Finally, Section 5 contains some more general comments and a conclusion is drawn.

## 2. Methodology

### 2.1. Simulation details

The molecular dynamics (MD) simulations were performed with the DL_POLY 2.0 code (Smith and Forester, 1996) in NPT Ensemble, i.e. pressure and temperature are fixed and lead to an adaptive cell length for the simulation box, and velocity rescaling, respectively. The equations of motions for atoms were solved with a time step of 1–2 fs ($10^{-15}$ s) by the leap-frog algorithm.

Liquid $Na_2O$–$2SiO_2$ has been simulated by placing 667 silicon, 667 sodium, and 1666 oxygen atoms in a cubic box with periodic boundary conditions. As the atoms are bearing charges (ions), the long range coulombic forces are evaluated by an Ewald sum. The atoms interact via a two-body potential (Born–Mayer type) parametrized by Teter (2003), see also Cormack et al. (2003), which writes

$$V_{ij}(r) = A_{ij}.exp\left(-r/\rho_{ij}\right) - C_{ij}/r^6 + z_i z_j/r, \tag{1}$$

where r is the distance between atoms i and j, $z_i$ is the effective charge associated with the ion i, and where $A_{ij}$, $\rho_{ij}$ and $C_{ij}$ are parameters describing repulsive and dispersive forces between the ions i and j. In the present report, we do not focus on structure and thermodynamic properties of liquid NS2 simulated with this potential and for a detailed analysis and comparison with experimental data we refer the reader to Du and Cormack (2004, 2005). Notice that at zero pressure and 300 K the density of the simulated NS2 glass is equal to 2.45 g/cm³, i.e. quite close to the experimental value (Vaills et al., 2001) 2.37 g/cm³.

The mid-ocean ridge basalt (MORB), a nine component system (0.13 wt.% $K_2O$, 2.94 wt.% $Na_2O$, 11.87 wt.% CaO, 7.77 wt.% MgO, 8.39 wt.% FeO, 1.15 wt.% $Fe_2O_3$, 15.11 wt.% $Al_2O_3$, 1.52 wt.% $TiO_2$ and 50.59 wt.% $SiO_2$), has been simulated with a two-body potential of the same form as Eq. (1). The chemical composition of the MORB melt and the potential parameters are those given by Guillot and Sator (2007a) in their simulation study of natural silicate melts (see Tables 1 and 2 therein). The simulated sample of MORB was composed of 3000 atoms (555 Si, 12 Ti, 195 Al, 9 $Fe^{3+}$, 60 $Fe^{2+}$, 126 Mg, 141 Ca, 63 Na, 3 K, and 1836 O) contained in a cubic box with periodic boundary conditions. The control parameters (time step, Ensemble, etc.) of the simulation are the same as for liquid NS2. The density of MORB at liquidus temperature and its equation of state (i.e. density versus pressure) are well reproduced by the MD calculation (for a detailed description of the properties of the MORB melt, see Guillot and Sator 2007a,b). Notice that long simulation runs (≃10 ns or $10^7$ time steps) were performed to reach good statistics when evaluating the viscosity by the Green–Kubo integrand.

As two different parametrized force fields have been used for the investigation of the two systems, one may wonder if the forthcoming results and obtained differences will arise from the parameters themselves, or from the investigated system. This underscores of course the question of the transferability of the force fields. One should first recall that force-fields are usually system dependent, i.e. their parameters are fitted in order to reproduce structural, thermodynamic or dynamic properties of a given system. However, to clarify this issue, we have also used the MORB potential (Guillot and Sator,

2007a) to simulate the NS2 liquid under pressure. Results (see below) show that while the absolute value of relevant properties may change slightly, the trends with pressure remain unchanged and therefore do not alter the more general conclusion of the paper. We motivate our choice simply by the fact that the Teter potential (Teter, 2003) appears to be highly accurate concerning the reproduction of experimental data on transport properties (diffusion, viscosity) as one will see below.

### 2.2. Simulation time and viscosity

Before presenting results, it is worthwhile to keep in mind some key data when one is about to calculate the viscosity of a supercooled melt. In using a high performance computer, the longest MD run that can be performed (in a reasonable time) for a system composed of ≃3000 atoms is about 1 μs (or $10^9$ MD steps). To observe on this timescale the diffusion of atoms in the simulation box, the mean square displacement of each atom after 1 μs has to be (on average) of the order of ≃10 Å² (the mean distance between two nearest neighbors is roughly 3 Å in a melt, so the diffusive regime is reached when each atom has interchanged its position with a nearest neighbor). Therefore, the smallest diffusion coefficient that can be evaluated over a 1 μs MD run is equal to ≃$2 \times 10^{-14}$ m²/s (from Einstein relation $D_{min} = <r_{min}^2>/6t_{max}$ where $<r_{min}^2> = 10$ Å² and $t_{max} = 10^{-6}$ s). In applying the Eyring theory to viscous flow, the viscosity η can be deduced from the diffusion coefficient D of network forming ions through the equation,

$$\eta = \frac{k_B T}{\lambda D} \tag{2}$$

where T is the temperature and λ a jump distance in the viscous flow. Experimentally it has been shown (Shimizu and Kushiro, 1984) that this equation works well with viscous liquids (e.g. silicates with high silica contents) provided that the D value is assigned to that of O or Si atoms and λ≃2.8 Å, the oxygen–oxygen mean distance in silicate melts. Using Eq. (2), a value of $D_O$ equal to $2 \times 10^{-14}$ m²/s leads to a corresponding viscosity of about 3000 Pa·s at 1473 K. We can use the Maxwell relation for which the relaxation time for viscous flow is related to the viscosity through the equation, $\tau_{relax} = \eta/G_\infty$, where $G_\infty \simeq 10^{10}$ Pa is the shear modulus at infinite frequency (Dingwell and Webb, 1989). So to fully relax a viscous melt of viscosity η≃$10^4$ Pa·s one needs to perform a MD run longer than $\tau_{relax} = 1$ μs, a finding consistent with the evaluation based on the self-diffusion. Although qualitative, these estimates are useful because they point out that only the low viscosity regime (i.e. η ≪ $10^4$ Pa·s) can be investigated by MD simulation, the highly viscous regime ($10^4$–$10^{12}$ Pa·s) being unreachable with usual numerical resources. In the present study our MD runs did not exceed 10 ns, which means that only a viscosity value smaller than ≃10 Pa·s could be investigated (notice that most of the MD studies published in the literature often do not exceed 1 ns run intervals).

## 3. Results

### 3.1. Diffusion coefficients

Self-diffusion constant is one of the very first quantities that can be accessed from MD simulations. There has been a long-standing effort to compute such quantity in systems of geological interest using MD. Rustad and co-workers (Rustad et al. 1990, 1991, 1992; Wasserman et al. 1993) have used such simulations to investigate the dynamics of simple glass-forming liquids, binary silicates and alumino-silicates under pressure. The behavior of diffusion has been correlated with structural and thermodynamic properties (Kubicki and Lasaga, 1988, 1991; Kubicki et al. 1990, 1992).