Thermal conductivity of molten and glassy NaAlSi$_3$O$_8$, CaMgSi$_2$O$_6$ and Mg$_2$SiO$_4$ by Non Equilibrium Molecular Dynamics at elevated Temperature and Pressure: Part 1 - Methods and Results

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Abstract

Non Equilibrium Molecular Dynamics simulations are used to compute the phonon thermal conductivity (k) for liquids and glasses of composition Mg$ _2 $SiO$ _4 $, CaMgSi$ _2 $O$ _6 $ and NaAlSi$ _3 $O$ _8 $ at 2000-4500 K and 0-30 GPa based on classical potentials. These compositions span the range of melt polymerization states in natural systems at ambient pressure based on the local coordination environment of oxygen with Si and Al. The NEMD results compare well with available laboratory measurements on molten NaAlSi$ _3 $O$ _8 $ and CaMgSi$ _2 $O$ _6 $ at 1-bar. Thermal conductivities decrease with increasing temperature, increase with increasing pressure and, at low pressure, increase slightly as the mean coordination number of Si and Al around oxygen increases, in the sequence MgSi$ _2 $O$ _4 $, CaMgSi$ _2 $O$ _6 $ and NaAlSi$ _3 $O$ _8 $. At 3500 K, the thermal conductivity of CaMgSi$ _2 $O$ _6 $ at 0, 10, 20 and 30 GPa is 1.1, 2.1, 2.5 and 3 W/m K, respectively. At ambient pressure (0.2 ± 0.15 GPa), k=1.2 and 0.5 W/m K at 2500 K and 4500 K, respectively for CaMgSi$ _2 $O$ _6 $. For NaAlSi$ _3 $O$ _8 $ composition, k varies from 1.7 W/m K to 2.7 W/m K at 3050 K for pressures of 6 and 30 GPa, respectively. Mg$ _2 $SiO$ _4 $ liquid at ambient pressure (0.07 ± 0.16 GPa ) is found to have thermal conductivities of 1.36 and 0.7 W/m K at 2500 K and 4500 K, respectively. Tables giving computed k values for all composition are included at all state points studied. The trade-off between T and P implies that the phonon thermal conductivity of silicate liquids at mantle depths increases substantially (factor of 2-3) along isentropes. In part II, these observations are used to constrain theoretical models and correlations between the thermal conductivity and melt properties including Grüneisen’s parameter and the isothermal compressibility.
INTRODUCTION

This is a two part series investigating the thermal conductivity (k) of molten and glassy silicates spanning the range of compositions and structural states relevant to molten silicates in the Earth, specifically the geoliquids Mg$_2$SiO$_4$, CaMgSi$_2$O$_6$ and NaAlSi$_3$O$_8$. In part I, details of the Non Equilibrium Molecular Dynamics (NEMD) method and results are presented for k in the temperature (T) and pressure (P) range ~2500-4500 K and 0-30 GPa, respectively, based on the classical effective pair potential of Matsui (1998). The comparison demonstrates that the NEMD method faithfully captures laboratory results and gives k- dependencies with temperature, pressure and structural state that are quantitative and reasonable. In part II, the NEMD results are used to test theories of thermal conductivity of glassy and molten silicates of geochemical importance, to relate phonon conductivity to melt structure at the atomic level and to provide correlations between thermodynamic melt properties and thermal conductivity. A tentative means of computing the thermal conductivity of multi-component silicate melts based on correlations with Equation of State (EOS) parameters is also suggested.

Knowledge of the phonon thermal conductivity of amorphous silicates (melts and glasses) over the range of compositions (X), P and T of the Earth’s crust and mantle is essential for analysis of geophysical and geochemical heat transfer problems. For example, heat transfer during nucleation and dissolution or growth of a crystal from a melt and between a magma body and surrounding crust is relevant to rates of magma crystallization, mechanisms of volatile-saturation and the dynamics and thermodynamics of partial melting. The conductive heat loss across a magma-wallrock contact is relevant to rates of assimilation and the generation of contact metamorphic rocks. Heat transport
from the Earth’s core to mantle, possibly modulated by a transient molten or partially molten ultra-low velocity zone (ULVZ), is relevant to the long-term thermal history of Earth and the thickness of thermal boundary layers along the core-mantle boundary and the strength and evolution of the earth’s magnetic field (Wen and Helmberger, 1998; Hernlund and Jellinek, 2010; Idehara, 2011; Anzellini et al, 2013; Olsen, 2013). Accurate values of the thermal diffusivity, $\kappa = k/\rho C_p$, where $\rho$ is the density and $C_p$ is the isobaric heat capacity, are needed to calculate transient geotherms and predict conditions for crustal anatexis and metamorphism in orogenic regions at non steady state conditions (e.g., Whittington et al., 2009). Finally, in ceramic and composite materials processing, knowledge of thermal conductivity is required (Kang and Morita, 2006). A better knowledge base for the thermal conductivity of molten and glassy silicates at elevated temperature and pressure is applicable to many problems and is clearly desirable. In this study, attention is mainly focused upon equilibrium (ergodic) liquids although a few calculations apply to nonequilibrium (non-ergodic) glass. The term amorphous is used here to refer to either glass or liquid when the distinction is not essential.

There are few reliable measurements of the thermal conductivity of molten silicates of any composition and fewer still of geosilicate liquids as a function of $X$ and $T$ at ambient $P$. We are aware of no experimental measurements describing the effect of pressure on $k$ for silicate liquids. Although there are measurements and theory related to the effects of $P$ on $k$ in crystalline silicates and oxides, liquids are structurally distinct with essentially no long range structure beyond $\sim 0.5$ nm (Kittel, 1949). Hence, one might expect some differences in modes of phonon excitation in liquids relative to ordered solids because, unlike solids, liquids undergo gradual changes in atomic structure.
as P increases. One of the goals of this study is to provide quantitative constraints on the P-dependence of the thermal conductivity of silicate liquids at elevated T. Very limited experimental data at 1-bar on molten silicates of varying atomic-level structure suggest that at fixed T and P, the more polymerized the melt (i.e., the lower the NBO/T ratio or the less fragile the liquid), the higher the thermal conductivity. A second goal of this work is to address this issue and (in part II) to explain the underlying melt structural basis that leads to this behavior. For crystalline solids, at constant P, k varies according to 1/T (Stackhouse and Stixrude, 2010). The validity of this scaling has not been studied for molten silicates in the T range 2000-5000 K applicable to most of Earth’s interior. The high-T scaling of k at fixed P is therefore also investigated here. In short, current knowledge of the thermal conductivity of geosilicate liquids is meager. In this study, we study of the effects of P, T and melt composition on the phonon thermal conductivity.

Obtaining accurate values for the phonon thermal conductivity proves difficult in the laboratory (e.g., Tritt and Weston, 2004). Many laboratory measurements are of limited value because: (1) they are contaminated by unwanted radiative (photon) heat transport, (2) include unwanted interfacial contact effects (hot-wire and hot-strip methods) or (3) are affected by convective heat transport. For example, measurements reported by Mc Birney and Murase (1973) on some natural glasses and geoliquids using the hot-wire method are dominated at temperatures above ~ 800-900 °C by radiative (photon) heat transport. Because the radiative component is so large it is impossible to reliably remove it to reveal the smaller phonon contribution. In hot-wire and hot-layer methods, thermal losses at contacts as well as radiative effects in transparent liquids introduce significant errors that are difficult to eliminate without additional assumptions.
and complex deconvolution of experimental data (Healy et al, 1976; Lee and Hasselman, 1985, Hammerschmidt and Sabuga, 2000). Hofmeister and co-workers (Pertermann and Hofmeister, 2006; Hofmeister, 2007; Hofmeister et al, 2009; Pertermann et al, 2008) give an account of these issues and present measurements of thermal conductivity at ambient pressure for a number of compounds. In particular, they note that recent advances in contact-free, laser-flash analysis using coatings and better mathematical treatments for data reduction (Degiovanni et al., 1994; Mehling et al., 1998) enable removal of direct radiative transfer effects and losses to the container and provide accurate phonon conductivities at ambient P and temperatures just above 1-bar melting points. Although these measurements by laser flash analysis on molten and glassy geosilicates eliminate undesired effects and exhibit excellent reproducibility, this technique is currently limited to 1-bar (10^4 GPa) pressure. It is clearly desirable to have a method for amorphous (glass and liquid) silicates that does not suffer from experimental issues that can be applied to systems of variable composition at elevated temperature and pressure for geological applications. Although high quality phonon conductivity data indicates that k decreases weakly with increasing T in the range ~1300-1600 K for silicate liquids, the behavior at higher temperature has not been studied and there are no data on the effects of pressure. A temperature range of only several hundred kelvins may not be large enough to reliably determine the T effect. Data on non-silicate liquids at high pressure (e.g., alkali halides and liquid metals) suggests the conductivity increases with pressure along an isotherm but the magnitude of this effect has not been thoroughly explored (e.g., Beck et al, 2007; Galamba et al, 2004; de Koker et al, 2012). Consequently, the trade-off between variations in T and P is unknown for liquid silicates. Finally, there is the issue of the
composition dependence of $k$. Although studies on CaO-Al$_2$O$_3$-SiO$_2$ liquids (Kang and Morita, 2006), as well as molten diopside and molten albite (Hofmeister et al., 2009) suggest that that polymerized or strong ‘network’ liquids exhibit higher $k$ at similar T and P compared to less polymerized ‘fragile’ liquids (Martinez and Angell, 2001), this compositional effect is not well quantified. Because differences in melt fragility correlate strongly with changes in second order thermodynamic properties at the glass transition (e.g., isothermal expansivity, isothermal compressibility, isobaric heat capacity), one might expect a correlation at fixed T and P between melt composition and phonon conductivity such that more fragile melts offer the greatest resistance to phonon propagation and hence exhibit lower conductivities compared to the network (strong) melts. This conjecture is tested by MD simulation in this study using liquid structural states, as encapsulated in radial distribution analysis and coordination statistics (e.g., Ghiorso and Spera, 2009; Spera et al, 2009). The compositions chosen in this study span the spectrum of polymerization and fragility states relevant to natural magmas. That is, in forsterite liquid the canonical fraction of bridging oxygen at low pressure, $X_{BO}$ ($=N_{BO}/(N_{BO}+N_{NBO})$, approaches zero whereas albite liquid is fully polymerized with each oxygen being shared between two distinct Si-Al tetrahedra (i.e., $X_{BO}=1$). Similarly, whereas the shear viscosity of liquid albite is quite Arrhenian over a broad temperature range (i.e., a classic ‘strong’ liquid), molten CaMgSi$_2$O$_6$ is distinctly non-Arrhenian, a classic high fragility liquid behavior. One of the most significant connections between structure and properties observed in all liquid silicates as shown in spectroscopic, X-ray and Molecular Dynamics studies is the increasing coordination of cations around oxygen (and of oxygen with itself) as pressure increases. This effect dominates a smaller but
opposing temperature effect of lengthening bond distances. As shown below, the higher mean coordination number of metals around oxygen gives rise to an increase in the thermal conductivity as pressure increases along an isotherm for all of the compositions studied here. Hence along a mantle adiabat, the thermal conductivity of a melt is expected to increase with depth. At crustal pressures ~ 0-2 GPa, composition effects will dominate. An important result of this study explored more fully in part II is that at the same T and crustal P, the thermal conductivity of silicic melt (e. g., a rhyolite) is larger by 25-100 % compared to basaltic melt.

The remainder of this paper is organized as follows. In the next section the MD technique and details of the NEMD formulation are described and illustrated for CaMgSi₂O₆ at a state point for which laboratory data from Hofmeister et al. (2009) are available for comparison. This is followed by presentation of results for liquids (and glass, when applicable) of forsteritic, diopsidic and albite composition at elevated T and P. The NEMD-derived values are then summarized in terms of T, X and P dependencies. The quantitative connection between melt structure, thermodynamic properties and phonon conductivity is explored in part II of this series.

METHODS

Classical Molecular Dynamics

The calculations presented in this study are based on classical Molecular Dynamics (MD) simulations. In classical MD, an empirical potential describing the energy between atom pairs is used to compute forces between atoms. This pairwise additive, radially symmetric potential is derived a priori and is not part of the MD simulation. Based on these forces, thousands of particles are moved to new positions
following the dictates of Newton’s second law of motion for several million femtosecond
($10^{15}$ s) time steps. From the locations and velocities of the particles, various
thermodynamic and transport properties are computed using the formalism of
macroscopic thermodynamics and statistical mechanics. The potential of Matsui (1998)
for the system Na$_2$O-CaO-MgO-SiO$_2$-Al$_2$O$_3$ was utilized in this study. This potential
incorporates Coulombic, Born and van der Waals energies and fractional charges on the
atoms. The Matsui potential has been used in previous studies to determine the equations
of state, tracer diffusivities and shear viscosities for liquid CaAl$_2$Si$_2$O$_8$, CaMgSi$_2$O$_6$,
MgSiO$_3$, Mg$_2$SiO$_4$, and melt of 1-bar eutectic composition in the system CaMgSi$_2$O$_6$-
CaAl$_2$Si$_2$O$_8$ (Creamer, 2013; Martin et al., 2012; Spera et al., 2011; Ghiroso and Spera,
2009; Spera et al., 2009; Nevins et al., 2009; Martin et al., 2009). The Matsui potential
provides a reasonable representation of these liquids up to circa 30 GPa based on
comparisons with laboratory data and results from first-principles MD simulations on
similar compositions (e.g., Sun et al, 2011; Karki et al, 2011; Stixrude et al, 2009).
Technical details of the basic MD methodology are described in Spera et al. (2009, 2011)
and follow standard MD protocols. The time step used in all simulations is 1 femtosecond
(1 fs). All NEMD calculations for the thermal conductivity start from a thermally
equilibrated initial state following the methods described in Spera et al. (2011).

Distinguishing Equilibrium Liquid from Non-equilibrium Glass

The pressure-temperature range of state points studied for both NaAlSi$_3$O$_8$ and
CaMgSi$_2$O$_6$ spans the transition from an equilibrium liquid to a non-equilibrium glass on
the timescale of the MD simulation. The simulations for Mg$_2$SiO$_4$ composition pertain
wholly to the liquid. It is important to make the distinction between glass and liquid (melt) because the properties of a glass depend on its thermal production history unlike that of an equilibrium or metastable liquid. Glass is a prime example of a nonequilibrium phase. When temperature is decreased rapidly on a sample and the relaxation time of the melt exceeds the laboratory experiment or simulation cooling timescale, the liquid falls out of equilibrium and undergoes a glass transition. The glass transition temperature \( T_g \) depends on the quench rate and pressure (Passaglia and Martin, 1964) for fixed composition. The glass transition is not a transition in the thermodynamic sense, but instead a kinetic phenomenon, where the amorphous solid is dynamically arrested. Glass is a non-equilibrium substance with properties that depend on the cooling and/or compression rate used in its preparation. At typical laboratory cooling rates of \( \sim 0.1-1 \) K/s, the \( T_g \) for albite and diopside liquids are 1036 K and 1023 K, respectively, at 1-bar (Arndt and Häberle, 1973, Reinsch et al, 2008). Because the effective quench rates used in MD simulations are vastly higher, of order \( \sim 10^2 \) K/ps \( (10^{14} \) K/s), the computer glass transition temperature is higher than the laboratory \( T_g \). For example, the computer \( T_g \) of CaAl\(_2\)Si\(_2\)O\(_8\) quenched from an ergodic liquid at 70-200 K/ps is \( \approx 2800 \) K (Morgan and Spera, 2000) which can be contrasted to the laboratory value of \( T_g = 1025 \) K (Arndt and Häberle, 1973). Vollmayr et al (1996) have shown that the computer \( T_g \) for silica varies between 2900 K and 3300 K for quench rates between 10 and 100 K/ps with the higher value of \( T_g \) at the faster cooling rate as expected. For comparison, the laboratory glass transition temperature of silica at 1-bar is 1483 K, 1535 K and 1543 K at laboratory cooling rates of 10 K/min, 40 K/min and 80 K/min, respectively, illustrating the effect of quench rate on \( T_g \) from laboratory studies (Brüning et al, 2005).
The transition from liquid to glass can be detected in MD simulations by several means. It has been noted previously that for ergodic dense liquids an excellent correlation exists between the molar or specific potential energy ($E_{\text{POT}}$) and $T^{3/5}$ along an isochore (Spera et al, 2009; Ghiorso and Spera, 2009; Martin et al, 2012; Cremer, 2012). This scaling relationship first posited by Rosenfeld and Tarazona (1998) is called RT-scaling. Glasses do not exhibit RT scaling; on plots of $E_{\text{POT}}$ vs $T^{3/5}$ deviations from linearity along isochores occur around $T_g$ and become more marked as $T$ decreases. A second method for detection of the glass transition is dynamical and is based on the mobility of atoms (tracer diffusivity). In an ergodic liquid, the mean square displacement (MSD) of an atom is a linear function of time; a plot of MSD vs. $t$ in logarithmic coordinates exhibits a slope of unity after a short (< 100 fs) inertial interval (Morgan and Spera, 2000). In contrast, glassy materials exhibit the phenomena of sub-diffusion. In the non-ergodic region where sub-diffusion holds, the MSD exhibits power-law behavior with MSD ~ $t^\delta$ following the short ballistic (inertial) interval. The exponent $\delta$ in a thermally arrested liquid (i.e., a glass) is characterized by $\delta$ $<$ 1 (Metzler and Klafter, 2004; Weeks and Weitz, 2002). Sub-diffusion arises when a system possesses memory, the hallmark of a non-equilibrium material such as glass. For CaMgSi$_2$O$_6$, the computer glass transition in our simulations occurs at ~ 2630 ± 50 K at 1-bar. For albite composition, $T_g$ is approximately 2800 K. The glass transition temperature depends on pressure in addition to quench rate. Experiments show that the change of $T_g$ with pressure is generally positive and can be crudely estimated treating the glass transition as a second-order isentropic Ehrenfest phase transition by \( \left( \frac{\partial T}{\partial P} \right)_S = \frac{\Delta \alpha T}{\Delta \rho \Delta C_p} \) (Prigogine and Defay, 1954). The variation of the computer glass transitions with pressure for CaMgSi$_2$O$_6$ and NaAlSi$_3$O$_8$ found here
empirically lies in the range 10-30 K/GPa approximately in agreement with a second-order isentropic Ehrenfest phase transition using available or estimated thermodynamic data. In the Tables below for thermal conductivity, glasses are distinguished from liquids based on the RT scaling and the power-law dependence of the MSD. The emphasis in this study is on equilibrium ergodic liquids, although some glass results are included.

Non-Equilibrium Molecular Dynamics

Calculations of thermal conductivity from MD simulations can be performed in two ways: Equilibrium MD (EMD) or NEMD. The Green-Kubo method, an EMD approach, uses heat current fluctuations to compute the thermal conductivity via the fluctuation-dissipation theorem (Kubo, 1966). The microscopic definition of the heat flux for EMD involves interparticle dynamic correlations requiring evaluation of pair velocities and particle energies that are computationally expensive to evaluate and subject to large fluctuations (Rapaport, 1995). Convergence of the current-current correlation function can be slow. Here we employ a NEMD method, which is relatively easy to implement, and has proved to be reliable (e.g., Müller-Plathe, 1997; Müller-Plathe and Bordat, 2004). In particular, the NEMD method has been successfully applied to liquids giving excellent results in comparison with laboratory measurements (Cao, 2008; Bedrov et al., 2000; Terao et al., 2007) and Green-Kubo (EMD) calculations (Vogelsang et al., 1987).

The essential idea of NEMD is to impose a known heat flux on the system by exchange of particle kinetic energies and then determine the resulting steady-state temperature gradient in the direction parallel to the heat flux. The thermal conductivity can then be expressed
where the integral is the cumulative heat flow imposed during a simulation of duration $t_0$ in the $z$ direction, $A$ is the cross-sectional area of the plane orthogonal to the $z$-axis, and the temperature derivative is the observed linear temperature gradient once a stationary thermal profile is achieved in the system. In order to impose a heat flux and compute the temperature profile, the simulation box is divided into $N$ slabs perpendicular to the $z$ direction. In the present work $N$ usually lies between 20-50; all layers are of identical volume. The heat flux is created by exchanging the barycentric velocities of identical type atoms (e.g., O for O, Ca for Ca, etc) between what becomes a cold layer located in the middle of the simulation box and what becomes a hot layer adjacent to one of the domain boundaries. In particular, the velocity exchange is accomplished by switching an atom with the largest kinetic energy (i.e., the hottest) from the cold slab with an atom of the same type with the lowest kinetic energy (coldest) in the hot layer. Serial application of this procedure induces a temperature gradient for a known quantity of heat exchange based on the kinetic energies of the exchanged atoms. The instantaneous local kinetic temperature $<T_k>$ in the $k^{th}$ slab is given by

$$T_k = \frac{1}{3k_Bn_k} \sum_{i=1}^{n_k} m_i v_i^2$$

(2)

where the sum extends over all $n_k$ atoms of each type of mass $m_i$ and velocity $v_i$ in the $k^{th}$ slab. This exchange mechanism produces an energy transfer computed from

$$\left\langle \int_0^{t_0} q_z(t) \, dt \right\rangle = \sum_{\text{transfers}} \left( v_c^2 - v_h^2 \right)$$

(3)
The heat transfer leads to a temperature difference between the designated layers and
gives rise to a steady-state temperature gradient across each half of the system. This
temperature gradient is the desired quantity of the NEMD simulation. Exchanging the
velocities of two atoms of equal mass (e.g., an O for an O, a Ca for a Ca, etc) leaves the
total linear momentum, total kinetic energy, melt composition and the internal energy
unchanged. After reaching the thermal steady state, the energy transfer imposed by the
velocity exchange is exactly balanced by the heat flux in the opposite direction effected
by the phonon thermal conductivity of the liquid. The thermal conductivity is then
computed from the expression

\[
 k = \frac{\sum_{\text{transfers}} (v_c^2 - v_h^2)}{2t_D L_x L_y (dT/dz)}
\]  

The sum is taken over all transfers over the duration \( t_D \) of the NEMD simulation starting
from an equilibrated initial state. All quantities in Eq. (4) are known exactly except the
temperature gradient that is obtained from Eq. (2) applied to each layer based on the
NEMD simulation. The simulation is terminated after a linear or nearly linear
temperature gradient is established. Typically this requires simulations of 1-5 ns duration.

In this study, tetragonal periodic primary MD ‘boxes’ with \( L_z > L_x = L_y \), as well as cubic
boxes are used. When cubic boxes are used, uncertainty in \( k \) is smaller, because more
atoms are being simulated and uncertainty of state point conditions scales according to
\( N_T^{-1/2} \) where \( N_T \) is the total number of atoms used in the simulation. At each state point
studied, simulations are performed for several different simulation cell sizes to take
account of finite-size effects (see below). Because of the mirror plane at \( z = L_z/2 \), each
simulation provides \( 2N \) temperatures over distance \( L_z \). The thermal gradient is
determined by linear regression of these 2N values each at a specific value of z corresponding to the mid-point of the layer. The uncertainty of the thermal conductivity ($\sigma_k$) is found by propagation of error of the temperature gradient found by regression of T against z. The value of k computed from Eq (4) corresponds to the thermal conductivity at the mean temperature and pressure of the simulation. Typically, with systems of 8000 atoms the uncertainty in T and P are ± 30 K and ± 0.25 GPa, respectively. These uncertainties can be made smaller by using more particles since $\sigma_T$ and $\sigma_P$ scale according to $N^{-1/2}$. For example, with $N=24,000$ particles, 1σ fluctuations in T and P are $\sigma_T \approx 18$ K and $\sigma_P \approx 0.15$ GPa, respectively. In this study $N_T$ varied from 2500 to 350,000 and weighted regression has been used to find the best statistical fits.

Critical NEMD parameters

There are two critical parameters in an NEMD simulation used to compute k: the duration between particle swaps ($\Omega$) or its reciprocal, the swap frequency, and the longest dimension of the MD rectangular domain ($L_z$). Tuning of these parameters insures good precision in k and efficient use of computational resources. In order to find the trade-off in a computationally efficient manner, a number of simulations for molten diopside at ambient pressure and high T at various $\Omega$ and $L_z$ were conducted. Comparison with the laboratory measurements from Hofmeister et al. (2009) at identical (within uncertainty) state points for CaMgSi$_2$O$_6$ affords an objective evaluation of the quality of the NEMD simulations. Additional NEMD simulations were run on crystalline and supercritical argon, a benchmark material in MD studies, in an earlier phase of this research; these results are presented elsewhere (Tikunoff, 2013).
Role of swap period ($\Omega$)

$\Omega$ is the period, in units of femtoseconds (fs), between particle velocity swaps during the NEMD calculation. The calculated conductivity of amorphous CaMgSi$_2$O$_6$ at ambient pressure ($10^{-4}$ GPa) and 1700 K in a box of fixed $L_z$ with its one-sigma error ($\sigma_k$) is plotted against $\Omega$ in Figure 1.1. For the limiting value of $\Omega = 1$ (not shown on Figure 1), or one swap per 1 fs time step, the system does not have sufficient time between velocity exchanges for thermal relaxation and relatively large statistical fluctuations for the thermal gradient occur that obfuscate determination of the conductivity. In contrast, for low swap periods ($\Omega = 100$ or one exchange every 100 fs) long simulation times are required for the system to achieve a steady-state temperature profile since relatively little heat is transferred per swap. In this case, for fixed simulation duration $t_D$, the uncertainty $\sigma_k$ is relatively large, roughly 10-15 %, relative due to slow convergence. Values of $\Omega$ between 20-40 give $\sigma_k$ errors in the 2-6 % range, relative. In light of the trade-off between computational burden and desired precision, values for $\Omega$ in this range appear optimal and have been used here. Similar results were found for argon fluid (Tikunoff, 2013). For $\Omega$ in this range, $k$ can be found with statistical uncertainty of several percent, approximately equal to or less than experimental uncertainties in $k$ for silicate liquids of ~5% relative (Pertermann et al., 2008).

Role of Simulation Cell Length ($L_z$)

The thermal conductivity $k$ exhibits a dependence on the size of the simulation cell in the direction of the heat flux $L_z$ when the size of the simulation volume is of the same order as the longest phonon path length. This variation is explained by the increase in the number of active phonon modes available as the system size increases as well as
the result of scattering that occurs at the interfaces of the heat source and sink in the NEMD system. The interface scattering effect is well known in MD studies and methods have been developed to account for it and hence obtain values of k appropriate for macroscopic systems (Chantrenne and Barrat, 2004; Varshney et al. 2009; Stackhouse and Stixrude, 2010). Finite-size effects are especially apparent in crystalline materials because the long-range order intrinsic to crystals gives rise to long mean free phonon path lengths that can exceed the size of the MD domain. In liquid and glassy materials, this is less of a problem because phonon mean free path lengths (\( \Lambda \)) are of the same order as the scale of short range order, approximately 0.3-0.6 nm for typical geosilicate liquids and glasses without a great deal of variation (Kittel, 1949). Since the scale of short range order is considerably less than the size of a typical MD simulation box filled with \( \sim 10^4 \) atoms of \( \sim 5-10 \) nm in our simulations, finite-system-size effects are less pronounced compared to crystals. However, for the best precision it is still desirable to account for finite-system-size effects since variations in \( L_z \) constrain the magnitudes of \( L_x \) and \( L_y \), necessarily, when tetragonal NEMD domains are utilized. The critical issue is the phonon mean free path length in an infinite (macroscopic) system (\( \Lambda_{\infty} \)) relative to the z-dimension of the MD simulation box of length \( L_z \). If the distance between the layers undergoing velocity exchange (\( L_z/2 \)) is comparable with \( \Lambda_{\infty} \), then an effective mean free path \( \Lambda_{\text{eff}} \) can be defined (Schelling et al., 2002; Yoon et al., 2004) according to:

\[
\frac{1}{\Lambda_{\text{eff}}} = \frac{1}{\Lambda_{\infty}} + \frac{1}{L_z}
\] (5)
From kinetic theory, the phonon mean free path (MFP) is related to the sonic speed and specific isochoric heat capacity of the material by (Bridgman, 1914; Kittel and Kroemer, 1980)

$$k = \frac{1}{2} \rho C_v c \Lambda_{\text{eff}} \quad (6)$$

where $\rho$ is the melt density (kg/m$^3$), $C_v$ is the isochoric specific heat capacity (J/kg K) and $c$ is the sonic velocity (m/s). Substituting Eq. (5) into Eq. (6) gives a relation between $k$ and $L_z$:

$$\frac{1}{k} = A \left( \frac{1}{\Lambda_{\infty}} + \frac{1}{L_z} \right) \quad (7)$$

where $A = 3(\rho C_v c)^{-1}$ is constant at any given state point and composition. Eq. (7) is of the form $1/k = C_1 + C_2/L_z$ where $C_1$ and $C_2$ are constants. To account for finite-system-size effects, NEMD conductivities from simulations performed in different sized boxes are plotted in $1/k$-$1/L_z$ coordinates. Extrapolation as $1/L_z \rightarrow 0$ gives the desired value of $k$ applicable to a macroscopic system. An example is illustrated in Figure 2 where the inverse of the thermal conductivity as a function of simulation cell length is plotted for CaMgSi$_2$O$_6$ at fixed $P$ and $T$. Extrapolation of the regression line to an infinite size system gives the phonon thermal conductivity $k = 1.143 \pm 0.004$ (1σ) W/m K. This compares to the laboratory value at 2000 K and ambient pressure of $1.159 \pm 0.058$ from Hofmeister et al. (2009) quite well. As another example, the NEMD value of $k$ for diopside composition at 1763 K and 1-bar of 1.186 $\pm 0.019$ W/m K, in this case uncorrected for a small finite-size effect, is within 1% of the laboratory value of 1.178 $\pm 0.06$ W/m K also from Hofmeister et al. (2009). Finally, extrapolation of the 1800 K (1-
bar) laboratory measurement for molten albite from Hofmeister et al (2009) gives a value of 1.55 W/m K that can be compared to the NEMD value at 2091 K and 1-bar (Table 2) of 1.498 W/m K. In conclusion, values computed for NaAlSi$_3$O$_8$ and CaMgSi$_2$O$_6$ compositions from NEMD compare quite well with laboratory results at ambient pressure. Evidently, the Matsui potential can recover accurate thermal conductivities at ambient pressure for these compositions using the NEMD method.

All of the thermal conductivity values reported below for Mg$_2$SiO$_4$, CaMgSi$_2$O$_6$ and NaAlSi$_3$O$_8$ have been analyzed as a function of simulation cell length as outlined above to obtain the desired macroscopic k from Eq. (7) using an optimal swap rates of $\Omega$ ~ 20-40 fs. Additional details on the NEMD method and statistical treatment of data may be found in Tikunoff (2013)

**RESULTS**

Values of the thermal conductivity at all state points for all compositions including the fluctuations in T and P and the $1\sigma$ uncertainties in k are collected in Tables 1, 2 and 3 for CaMgSi$_2$O$_6$, NaAlSi$_3$O$_8$ and Mg$_2$SiO$_4$, respectively. NEMD simulations for glassy materials, based on the criteria given earlier, are identified explicitly in the Tables. All others are for equilibrium or metastable liquids. Here we summarize the effects of T, P and composition on the thermal conductivity. In Part II, the theoretical basis for these variations is explored in the context of melt structure, specifically the systematic changes in melt structure with T, P and composition and with thermodynamic properties such as Grüneisen’s parameter, melt density and isothermal compressibility derived from the MD simulations based on theoretical models derived from condensed matter considerations.
All calculated k values for CaMgSi$_2$O$_6$ composition (both liquids and glass) are plotted on Figure 3. As T increases, k decreases, at all pressures although the effect is diminished as P increases. Figure 4 illustrates that a T increase from 3000 K to 4500 K decreases k by ~25% from 1.02 W/m K to 0.72 in diopside liquid at ambient pressure. At higher pressure (~10 GPa), the T-dependence of k is substantially weaker. At ~20 GPa, k remains relatively T-independent and assumes a value of ~2.4 W/m K (Table 1). In diopside liquid at 3500 K, a pressure increase from ambient to ~20 GPa increases k rather dramatically from ~1.15 W/m K to 2.5 W/m K, an increase of more than 100%. The increase in k with increasing P along an isotherm only slightly depends upon T. For example, at ~4500 K, k increases from 0.73 W/m K at ambient pressure to 2.28 W/m K at ~20 GPa, an increase by a factor >3 which is larger than, but comparable to, the increase at lower T. This weak T dependence is consistent with the well known result that pressure rather than T plays the dominant role in governing melt structure at the atomic level (e.g., Spera et al, 2009). The magnitude of k is strongly controlled by melt structure, which depends mainly on composition and pressure at high T. This phenomenon is quantitatively explored in part II.

In summary, k decreases with increasing temperature along an isobar and the effect becomes muted as pressure increases. The effect of increasing pressure on k along an isotherm is rather significant: a factor of ~2-3 as P increases from ambient to ~30 GPa. The trade-off between the opposing effects of increasing T and P on thermal conductivity for molten diopside can be evaluated by computing the change in k along the diopside liquid 2000 K isentrope. Temperature along the isentrope is given by
\[ T = T_0 \exp(\alpha P / \rho C_p) \], where \( \alpha \) is the isobaric expansivity, \( \rho \) is the melt density and \( C_p \) is the isobaric specific heat capacity. Adopting MD-derived mean values of density, heat capacity and expansivity along the isentrope for liquid diopside from Creamer (2012), one finds that \( k \) increases by a factor of 2.2 as pressure increases to 30 GPa along the 2000 K isentrope. This indicates that thermal conductivity in a magma ocean will be dominated by the pressure effect, ultimately governed by atomic level melt structure, and hence, increase with depth.

*Liquid albite*

Albite liquid exhibits \( k \)-\( P \)-\( T \) dependence that is qualitatively similar to molten diopside: a decrease of \( k \) with increasing \( T \) along an isobar and a strong increase in \( k \) with increasing \( P \) along an isotherm (Figure 5). For example, at \( \sim 4000 \) K, \( k \) increases from 0.9 to 2.6 W/m K from near ambient pressure to \( \sim30 \) GPa whereas at ambient \( P \), in the \( T \) range 2100-4024 K, \( k \) decreases from 1.45 W/m K to 0.89 W/m K. Similarly, at \( \sim30 \) GPa, as \( T \) increases in the sequence 2060 K, 3068 K, 4034 K, thermal conductivity decreases in the sequence 2.88 W/m K, 2.72 W/ m K, 2.60 W/m K, respectively. In general, thermal conductivity for albite liquid exceeds that for liquid diopside when compared at identical (or nearly so) \( T \)-\( P \) conditions, although differences become small as \( P \) increases.

*Liquid forsterite*

Liquid forsterite shows the strongest negative correlation of \( k \) with \( T \) at ambient pressure of the three liquid compositions studied. The conductivity decreases from 1.37 W/ m K at 2560 K to 0.68 W/ m K at 4580 K (Figure 6). Similar to the other compositions, along an isotherm, \( k \) increases substantially as pressure increases. For example, at \( \sim3550 \) K, \( k \) increases from 0.90 W/ m K to 2.12 W/ m K as pressure
inches from ambient to from ambient to 11 GPa pressure, an increase by a factor of 2.4, similar to the behavior in diopside and albite melts.

Glass

For CaMgSi$_2$O$_6$ at 2076 K and 2551 K and for NaAlSi$_3$O$_8$ at 2070 K and 3056 K, T is below the computer glass transition at all pressures. For glassy diopside at fixed pressure, there is a very slight T-dependence of k such that as T increases, k decreases. In contrast, along an isotherm k increases appreciably as pressure increases. For example, at T=2076 K, k increases from 1.14 W/m K at zero pressure to 2.89 W/m K at ~30 GPa, an increase by a factor of ~ 2.5. Glassy albite exhibits similar behavior: a weak, almost negligible, negative dependence of thermal conductivity with temperature but a rather strong increase in k as pressure increases along an isotherm. The weak isobaric thermal dependence of the thermal conductivity of albite and diopside glass is consistent with the experimental findings of Hofmeister et al (2009) as is the observation that glass k values are larger than values for corresponding liquids when compared at temperatures around the glass transition. Because the properties of a glass depend on its preparation (thermal) history, direct comparison between NEMD values and laboratory results is not meaningful given the enormously different cooling rates during preparation of computer versus laboratory glasses. Additional NEMD simulations on the glasses are needed to quantify the effects of preparation history on glass thermal conductivity. Diopsidic and albitic glasses have thermal conductivities of k=1.14 W/m K and k=1.50 W/m K, respectively, at similar state points (e.g., T=2059 ±12 K, P=-0.04 ±0.14 GPa and T=2091 ±20 K, P=0.20 ±0.23 GPa, respectively). The more polymerized NaAlSi$_3$O$_8$ composition in which each oxygen has two nearest neighbors of Si and/or Al at low pressure is a
better thermal conductor than the less polymerized compositions. The relationship between glass or melt atomic structure and phonon conductivity is discussed more fully in Part II. Here we note that as pressure increases, this effect becomes quantitatively muted since, at high pressures structures approximately converge being dominated by high coordination numbers.

**IMPLICATIONS**

Although quantitative knowledge of the effects of temperature, pressure and composition on the phonon conductivity of geosilicate liquids is critical for the analysis of many geophysical and petrological problems, very few measurements exist due to experimental difficulties. There are virtually no measurements on the effects of pressure on thermal conductivity of silicate liquids. In this study, we have implemented a Non-Equilibrium Molecular Dynamics (NEMD) technique within the context of classical Molecular Dynamics to study the phonon conductivities of amorphous (molten and glassy) Mg$_2$SiO$_4$, CaMgSi$_2$O$_6$ and NaAlSi$_3$O$_8$ at elevated temperatures (2500-4500 K) and pressures (0-30 GPa). The NEMD method takes account of finite-size effects and faithfully captures experimental thermal conductivities for simple fluids such as Ar and alkali halide liquids. The NEMD results compare very well with ambient pressure experimental values for liquid CaMgSi$_2$O$_6$ and NaAlSi$_3$O$_8$ from Hofmeister et al (2009). For example, experimental values at 1-bar for CaMgSi$_2$O$_6$ and NaAlSi$_3$O$_8$ at 2000 K of 1.15 W/m K and 1.55 W/m K compare well with the NEMD values at the same state point of 1.14 W/m K and 1.45 W/m K, respectively. In the temperature range of this study all compositions exhibit a negative dependence of k with temperature and a strong
positive dependence of k with pressure. There is also a discernable effect at low pressure and identical temperatures such that the thermal conductivity increases as the extent of polymerization increases. For example, molten albite, in which every oxygen is linked to two TO₄ (T=Si, Al) tetrahedra exhibits a greater thermal conductivity than molten Mg₂SiO₄ for which each oxygen has only one nearest neighbor of Si at low pressure. As pressure increases this polymerization effect is damped presumably because the effect of pressure is to increase the coordination number of oxygen around a central Si and likewise the coordination number of Si and other cations around a central oxygen, As P increases, all compositions become closer in structure and hence the structural control on k diminishes. In part II of this study, the MD-derived thermal conductivities are related to macroscopic thermodynamic properties and melt structures.
References


54. Martin G.B., Ghiorso, M., and Spera, F. (2012) Transport properties and equation of 1954state of 1-bar eutectic melt in the system CaAl$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ by molecular dynamics simulation. American Mineralogist, 97, 1155-1164.

57. TERAO ET AL 2007
58. CREAMER ET AL 2012
59. HOFMEISTER 19XX, 19XY

Figure Legends
Figure 1: Phonon thermal conductivity of CaMgSi$_2$O$_6$ ($\rho=2569$ kg/m$^3$ at P=0.36 ±0.17 GPa and T=1764 ±13 K) versus particle swap time interval $\Omega$ in femtoseconds. Aspect ratio of the NEMD box equals unity (i.e., $k$ has not been corrected for finite-system-size effects). For large values of $\Omega$, the uncertainty in $k$ is relatively large although its mean value is not very different from the best estimate of 1.154 ±0.02 W/m K at $\Omega=20$. The laboratory value from Hofmeister et al. (2009) at 1764 K and 1 bar is 1.17 ±0.06 W/m K. Applying a finite-system-size correction increases the value of $k$ whereas the effect of pressure is to increase $k$ from its one-bar value. These effects approximately cancel in this case. In the remainder of this work the duration between swap events is between 10 and 30 fs, and the total duration of NEMD simulation is 2 ns.

Figure 2: Inverse phonon thermal conductivity ($k^{-1}$) versus inverse system cell length $L_z$ for CaMgSi$_2$O$_6$ at T=2060 ±15 K, P= -0.04 ±0.15 GPa and $\rho=2392$ kg/m$^3$. Extrapolation in the limit $L_z \to 0$, the intercept, gives the value $k=1.143 \pm 0.004$ W/m K. This can be compared to the laboratory value at 2000 K and ambient pressure of 1.159 ±0.058 from Hofmeister et al. (2009). The number of particles $N$ used in the simulations for $L_z = 4.22$ nm, 8.44 nm, 12.66 nm and 16.88 nm are 5000,10000,15000 and 20000, respectively. In all cases the swap time interval is $\Omega= 20$ fs and the total simulation duration $t_{D}= 2$ ns.

Figure 3: Thermal conductivity for amorphous diopside (glass and liquid) versus pressure along quasi-isotherms ~2000 K, 2500 K, 3500 K and 4500 K. Raw data is in Table 1. Data at the highest pressure are near the limits of the classical potential used in the simulations and are included for the purposes of completeness.

Figure 4: Variation of thermal conductivity at ambient conditions and at 10 GPa for CaMgSi$_2$O$_6$ composition. The effect of $T$ on $k$ is muted as pressure increases.

Figure 5: Thermal conductivity for amorphous albite (glass and liquid) versus pressure along three quasi-isotherms at ~2000 K, 3000 K and 4000 K. Raw data can be found in Table 2.

Figure 6: Thermal conductivity of molten Mg$_2$SiO$_4$ at $P = 0.07 \pm 0.16 GPa$ as a function of temperature.

Figure 7: Thermal conductivity of molten Mg$_2$SiO$_4$ as a function of pressure along the $T = 3548 \pm 18 K$ isotherm.

TABLES
Table 1: NEMD results for liquid and glassy CaMgSi₂O₆. Glass entries noted by k values in *italics*. Temperatures in bold are averages used in the Figures. 1σ fluctuations are reported for T and P of the NEMD run. 1σ errors for k are found by propagation of error of the computed T gradient and the deviation from linearity in 1/k versus 1/Lz.

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Table 2: NEMD results for liquid and glassy NaAlSi$_3$O$_8$. Glass entries noted by k values in *italics*. Temperatures in bold are averages used in the Figures. 1σ fluctuations are reported for T and P of the NEMD run. 1σ errors for k are found by propagation of error of the computed T gradient and the deviation from linearity in 1/k versus 1/L$_z$.

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Table 3: NEMD results for liquid Mg$_2$SiO$_4$ thermal conductivity values. Temperatures in bold are averages used in the Figures. 1σ fluctuations are reported for T and P of the NEMD run. 1σ errors for k are found by propagation of error of the computed T gradient and the deviation from linearity in 1/k versus 1/L$_z$.

<table>
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<tr>
<th>Density (kg/m$^3$)</th>
<th>T (K)</th>
<th>$\sigma_T$ (K)</th>
<th>P (GPa)</th>
<th>$\sigma_P$ (GPa)</th>
<th>k (W/mK)</th>
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FIGURES

Figure 1
Figure 2

\[ k^{-1} = 0.875 + 4.297 L_z^{-1} \]

\[ R^2 = 0.996 \]
Figure 3

![Graph showing data points for different temperatures (2076 K, 2551 K, 3538 K, 4517 K) plotted against pressure (P [GPa]) with corresponding thermal conductivity values (k [W/mK]).](image-url)
Figure 4

- $P = 0.19 \pm 0.15$ GPa
- $P = 10.38 \pm 0.23$ GPa

$k \text{ [W/mK]}$ vs. $T \text{ [K]}$
Figure 5
Figure 6

$P = 0.07 \pm 0.16 \text{ GPa}$
Figure 7

$k \ [\text{W/mK}]$

$P \ [\text{GPa}]$

$T=3548\pm18 \ K$