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Mg₂SiO₄ Liquid under High Pressure from Molecular Dynamics

Omar Adjaoud^a, G. Steinle-Neumann^{a,*}, Sandro Jahn^b

^a*Bayerisches Geoinstitut, University Bayreuth, 95440 Bayreuth, Germany*

^b*GeoForschungsZentrum Potsdam, Department 4, Telegrafenberg, 14473 Potsdam Germany*

Abstract

We use a flexible potential model to perform large-scale molecular dynamics simulations of Mg₂SiO₄ melt up to pressures of 24 GPa and at temperatures between 2390 K and 3200 K. We find that thermal pressure and the Grüneisen parameter γ increase linearly with density, independent on temperature. γ increases from 0.5 at ambient pressure to 0.75 at 24 GPa. While Si stays overwhelmingly in tetrahedral coordination, the coordination of Mg increases significantly under compression, from an average 5-fold coordination at room pressure to 7-fold coordination at 24 GPa. Medium range order in Mg₂SiO₄ as expressed by X-ray and neutron structure factors change considerably with pressure, with features at low wave-vectors q sharpening considerably and shifting to higher q . Diffusivity of the atomic species in Mg₂SiO₄ decrease uniformly with pressure and are well described by an Arrhenius law. For viscosity η we find good agreement with experiments at room pressure, and predict a rapid increase with pressure.

Key words: Mg₂SiO₄, melt structure, high pressure, high temperature, thermodynamics, diffusivity, viscosity

1 Introduction

Melting is a ubiquitous process in planetary interiors that has major consequences for their chemical and thermal evolution. The importance of melts in the Earth range from extraction of basalt at mid-ocean ridges to the large scale magma ocean that governed the dynamics of the early planet (Tonks

* Corresponding author.

Email address: g.steinle-neumann@uni-bayreuth.de (G. Steinle-Neumann).

6 and Melosh, 1993). As the major component of the Earth's upper mantle the
7 magnesium orthosilicate Mg_2SiO_4 is of considerable importance.

8 Despite this importance the knowledge of thermodynamic and transport prop-
9 erties of Mg_2SiO_4 melt is limited. This is partly caused by the high melting
10 point of Mg_2SiO_4 (2163 ± 25 K (Bowen and Andersen, 1914)) that has lead
11 to extrapolations of properties from supercooled liquids to high temperatures
12 (e.g. Tangemann *et al.*, 2001) or extrapolation from other compositions to
13 Mg_2SiO_4 (e.g. Lange and Carmichael, 1987; Rigden *et al.*, 1989). Such extrap-
14 olations produce conflicting results for a number of properties, such as heat
15 capacity (Stebbins *et al.*, 1984; Lange and Navrotsky, 1992; Tangemann *et al.*,
16 2001) or compressibility (Bottinga, 1985; Lange and Carmichael, 1987; Rivers
17 and Carmichael, 1987) (Table 1). As the melting temperature increases rapidly
18 with pressure (Ohtani and Kumazawa, 1981), high pressure experiments on
19 Mg_2SiO_4 melts are even more difficult and scarce.

20 Aside from the thermodynamic properties mentioned in the previous para-
21 graph transport properties of the melt, such as viscosity, are of central im-
22 portance as crystal growth (Solomatov and Stevenson, 1993a), crystal settling
23 (Solomatov and Stevenson, 1993b) and convection dynamics (Abe, 1997) crit-
24 ically depend on them. Despite this importance there is limited information
25 on melt viscosity, in particular at high pressure. At high pressure viscosity is
26 measured most directly by the "falling sphere" method, in which the sinking
27 velocity of a solid sphere through a liquid can be related to viscosity by Stokes'
28 law (Kushiro, 1978; Reid *et al.*, 2003; Liebske *et al.*, 2005). For low viscosity
29 depolymerized melts, such as diopside (Reid *et al.*, 2003), peridotite (Lieb-
30 ske *et al.*, 2005) or the Mg_2SiO_4 liquid studied here, the fast sinking velocity
31 makes the measurements challenging.

32 Ultimately, changes in physical properties must be caused by structural changes
33 in the melt that are difficult to monitor experimentally. For a quantitative
34 analysis using nuclear magnetic resonance for ^{27}Al , ^{29}Si or ^{17}O (Fiske *et al.*,
35 1998; Allwardt *et al.*, 2007; Kelsey *et al.*, 2007) samples must be synthesized at
36 high pressure and temperature, and the quenched glass can then be analyzed
37 at room pressure.

38 Alternatively, structure factors of quenched glasses can be measured with X-
39 rays or neutrons and reveal structural correlations between different compo-
40 nents. Such studies on Mg_2SiO_4 (Kohara *et al.*, 2004) reveal that glass/melt
41 connectivity result from Mg-O polyhedra. SiO_4 units, that typically serve as
42 network formers, show almost no connectivity, with Si_2O_7 dimers (Q^1 species)
43 coexisting with isolated SiO_4 units (Q^0 species). In analogy to the crystalline
44 phases, connectivity in the melt and coordination of Si can be expected to
45 increase with pressure, but quantitative experiments to this extent have not
46 been performed to date.

47 In light of these difficulties numerous molecular dynamics simulations on struc-
 48 ture and physical properties of silicate melts have been performed over the past
 49 few years, with the goal to predict physical properties and to relate structural
 50 properties with macroscopic observables. These include the properties men-
 51 tioned above, but the interpretation of integrated structural signals such as
 52 X-ray or neutron structure factors also depend critically on an understanding
 53 of the various partial contributions to the measured signal (Jahn and Madden,
 54 2007a).

55 Computations for liquids typically fall in two categories: electronic struc-
 56 ture (*ab-initio*) computations (Vocadlo *et al.*, 2000; Belonoshko *et al.*, 2005;
 57 Stixrude and Karki, 2005; Karki *et al.*, 2006, 2007; Wan *et al.*, 2007; de Koker
 58 *et al.*, 2008) and potential model simulations (Gale *et al.*, 1992; Matsui, 1994;
 59 Guillot and Sator, 2007a,b; Lacks *et al.*, 2007). *Ab-initio* computations provide
 60 an accurate description of bonding and electronic structure and are transfer-
 61 able between different structure types and to different thermodynamic condi-
 62 tions (e.g. high pressure). Computational requirements, however, pose severe
 63 limitations on the maximum simulation cell size and run duration: *Ab-initio*
 64 studies are typically limited to a few hundred atoms in the cell and run du-
 65 rations of a few picoseconds (ps). While such short run durations allow for
 66 the evaluation of thermodynamic properties, longer runs and larger cells are
 67 needed to reliably obtain transport properties. Pair potentials (Matsui, 1994)
 68 or shell models (Gale *et al.*, 1992) are often used to efficiently explore physical
 69 properties; large system sizes and long run durations are readily accessible.
 70 However, such potentials suffer from the fact that they are typically fit to a
 71 set of experimental data and their transferability to different compositions or
 72 different thermodynamic conditions is limited.

73 Both of these simulation approaches have limitations for a comprehensive
 74 study of thermodynamic and transport properties of melts at high pressure
 75 and temperature, and here we attempt to bridge the gap between them. We
 76 apply an advanced ionic model that is derived from electronic structure cal-
 77 culations. The so called Aspherical Ion Model (AIM) (Aguado *et al.*, 2003;
 78 Madden *et al.*, 2006) has been applied successfully before for oxide melts,
 79 e.g. MgO melt (Aguado and Madden, 2005), Al₂O₃ melt (Jahn and Madden,
 80 2007a) and MgO-Al₂O₃ melts (Jahn, 2008). Recently, a set of AIM-type po-
 81 tentials was constructed for silicates, which has successfully been applied to
 82 study crystalline magnesiosilicate materials in a wide range of pressures and
 83 temperatures (Jahn and Madden, 2007b). Here we explore structural, thermo-
 84 dynamic, and transport properties of Mg₂SiO₄ liquid over a wide pressure and
 85 temperature range of 0-24 GPa and 2390-3200 K, respectively. The current
 86 manuscript is organized as follows: after briefly introducing the method and
 87 computational setup we explore the thermodynamics of the melt using a Mie-
 88 Grüneisen description of the thermal equation of state. We look at structural
 89 properties and transport properties in the melt along an isotherm of 2800 K.

Results are compared to experimental data where available, and the behavior predicted is discussed. In the final section, conclusions are given.

2 Model and computational details

Details of the AIM interaction model and its parameterization are described elsewhere (Aguado *et al.*, 2003; Madden *et al.*, 2006). In short, the AIM interatomic potential V is constructed from four components

$$V = V^{qq} + V^{disp} + V^{rep} + V^{pol} \quad (1)$$

The first two components, the charge-charge (V^{qq}) and dispersion (V^{disp}) interactions, are purely pairwise additive:

$$V^{qq} = \sum_{i \leq j} \frac{q^i q^j}{r_{ij}}, \quad (2)$$

$$V^{disp} = - \sum_{i \leq j} [f_6^{ij}(r_{ij}) C_6^{ij} / r_{ij}^6 + f_8^{ij}(r_{ij}) C_8^{ij} / r_{ij}^8], \quad (3)$$

where q^i is the formal charge on ion i (+4 for Si, +2 for Mg and -2 for O), C_6^{ij} and C_8^{ij} are the dipole-dipole and dipole-quadrupole dispersion coefficients respectively, and f_n^{ij} are Tang-Toennies dispersion damping functions (Tang and Toennies, 1984), which describe short-range corrections to the asymptotic dispersion term.

The overlap repulsion component (V^{rep}) is given by

$$\begin{aligned} V^{rep} = & \sum_{i \in O, j \in Mg, Si} [A^{-+} e^{-a^{-+} \rho^{ij}} + B^{-+} e^{-b^{-+} \rho^{ij}} + C^{-+} e^{-c^{-+} r_{ij}}] \\ & + \sum_{i, j \in O} A^{--} e^{-a^{--} r_{ij}} \\ & + \sum_{i \in O} [D(e^{\beta \delta \sigma^i} + e^{-\beta \delta \sigma^i}) + (e^{\zeta^2 |\nu^i|^2} - 1) + (e^{\eta^2 |\kappa^i|^2} - 1)], \end{aligned} \quad (4)$$

with

$$\rho^{ij} = r_{ij} - \delta \sigma^i - S_\alpha^{(1)} \nu_\alpha^i - S_{\alpha\beta}^{(2)} \kappa_{\alpha\beta}^i, \quad (5)$$

and summation of repeated indexes is implied. The variable $\delta \sigma^i$ characterizes the deviation of the radius of oxide anion i from its default value, $\{\nu_\alpha^i\}$ are a set

of three variables describing the Cartesian components of a dipolar distortion of the ion, and $\{\kappa_{\alpha\beta}^i\}$ are a set of five independent variables describing the corresponding quadrupolar shape distortions ($|\kappa|^2 = \kappa_{xx}^2 + \kappa_{yy}^2 + \kappa_{zz}^2 + 2(\kappa_{xy}^2 + \kappa_{xz}^2 + \kappa_{yz}^2)$ with a traceless matrix κ). $S_{\alpha}^{(1)} = r_{ij,\alpha}/r_{ij}$ and $S_{\alpha\beta}^{(2)} = 3r_{ij,\alpha}r_{ij,\beta}/r_{ij}^2 - \delta_{\alpha\beta}$ are interaction tensors. The last summations include the self-energy terms, representing the energy required to deform the anion charge density, with β , ζ and η as effective force constants. The extent of each ion's distortion is determined at each molecular dynamics time-step by energy minimization.

The polarization part of the potential incorporates dipolar and quadrupolar contributions (Wilson *et al.*, 1996),

$$\begin{aligned}
V^{pol} = & \sum_{i,j \in O} \left((q^i \mu_{\alpha}^j - q^j \mu_{\alpha}^i) T_{\alpha}^{(1)} + \left(\frac{q^i \theta_{\alpha\beta}^j}{3} + \frac{\theta_{\alpha\beta}^i q^j}{3} - \mu_{\alpha}^i \mu_{\beta}^j \right) T_{\alpha\beta}^{(2)} \right. \\
& \left. + \left(\frac{\mu_{\alpha}^i \theta_{\beta\gamma}^j}{3} + \frac{\theta_{\alpha\beta}^i \mu_{\gamma}^j}{3} \right) T_{\alpha\beta\gamma}^{(3)} + \frac{\theta_{\alpha\beta}^i \theta_{\gamma\delta}^j}{9} T_{\alpha\beta\gamma\delta}^{(4)} \right) \\
& + \sum_{i \in O, j \in Mg, Si} \left(q^j \mu_{\alpha}^i [1 - g_D(r^{ij})] T_{\alpha}^{(1)} + \frac{\theta_{\alpha\beta}^i q^j}{3} [1 - g_Q(r^{ij})] T_{\alpha\beta}^{(2)} \right) \\
& + \sum_{i \in O} \left(k_1 |\vec{\mu}^i|^2 + k_2 \mu_{\alpha}^i \theta_{\alpha\beta}^i \mu_{\beta}^i + k_3 \theta_{\alpha\beta}^i \theta_{\alpha\beta}^i + k_4 |\vec{\mu}^i \cdot \vec{\mu}^i|^2 \right), \quad (6)
\end{aligned}$$

where $k_1 = \frac{1}{2\alpha}$, $k_2 = \frac{B}{4\alpha^2 C}$, $k_3 = \frac{1}{6C}$, $k_4 = \frac{-B^2}{16\alpha^4 C}$, α , B and C the dipole, dipole-dipole-quadrupole and quadrupole polarizabilities of the oxygen ion, respectively, and $T_{\alpha\beta\gamma\delta} = \nabla_{\alpha} \nabla_{\beta} \nabla_{\gamma} \nabla_{\delta} \dots \frac{1}{r_{ij}}$ are the multipole interaction tensors (Stone, 1996). The instantaneous values of these moments are obtained by minimization of this expression. The charge-dipole and charge-quadrupole cation-anion asymptotic functions include terms which account for penetration effects at short-range by using Tang-Toennies damping functions (Tang and Toennies, 1984) of the form,

$$g_D(r^{ij}) = c_D e^{-b_D r^{ij}} \sum_{k=0}^4 \frac{(b_D r^{ij})^k}{k!}, \quad (7)$$

$$g_Q(r^{ij}) = c_Q e^{-b_Q r^{ij}} \sum_{k=0}^6 \frac{(b_Q r^{ij})^k}{k!}, \quad (8)$$

with D and Q standing for dipolar and quadrupolar parts. While the parameters b_D and b_Q determine the range at which the overlap of the charge densities affects the induced multipoles, the parameters c_D and c_Q determine the strength of the ion response to this effect. Only oxygen ions are considered polarizable.

136 The set of AIM potentials used here was parameterized for the Ca-Mg-Al-Si-O
 137 system by reference to electronic structure calculations. The model was shown
 138 to be accurate and transferable in a wide range of pressures, temperatures and
 139 compositions (Jahn and Madden, 2007b). Here, the same set of interatomic
 140 potentials and the same AIM code is used.

141 Molecular dynamics (MD) simulations are performed using a cubic simula-
 142 tion box with 2016 ions (288 formula units). At each MD step, the energy
 143 of the 'electronic degrees of freedom' (ionic polarization and deformation) is
 144 minimized before the ions are moved. This effectively describes many-body
 145 interactions (for more details see Aguado *et al.* (2003)). To integrate New-
 146 ton's equation of motion for the ions the code uses the Leapfrog algorithm
 147 (Allen and Tildesley, 1987), and we choose a time step of 1 fs. The starting
 148 configuration was obtained from a disordered structure of an aluminate melt
 149 by replacing the respective cations, which was followed by a 200 ps equili-
 150 bration run at high temperature (3000 K). In the second half of this run, no
 151 measurable changes in the structural and dynamic properties of interest are
 152 observed and hence we concluded that equilibrium was achieved. At each pres-
 153 sure and temperature, additional equilibration runs of 50 ps are performed in
 154 the NPT ensemble using an isotropic barostat (Martyna *et al.*, 1994) coupled
 155 to a Nosé-Hoover thermostat (Nosé and Klein, 1983) with a relaxation time of
 156 6 ps. After equilibration, the barostat is switched off and production runs of
 157 150 ps length are started in the NVT ensemble. Trajectories, the stress tensor
 158 and other properties are recorded every 10 time steps, i.e. with time interval
 159 of 10 fs. We explore a pressure range from 0 to 24 GPa, with step of 4 GPa,
 160 and temperatures of 2390, 2600, 2800, 3000 and 3200 K.

161 3 Results and Discussion

162 3.1 Thermodynamics properties

163 In order to describe the thermodynamic properties of the Mg_2SiO_4 liquid we
 164 fit the results from the simulations with the thermal equation of state:

$$165 \quad P(V, T) = P_{iso}(V, T_{ref}) + P_{therm}(V, T), \quad (9)$$

166 where the isothermal equation of state $P_{iso}(V, T_{ref})$ is evaluated at $T_{ref} = 2800$
 167 K by a third order finite strain (Birch-Murnaghan) equation of state (Birch,
 168 1952):

$$169 \quad P_{iso}(V, T_{ref}) = 3K_0f(1 + 2f)^{5/2} \left[1 + \frac{3}{2}(K'_0 - 4) \right], \quad (10)$$

170 with the Eulerian finite strain

$$171 \quad f = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]. \quad (11)$$

172 V_0 , K_0 , and K'_0 are the volume, isothermal bulk modulus (K_T), and its pressure
 173 derivative at zero pressure, respectively. The third order finite strain equation
 174 of state is found to represent well the results from the simulations for all
 175 temperatures considered (Fig. 1). Equation-of-state parameters for T_{ref} are
 176 $V_0 = 55.0 \pm 0.3 \text{ cm}^3/\text{mol}$ (or $\rho_0 = 2.56 \text{ g/cm}^3$), $K_0 = 26 \pm 2 \text{ GPa}$, and
 177 $K'_0 = 5.8 \pm 0.5$.

178 We approximate the thermal pressure P_{therm} by the Mie-Grüneisen model:

$$179 \quad P_{therm} = \left(\frac{\partial P}{\partial T} \right)_V (T - T_{ref}). \quad (12)$$

180 Through Maxwell relations the prefactor $(\partial P/\partial T)$ is related to K_T , the ther-
 181 mal expansivity (α), the Grüneisen parameter (γ) and the isochoric heat ca-
 182 pacity (C_V):

$$183 \quad \left(\frac{\partial P}{\partial T} \right)_V = \alpha K_T = \frac{\gamma C_V}{V}. \quad (13)$$

184 We evaluate $\partial P/\partial T$ by fitting isothermal equations of state for all simulation
 185 temperatures to obtain K_T and compute the thermal expansion coefficient
 186 from the volume-temperature relation at constant pressure:

$$187 \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P. \quad (14)$$

188 Similar to solids (e.g. Chopelas, 1990) we find α to decrease rapidly with
 189 pressure. In our simulations it is, however, essentially independent on temper-
 190 ature for the range considered (Fig. 2). This is similar to results by Guillot
 191 and Sator (2007b) that find thermal expansivity constant for a wide range of
 192 melt compositions and a fairly large temperature range.

193 From considering the energetics (enthalpy H) of our simulations we are able
 194 to compute the isobaric heat capacity (C_P) of the liquid:

$$195 \quad C_P = \left(\frac{\partial H}{\partial T} \right)_P. \quad (15)$$

196 As for α we find C_P to be independent on T , and use C_P , α , K_T , and V to
 197 compute C_V :

$$198 \quad C_V = C_P - VT\alpha^2 K_T. \quad (16)$$

199 We find an isochoric heat capacity of $C_V = 3.75 \pm 0.1$ R. C_V is not only
 200 temperature- but also pressure-independent in our simulations, and we can
 201 readily invert eq. 13 for γ and find it is best described by a linear volume
 202 dependence (Fig. 3):

$$203 \quad \gamma = \gamma_{ref} + \gamma' (V - V_{0,ref}), \quad (17)$$

204 where we choose again $T = 2800$ K as the reference temperature. Fitting eq.
 205 17 we obtain $\gamma_0 = 0.50 \pm 0.05$ and $\gamma' = -0.016 \pm 0.003$ mol/cm³.

206 To compare our results with previous experimental (Stebbins *et al.*, 1984;
 207 Bottinga, 1985; Lange and Carmichael, 1987; Rivers and Carmichael, 1987;
 208 Lange, 1997; Tangemann *et al.*, 2001) and computational estimates (Guillot
 209 and Sator, 2007b; Lacks *et al.*, 2007; de Koker *et al.*, 2008) on thermodynamic
 210 data we have compiled a table with physical properties, combining different
 211 experiments where necessary to compute properties (Table 1).

212 We find our results to be consistent with the *ab-initio* computations (de Koker
 213 *et al.*, 2008), except for heat capacity C_V where we predict a value considerably
 214 smaller (3.75 R compared to 4.4 R in the *ab-initio* results). The simulations
 215 using classical potentials (Guillot and Sator, 2007b; Lacks *et al.*, 2007) un-
 216 fortunately do not report a full set of thermodynamic properties, but only
 217 isothermal equations-of-state (Table 1); in these calculations, however, the
 218 zero pressure volume is predicted larger, accompanied in part by a smaller
 219 bulk modulus.

220 The results for the thermal equation-of-state are consistent with experimen-
 221 tal data, although some of the compressional parameters (bulk modulus K_0
 222 and its pressure derivative K'_0 show large variations between different exper-
 223 iments. K_0 from Rivers and Carmichael (1987) is in good agreement with
 224 all computational results, while values from Lange and Carmichael (1987)
 225 and Bottinga (1985) are significantly more and less compressible, respectively.
 226 The one experimental value reported for $K'_0 = 3.8$ (Bottinga, 1985) is consid-
 227 erably smaller than all computational results, making the melt less compress-
 228 ible at higher pressure. The difference in bulk moduli is also reflected in the
 229 Grüneisen parameter γ where good agreement between computational results
 230 and experiments can only be obtained with the bulk modulus from Rivers and
 231 Carmichael (1987). For heat capacity our results are consistent with lower es-
 232 timates, but the majority of values based on the experimental literature are
 233 larger, in good agreement with the *ab-initio* results (de Koker *et al.*, 2008).

234 The increase of γ with pressure predicted here agrees with the recent *ab-*
235 *initio* results on Mg_2SiO_4 melt (de Koker *et al.*, 2008), although the increase
236 predicted here is somewhat smaller (Fig. 3). It also follows systematics of
237 other recent simulations on MgSiO_3 melt (Stixrude and Karki, 2005) and
238 MgO (Karki *et al.*, 2006). Such behavior is in contrast to solids where the
239 Grüneisen parameter generally decreases with increasing pressure (Karki *et*
240 *al.*, 2000), and only structural changes can lead to an increase of γ , e.g. for
241 the α to β transition in Mg_2SiO_4 (Stixrude and Lithgow-Bertelloni, 2007).
242 Shock wave experiments on Mg_2SiO_4 (Mosenfelder *et al.*, 2007) also infer a
243 strong increase of γ for the melt with pressure and obtain $\gamma \sim 2.6$ at pressures
244 between 150-200 GPa.

245 A significant increase of γ has considerable bearings on the thermal state of a
246 magma ocean as it would result in a much steeper adiabat in the magma ocean
247 (Mosenfelder *et al.*, 2007) than conventionally thought (Miller *et al.*, 1991).
248 As Mosenfelder *et al.* (2007) demonstrate this could lead to a crystallization
249 of the magma ocean beginning near the surface or at depths of the transition
250 zone.

251 3.2 Structural properties

252 Structural changes in the liquid are likely to be the underlying cause for the
253 increase in γ discussed above and therefore we explore the structure of the
254 liquid as a function of pressure from our simulations. From particle positions
255 we compute the partial radial distribution functions $g_{ij}(r)$ ($i, j \in [\text{Mg}, \text{Si}, \text{O}]$).
256 Oscillations in $g_{\text{SiO}}(r)$ only extend to the next nearest neighbor distance (~ 4.2
257 Å) (Fig. 4) showing the SiO_4 structural unit behave rather rigidly. This holds
258 not only for low pressures, but persists to 24 GPa; up to this pressure $\sim 80\%$ of
259 the Si is in four-fold coordination (see discussion below). $g_{\text{MgO}}(r)$ and $g_{\text{OO}}(r)$
260 show fluctuations well beyond that range, indicating an ionic-like character
261 of the liquid (Fig. 4). While the nearest neighbor cation-oxygen distances are
262 almost unaffected by pressure, the oxygen-oxygen and second neighbor cation-
263 oxygen distances are considerably shifted to lower r with increasing pressure.

264 Cation coordination numbers are obtained by counting the number of oxygens
265 within the first coordination shell. The cutoff distance is defined by the first
266 minimum in the respective $g_{ij}(r)$. We find only a modest increase in Si-O
267 coordination, with an average coordination increase from 4.0 at 0 GPa to 4.2
268 at 24 GPa (Fig. 6). This stems from the fact that in our simulations $\sim 80\%$
269 of the Si remain four-fold coordinated while the rest of the Si are five-fold
270 coordinated. Even at 24 GPa there is only a negligible amount of the Si in
271 six-fold coordination. This is in contrast to the *ab-initio* results (de Koker *et*
272 *al.*, 2008) that show a stronger increase in coordination (and connectivity).

273 The rigid ion molecular dynamics (Guillot and Sator, 2007b) also predicts a
274 rapid increase with pressure, capturing structural changes in the melt well.

275 Coordination for Mg increases considerably with pressure, and here our results
276 agree with those of the *ab-initio* computations (de Koker *et al.*, 2008) and the
277 rigid ion model (Guillot and Sator, 2007b) (Fig. 6).

278 Apparently, the atomic structure of the melt depends in a sensitive way on
279 the details of the interaction model. The high stability of the SiO₄ suggests
280 that the Si-O interaction in the AIM potential may be slightly too strong.

281 In the pressure range considered, compression in the melt structure is taken
282 up mostly by rearrangements of the second neighbor Si-O and O-O distances
283 which is also represented by a rearrangement in the Si-O-Si bond angle (Fig. 5).
284 Under compression the Si-O-Si angle distribution is shifted to smaller angles,
285 allowing for a more dense packing of the SiO₄ tetrahedra.

286 In experiments the radial distribution function can not be obtained directly,
287 but its Fourier transform is accessible in diffraction experiments where the
288 total X-ray ($S^{X-ray}(q)$) or neutron structure factors ($S^{neu}(q)$) are measured.
289 For a multicomponent system, the total structure factor is a weighted sum of
290 partial structure factors, which represent structural correlations between the
291 different components.

292 Since X-ray scattering gives almost equal weight to all three different species
293 (O²⁻, Mg²⁺ and Si⁴⁺ are isoelectronic), and neutrons are particularly sensitive
294 to the positions of the oxygen ions, these two techniques give complementary
295 structural information. The X-ray weighted structure factor, $S^{X-ray}(q)$, is de-
296 termined from partial structure factors $S_{\alpha\beta}(q)$ by weighting them with X-ray
297 form factors,

$$298 \quad S^{X-ray}(q) = \frac{1}{\sum_{\alpha} N_{\alpha} f_{\alpha}^2(q)} \sum_{\alpha\beta} \sqrt{N_{\alpha} N_{\beta}} f_{\alpha}(q) f_{\beta}(q) S_{\alpha\beta}(q), \quad (18)$$

299 with $\alpha, \beta \in [Mg, Si, O]$ and $N_{\alpha, \beta}$ being the total number of ions of type α and
300 β , respectively. The form factors $f_{\alpha}(q)$ depend on the magnitude of the wave-
301 vector q . Note that the $f_{\alpha}(q)$ are taken from the literature (Cromer and Waber,
302 1974). Similarly, the neutron weighted structure factor, $S^{neu}(q)$, is determined
303 by weighting them with the experimental coherent neutron scattering lengths
304 $b_{\alpha}(\alpha \in [Mg, Si, O])$ (Sears, 1992):

$$305 \quad S^{neu}(q) = \frac{1}{\sum_{\alpha} N_{\alpha} b_{\alpha}^2} \sum_{\alpha\beta} \sqrt{N_{\alpha} N_{\beta}} b_{\alpha} b_{\beta} S_{\alpha\beta}(q). \quad (19)$$

306 Hence, the partial structure factors are needed to interpret diffraction data

of complex melts but they are very difficult to obtain experimentally. However, the $S_{\alpha\beta}(q)$ are readily available from molecular dynamics simulations. At ambient pressure both $S^{X-ray}(q)$ and $S^{neu}(q)$ of Mg_2SiO_4 melt show few distinct features (Fig. 7). In $S^{X-ray}(q)$ two peaks at $q \sim 2.3 \text{ \AA}^{-1}$ (A) and $q \sim 4.5 \text{ \AA}^{-1}$ (C) can be identified. Contributions to (A) and (C) are from Mg-Mg and Mg-Si interactions primarily, with negative (canceling) contributions from Mg-O. In $S^{neu}(q)$ only (C) is clearly identifiable. At higher pressure the peaks sharpen, and an additional peak (B) becomes visible in $S^{X-ray}(q)$. This peak has significant contributions from O-O and Mg-O pairs, and is located in between the peaks of these two partial structure factors. At low pressure the broad O-O peak makes (B) invisible. Due to the smaller amplitude of the Mg-Mg and Mg-Si pairs in $S^{neu}(q)$, with the negative contribution from Mg-O essentially the same (A) can not be observed in $S^{neu}(q)$. The q position of the peak (A) at 0 GPa ($\sim 2.3 \text{ \AA}^{-1}$) is in good agreement with the experimental data of Kohara *et al.* (2004) on the structure of Mg_2SiO_4 glasses ($\sim 2.2 \text{ \AA}^{-1}$).

The first Si-O peak at 0 GPa ($\sim 1.6 \text{ \AA}^{-1}$), only visible in the partial structure factor is comparable to the position of the Si-O peak in vitreous silica and other nonorthosilicate glasses and melts ($< 1.8 \text{ \AA}^{-1}$) (Waseda, 1980; Kohara and Suzuya, 2003).

Changes in the shapes of both $S^{X-ray}(q)$ and $S^{neu}(q)$ with pressure are significant: amplitudes of (A), (B) and (C) increase and shift to higher q .

3.3 Transport properties

Due to the long run durations and large system size we can reliably compute the diffusion coefficient D of the individual atomic species from the molecular dynamics runs via the Einstein relation (Allen and Tildesley, 1987):

$$D_\alpha = \lim_{t \rightarrow \infty} \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \frac{\langle (\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0))^2 \rangle}{6t}, \quad (20)$$

where $\mathbf{r}_i$ is the position of i^{th} ion of species α at time t after origin time t_0 , and ensemble averages of the mean square displacements are taken for a specific species with a total number of ions N_α . As in the case for solid Mg_2SiO_4 (Andersson *et al.*, 1989) we find that the network modifying ion (Mg) diffuses much faster than the network forming cation (Si): $D_{Mg} \gg D_O \gg D_{Si}$ (Fig. 8).

We analyze our time series of mean square displacement in terms of uncertainty and found a standard deviation that is smaller than the symbol size in Fig. 8.

341 The diffusion coefficients decrease with pressure following an Arrhenius law
 342 (Fig. 8), and unlike for more polymerized melts (Karki *et al.*, 2007) there is no
 343 initial increase in D . Diffusivities computed from *ab-initio* by de Koker *et al.*
 344 (2008) and the potential model by Lacks *et al.* (2007) report diffusivities larger
 345 by ~ 0.5 log units, and there is good agreement between the potential model
 346 and the *ab-initio* results. The *ab-initio* results show a much larger uncertainty
 347 in the diffusion constants, due to the smaller simulation cell. Experimental
 348 data on melt diffusivities are not available at the present time.

349 We compute the shear viscosity η from the Green-Kubo relation (Allen and
 350 Tildesley, 1987) which involves integration over time of the autocorrelation
 351 function for the off-diagonal components of the stress tensor:

$$352 \quad \eta = \frac{V}{k_B T} \int_0^\infty dt \langle \sigma_{ij}(t + t_0) \sigma_{ij}(t_0) \rangle. \quad (21)$$

353 Here $\langle - \rangle$ denotes the thermal average, k_B is the Boltzmann constant, and σ_{ij}
 354 ($i \neq j$) are the off-diagonal components of the stress tensor σ_{ij} . The three
 355 components of the stress tensor are averaged to obtain η . Uncertainties in η
 356 are estimated from fluctuations in the stress tensor.

357 The computed viscosity of Mg_2SiO_4 liquid at 2800 K at zero pressure is con-
 358 sistent with experimental data at ambient pressure (Urbain *et al.*, 1982) ex-
 359 trapolated to 2800 K (Fig. 9).

360 Within the standard deviations we can fit the pressure dependence of viscosity
 361 with an exponential function, increasing with pressure. In the rigid ion model
 362 (Lacks *et al.*, 2007) the viscosity is computed considerably smaller, consistent
 363 with their larger values for D .

364 This is in contrast to experimental estimates on melt viscosity for depolymer-
 365 ized melts, where for both diopside (Reid *et al.*, 2003) and peridotite (Liebske
 366 *et al.*, 2005) viscosity initially increase with pressure, then decrease. In Liebske
 367 *et al.* (2005) the initial increase was attributed to a redistribution of intertetra-
 368 hedral angle, while the subsequent decrease was interpreted as an increase in
 369 coordination of network-forming cations. However, here we do not find any in-
 370 dication of sudden changes in coordination, but a continuous change, as many
 371 other computational studies (Stixrude and Karki, 2005; Karki *et al.*, 2006;
 372 Guillot and Sator, 2007b; Karki *et al.*, 2007; de Koker *et al.*, 2008) although
 373 to a smaller extent (Fig. 6).

374 In order to elucidate the experimentally observed anomaly by computations
 375 careful studies will be necessary, with a dense simulation grid in pressure and
 376 temperature, in order to pinpoint an anomaly closely. Also, the fluctuations
 377 in the stress tensor will need to be decreased considerably in order to improve

the uncertainty in viscosity. From our simulations we find that longer run durations will do little to decrease the standard deviation, simulations on yet larger cells may be necessary.

4 Conclusions

Here we perform molecular dynamics simulations on Mg_2SiO_4 melt on a dense pressure - temperature grid over a wide pressure (0-24 GPa) and temperature (2390 - 3200 K) range, using a flexible potential model that has been successfully applied for high pressure and temperature properties of solids in the CMAS system and in oxide melts. We find that over the pressure range considered structural changes in the Mg_2SiO_4 melt are continuous, with only a slight increase in coordination of Si, and considerable coordination change in Mg. The observed change in Si coordination is smaller than in *ab-initio* (de Koker *et al.*, 2008) and rigid ion (Guillot and Sator, 2007b) simulations, hinting at a Si-O bond that is too strong in our potential model. Structural changes predicted by the present model should be observable in X-ray and neutron experiments as significant changes in the respective static structure factors occur, mostly driven by changing Mg coordination and interactions in the melt.

Contrary to solids under pressure we find thermal pressure and the Grüneisen parameter to increase with compression, consistent with recent shock wave experiments (Mosenfelder *et al.*, 2007) and simulations in Mg_2SiO_4 (de Koker *et al.*, 2008) and other depolymerized silicate (and oxide) melts (Stixrude and Karki, 2005; Karki *et al.*, 2006, 2007).

Large simulation cells and long run durations allow us to analyze the simulations in terms of transport properties of the melt, diffusivity and viscosity and estimate uncertainties on these properties from the simulations. We find that Mg is the fastest diffusing species over the whole compression range, but the difference between O- and Mg-diffusivity decreases considerably at high pressure. Diffusivities obtained are somewhat smaller than those of other recent *ab-initio* (de Koker *et al.*, 2008) and potential (Lacks *et al.*, 2007) simulations. The diffusivities computed can be fit readily with an Arrhenius law. For viscosity we find good agreement between the value computed from the Kubo-Green relations in the simulations and experiments at room pressure. Viscosity increases as a function of pressure.

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Table 1

Thermodynamic parameters for Mg_2SiO_4 melt at 0 GPa and 2390 K, comparing our fit to experimental data, extrapolated to 2390 K. Experimental data at other temperatures are included for comparison and the temperature are included. Equation of state parameters are also included for recent *ab-initio* and rigid ion molecular dynamics.

Property	AIM (2390 K, 0 GPa)	Experiment	Simulations Olivine ^{*,g} Mg_2SiO_4 ^h	<i>ab initio</i> ⁱ
V_0 (cm^3/mol)	53.5 ± 0.2	54.9 ± 0.2 ^a 53.6 ± 0.3 ^b	56.3 ^g (2273 K) 58.1 ^h (3000 K)	53.55 (2163 K)
K_0 (GPa)	27 ± 3	11 ^b 59 ^c (2494 K) 20 ± 1 ^e	18 ^g (2273 K) 16 ^h (3000 K)	23 ± 8 (2163 K)
K'_0	6.3 ± 0.5	3.8 ^c (2494 K)	7.2 ^g (2273 K) 6.4 ^h (3000 K)	7 ± 1 (2163 K)
α (10^{-6} K^{-1})	74 ± 15	119 ± 7 ^a 82 ^c (2163 K)		121 ± 50 (2163 K)
C_V (R)	3.75 ± 0.1	4.5 ± 0.4 ^{a,b,d} 3.5 ^{a,b,f} 4.2 ± 0.2 ^{a,d,e}		4.4 ± 0.5 (2163 K)
γ	0.50 ± 0.08	0.27 ± 0.05 ^{a,b,d} 0.34 ± 0.03 ^{a,b,f} 0.52 ± 0.08 ^{a,d,e}		0.6 ± 0.1 (2163 K)

* composition close to Fo90

^a Lange, 1997

^b Lange and Carmichael, 1987

^c Bottinga, 1985

^d Stebbins *et al.*, 1984

^e Rivers and Carmichael, 1987

^f Tangemann *et al.*, 2001

^g Guillot and Sator, 2007b

^h Lacks *et al.*, 2007

ⁱ de Koker *et al.*, 2008

Fig. 1

Fig. 1. (color online) Pressure-volume equation of state for Mg_2SiO_4 liquid. Results from the molecular dynamics simulations (open symbols) and third-order Birch–Murnaghan equation of state fits (lines) at 3200 K (purple, triangles), 2800 K (green, squares), and 2390 K (black, circles) are shown. For comparison *ab-initio* (de Koker *et al.*, 2008) (red, crosses) and rigid ion simulation results (Lacks *et al.*, 2007) at 3000 K are included (blue, stars).

Fig. 2

Fig. 2. Thermal expansion (α) as a function of pressure for Mg_2SiO_4 liquid. α is found independent on temperature.

Fig. 3

Fig. 3. Grüneisen parameter γ as a function of volume for Mg_2SiO_4 liquid. Values for different temperature simulations are shown by the symbols, and a linear fit to the results is included. For comparison γ from recent *ab-initio* results (de Koker *et al.*, 2008) are included.

Fig. 4

Fig. 4. (color online) Radial distribution functions of Si-O (black), Mg-O (blue) and O-O (red) at 0 GPa (solid lines) and 24 GPa (dashed lines) at 2800 K.

Fig. 5. (color online) Bond-angle distribution of Si-O-Si bonds at 0 GPa (solid black line) and 24 GPa (dashed red line) at 2800 K. Vertical lines show the maximum in the distribution function.

Fig. 6

Fig. 6. (color online) Average Si (a) and Mg (b) coordination numbers of Mg_2SiO_4 . Closed circles present our results at 2800 K. For comparison we have included simulation results from *ab-initio* (de Koker *et al.*, 2008) at 3000 K (black squares) and rigid ion simulations (Guillot and Sator, 2007b) on peridotite liquid at 2273 K (blue line).

Fig. 7

Fig. 7. (color online) Neutron (a) and X-ray (b) weighted total structure factors of Mg_2SiO_4 liquid at 2800 K and four different pressures. Contribution of partial structure factors to the neutron (c) and X-ray (d) total structure factor at 8 GPa.

Fig. 8

Fig. 8. (color online) Diffusivity of the atomic species in Mg_2SiO_4 melt as a function of pressure. The upper panel shows the diffusivity for Mg, the middle panel for Si and the lower panel for O. Open red triangles present our results at 2800 K. Filled blue circles are from the rigid ion simulations Lacks *et al.* (2007) and open diamonds from the *ab-initio* molecular dynamics by de Koker *et al.* (2008), both at 3000 K.

Fig. 9

Fig. 9. (color online) Viscosity of Mg_2SiO_4 melt as a function of pressure. Open red diamonds show our results at 2800 K, including an estimate of uncertainty.. Filled blue circles are from the rigid ion simulations of Lacks *et al.* (2007) at 3000 K. The star shows the experimental viscosity of Urbain *et al.* (1982) at 0 GPa, extrapolated to 2800 K.