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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

Dane Tikunoff$^1$ and Frank J. Spera$^{1*}$

$^1$Department of Earth Science, University of California-Santa Barbara,

*E-mail: spera@geol.ucsb.edu
Abstract

Non Equilibrium Molecular Dynamics (NEMD) simulations are used to compute the phonon thermal conductivity ($k$) for liquids and glasses of composition $\text{Mg}_2\text{SiO}_4$, $\text{CaMgSi}_2\text{O}_6$ and $\text{NaAlSi}_3\text{O}_8$ 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. The NEMD results compare well with available laboratory measurements on molten $\text{NaAlSi}_3\text{O}_8$ and $\text{CaMgSi}_2\text{O}_6$ at 1-bar. Thermal conductivities decrease with increasing temperature ($T$), increase with increasing pressure ($P$) and, at low pressure, increase slightly as the mean coordination number of Si and Al around oxygen increases, in the sequence $\text{Mg}_2\text{SiO}_4$, $\text{CaMgSi}_2\text{O}_6$ and $\text{NaAlSi}_3\text{O}_8$. At 3500 K, the thermal conductivity of $\text{CaMgSi}_2\text{O}_6$ at 0, 10, 20 and 30 GPa is 1.1, 2.1, 2.5 and 3 W/m K, respectively. At ambient pressure ($0.2 \pm 0.15$ GPa), $k=1.2$ and 0.5 W/m K at 2500 K and 4500 K, respectively for $\text{CaMgSi}_2\text{O}_6$. For $\text{NaAlSi}_3\text{O}_8$ 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. $\text{Mg}_2\text{SiO}_4$ liquid at ambient pressure ($0.07 \pm 0.16$ 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 compositions are included for 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.
INTRODUCTION

Knowledge of the phonon thermal conductivity of amorphous silicates (melts and glasses) over the range of composition (X), P and T of the Earth’s crust and mantle is essential for analysis of many geophysical and geochemical problems. For example, heat transfer during nucleation and dissolution or growth of a crystal from a melt is a significant factor governing rock texture. Similarly, heat exchange between magma and its surroundings is relevant to rates of magma crystallization, mechanisms of volatile-saturation and the thermodynamics of partial melting. 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, 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, \( C_p \) is the isobaric specific heat capacity, and \( k \) is the phonon thermal conductivity, are needed to calculate transient geotherms and predict conditions for crustal anatexis and metamorphism in orogenic regions (e.g., Whittington et al., 2009). Finally, in ceramic and composite materials processing, knowledge of thermal conductivity is required (Kang and Morita, 2006). Of special concern is the lack of any estimates of the effects of pressure on phonon conduction in silicate liquids. In this study, attention is mainly focused upon equilibrium silicate liquids of petrological significance although a few results relevant to glasses are included. 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 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 pressure on thermal conductivity in crystalline silicates and oxides, liquids are structurally distinct with essentially no long range structure beyond ~ 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 structure as P increases. One of the goals of this study is to provide quantitative constraints on the pressure-dependence of the thermal conductivity of silicate liquids at elevated temperature. 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 (e.g., the lower the NBO/T ratio), the higher the thermal conductivity (Kang and Morita, 2006). A second goal of this work is to therefore examine, at fixed temperature and pressure, the correlation of thermal conductivity with NBO/T ratio. Finally, although for crystalline solids at constant pressure, thermal conductivity varies according to 1/T (e.g., see summary in Stackhouse and Stixrude, 2010) the validity of this scaling of conductivity with temperature, $k \propto 1/T$, has not been experimentally or numerically studied for molten silicates in the range 2000-5000 K. The high-T scaling of k at fixed P is therefore also investigated here. In short, current knowledge of the thermal conductivity of silicate liquids is meager. In this study, we study 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 measurements are of restricted value.
because: (1) they are contaminated by unwanted radiative (photon) transport, (2) include unwanted interfacial contact effects or (3) are affected by convective heat transport. For example, measurements reported by McBirney and Murase (1973) using the hot-wire method are dominated by radiative effects that act to conceal the smaller phonon contribution. Additionally, in hot-wire and hot-layer methods, thermal losses at contacts introduce significant errors difficult to eliminate without complex deconvolution (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) present measurements of thermal conductivity at ambient pressure for a number of compounds. They note that recent advances in contact-free, laser-flash analysis and better data reduction methods (Degiovanni et al., 1994; Mehling et al., 1998) enable removal of direct radiative transfer effects and losses to the container and hence provide accurate phonon conductivities at ambient P and temperatures just above 1-bar melting points. Unfortunately, these measurements are limited to 1-bar (10^{-4} GPa) pressure. Although these data indicate that k decreases weakly with increasing T in the range \sim1300-1600 K for silicate liquids, the behavior at higher temperature has not been studied and there are no data on the effects of pressure. Data on alkali halides and metal liquids (e.g., Beck et al, 2007; Galamba et al, 2004; de Koker et al, 2012) suggests that conductivity increases with pressure along an isotherm but for silicate liquids the effects of pressure are unknown. Consequently, the trade-off between variations in T and P is unknown for liquid silicates. Finally, although studies on CaO-Al_2O_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
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T and P compared to less polymerized ‘fragile’ liquids (Martinez and Angell, 2001), the role of composition and its correlative melt polymerization is not well quantified. Because melt structural states correlate with changes in second order thermodynamic property differences between liquid and glass (e.g., isothermal expansivity, isothermal compressibility, isobaric heat capacity), (Giordano and Dingwell, 2003) one might expect a correlation at fixed T and P between melt composition and phonon conductivity such that more fragile melts possess lower conductivities compared to the network (strong) melts. This conjecture can be addressed using liquid structural states, encapsulated in radial distribution analysis and coordination statistics derived from MD simulations (e.g., Ghiorso and Spera, 2009; Spera et al, 2009). The compositions chosen in this study span the spectrum of polymerization states relevant to natural magmas (Mysen and Richet, 2005; Hendersen et al, 2006; Hofmeister et al, 2009). 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., \(X_{BO}=1\)). Diopside liquid is intermediate in the stoichiometric sense with \(X_{BO}=1/3\) at 1-bar pressure. One of the most significant connections between structure and properties observed in all liquid silicates both experimentally and in Molecular Dynamics simulations is the increasing coordination of cations around oxygen (and of oxygen with itself) as pressure increases (e.g., Daniel et al, 1996; Allwardt et al, 2007; Spera et al, 2011). 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 \( \sim 0-2 \text{ GPa} \), composition effects will dominate. An important result of this study explored more fully in part II is that at the same temperature and crustal pressure, the thermal conductivity of silicic melt (e.g., a rhyolite) is larger by 25-100\% compared to basaltic melt. In summary, the effects of composition, temperature and pressure on thermal conductivity in silicate liquids are largely unknown over the range of states relevant to the Earth. The main purpose of this study is to address these issues.

**METHODS**

Classical Molecular Dynamics

The calculations in this study are based on classical Molecular Dynamics (MD) simulations. In classical MD, an empirical relation describing the potential 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, particles are moved to new positions following the dictates of Newton’s second law of motion for several million femtosecond \( (10^{-15} \text{ s}) \) 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 \( \text{Na}_2\text{O-CaO-MgO-SiO}_2-\text{Al}_2\text{O}_3 \) 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 equation of state, tracer diffusivity and shear viscosity for \( \text{CaAl}_2\text{Si}_2\text{O}_8, \text{CaMgSi}_2\text{O}_6, \text{MgSiO}_3, \text{Mg}_2\text{SiO}_4, \) and 1-bar eutectic
composition (system CaMgSi$_2$O$_6$-CaAl$_2$Si$_2$O$_8$) liquid (Creamer, 2012; Martin et al., 2012; Spera et al., 2011; Ghiorso 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 history unlike that of an equilibrium or metastable liquid (Donth, 2001). When temperature is decreased rapidly on a liquid and its intrinsic relaxation time exceeds the laboratory or simulation quenching timescale, the liquid falls out of equilibrium and undergoes a kinetic transition to a glass. The glass transition temperature ($T_g$) for a given composition depends on both quench rate and pressure (Passaglia and Martin, 1964). The glass transition is not a transition in the thermodynamic sense, but instead a kinetic phenomenon, where the amorphous solid with
crystal-like vibrational properties is dynamically arrested and hence preserves the disorder of the liquid (Roland et al, 2005; Langer, 2014). At typical laboratory cooling rates of ~0.1-1 K/s, the glass transition temperature ($T_g$) for NaAlSi$_3$O$_8$ and CaMgSi$_2$O$_6$ 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 greater, of order ~ $10^2$ K/ps ($10^{14}$ K/s), the computer glass transition temperature is significantly higher. For example, the computer $T_g$ of CaAl$_2$Si$_2$O$_8$ defined by analysis of the mean square displacement versus time (see below) is approximately 2800 K for a quench rate of 70-200 K/ps (Morgan and Spera, 2001). This is significantly higher than the laboratory value of $T_g = 1025$ K (Arndt and Häberle, 1973).

The transition from liquid to glass can be detected in MD simulations by two means. For ergodic liquids an excellent correlation exists between the potential energy ($E_{\text{POT}}$) and $T^{3/5}$ at constant density (Spera et al, 2009; Ghiorso and Spera, 2009; Martin et al, 2012; Creamer, 2012). This scaling relationship, proposed by Rosenfeld and Tarazona (1998), is called RT-scaling. Glasses exhibit imperfect RT scaling; on plots of $E_{\text{POT}}$ vs $T^{3/5}$ deviations from linearity along isochores occur around $T_g$ and become more pronounced as $T$ decreases. A dynamical method for detection of the glass transition is based on the mobility of atoms (tracer diffusivity) in Euclidean space. 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) ballistic interval (Morgan and Spera, 2001). In contrast, glassy materials exhibit the phenomena of sub-diffusion; a diffusion process with a non-linear relationship to time, in contrast to a normal diffusion process in which the mean squared displacement (MSD) of
a particle is a linear function of time (Wang et al., 2012). In particular, in the non-ergodic region where sub-diffusion holds, the MSD exhibits power-law behavior with MSD \( \sim t^\delta \) following a short ballistic 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 CaMgSi2O6 the computer glass transition in our simulations occurs at \( \sim 2630 \pm 50 \) K at 1 bar. For NaAlSi3O8 composition, \( T_g \) is approximately 2800 K based on the RT scaling and MSD criteria. The glass transition temperature depends on pressure in addition to quench rate. The variation of the computer glass transitions with pressure for CaMgSi2O6 and NaAlSi3O8 found here empirically lies in the range 10-30 K/GPa. In the Tables below for thermal conductivity, glasses are distinguished from liquids based on the RT and MSD analysis outlined above for compositions NaAlSi3O8 and CaMgSi2O6. 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 Kubo relations (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 Non Equilibrium Molecular Dynamics (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 the NEMD method used to obtain $k$ 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

$$ k = \frac{\int_0^t \mathbf{q}_z(t) \, dt}{2 A t_D (dT/\, dz)} $$

(1)

where the integral is the cumulative heat flow imposed during a simulation of duration $t_D$ 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 $N$ 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
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243 this procedure induces a temperature gradient for a known quantity of heat exchange
244 based on the kinetic energies of the exchanged atoms. The instantaneous local kinetic
245 temperature \(<T_k>\) in the \(k^{th}\) slab is given by
246
\[
T_k = \frac{1}{3k_B n_k} \sum_{i=1}^{n_k} m_i v_i^2
\]

247 where the sum extends over all \(n_k\) atoms of each type of mass \(m_i\) and velocity \(v_i\) in the \(k^{th}\)
248 slab. This exchange mechanism produces an energy transfer computed from
249
\[
\left\langle \int_{0}^{t_D} q_x(t) \, dt \right\rangle = \sum_{\text{transfers}} (v^2_c - v^2_h)
\]

249 The heat transfer leads to a temperature difference between the designated layers and
250 gives rise to a steady-state temperature gradient across each half of the system. This
251 temperature gradient is the desired quantity of the NEMD simulation. Exchanging the
252 velocities of two atoms of equal mass (e.g., an O for an O, a Ca for a Ca, etc) leaves the
253 total linear momentum, total kinetic energy, melt composition and the internal energy
254 unchanged. After reaching the thermal steady state, the energy transfer imposed by the
255 velocity exchange is exactly balanced by the heat flux in the opposite direction effected
256 by the phonon thermal conductivity of the liquid. The thermal conductivity is then
258 computed from the expression
259
\[
k = \frac{\sum_{\text{transfers}} (v^2_c - v^2_h)}{2t_D L_x L_y (dT/dz)}
\]

260 The sum is taken over all transfers over the duration \(t_D\) of the NEMD simulation starting
261 from an equilibrated initial state. All quantities in Eq. (4) are known exactly except the
262 temperature gradient that is obtained from Eq. (2) applied to each layer. The simulation is
263 terminated after a linear or nearly linear temperature gradient is established.
Representative thermal profiles are given in Tikunoff (2013). Attainment of a linear $T$ profile typically 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 $\pm 30$ K and $\pm 0.25$ 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, 1$\sigma$ 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 in all cases 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, 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 (see below). 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) where additional technical details may be found.

Role of swap period ($\Omega$)

The swap period ($\Omega$) 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. 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
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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 $\sim$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 silicate 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 good 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 to $\Lambda_\infty$, an effective mean free path $\Lambda_{\text{eff}}$
can be defined (Schelling et al., 2002; Yoon et al., 2004) according to:

$$\frac{1}{\Lambda_{\text{eff}}} = \frac{1}{\Lambda_\infty} + \frac{1}{L_z} \quad (5)$$

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)

$$k = \frac{1}{3} \rho C_V c \Lambda_{\text{eff}} \quad (6)$$

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 $1/L_z \to 0$ gives the desired value of $k$
applicable to a macroscopic system. All of the thermal conductivity values reported
below for Mg$_2$SiO$_4$, CaMgSi$_2$O$_8$ and NaAlSi$_3$O$_8$ have been analyzed as a function of
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simulation cell length as outlined above to obtain the desired macroscopic k from Eq. (7) using an optimal swap rates of $\Omega \sim 20$-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. Figure 2 illustrates the calculation of finite-size effects, 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 $k=1.143 \pm 0.004$ ($1\sigma$) 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 well with laboratory results at ambient pressure. Evidently, the Matsui potential can recover accurate thermal conductivities at ambient pressure for these compositions. 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.

\[ \text{CaMgSi}_2\text{O}_6 \]

All calculated k values for CaMgSi_2O_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 depends weakly on temperature 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 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 greater than 3 which is comparable to the increase with pressure at lower T.

In summary, for CaMgSi_2O_6 k decreases with increasing temperature along an isobar. The effect of increasing pressure on k along an isotherm is rather significant: a factor of ~2-3 as pressure 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
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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.

Liquid albite

Albite liquid exhibits $k$-P-T dependence that is qualitatively similar to molten diopside; all values are listed in Table 2 and depicted in Figure 5. The thermal conductivity decreases with increasing $T$ along an isobar and strongly increases as pressure increases along an isotherm. For example, at ~ 4000 K, $k$ increases from 0.9 to 2.6 W/m K from near ambient pressure to ~30 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 ~30 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 smaller 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 (Figure 7). For example, at ~3550 K, $k$ increases from 0.90 W/m K to 2.12 W/m K as pressure increases 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, the temperature 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, to first order, each oxygen has two nearest neighbors of Si and/or Al (at low pressure) is a better thermal conductor than the less polymerized composition CaMgSi$_2$O$_6$ in which, to first order, two of the three oxygens of the metasilicate (SiO$_3$) backbone have one nearest neighbor of Si and the remaining oxygen
is bridging oxygen. 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 silicate 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 that we are aware of. In this study, we have
implemented a Nonequilibrium Molecular Dynamics 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) and provide estimates of this important geophysical
parameter in these liquids. 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, exhibits a greater thermal conductivity than molten $\text{Mg}_2\text{SiO}_4$ when compared at comparable state points. 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 pressure increases, all compositions become closer in structure and hence the structural control on thermal conductivity diminishes. In part II of this study, the MD-derived thermal conductivities are related to macroscopic thermodynamic properties and melt structures.
References


Revision 2


Martin G.B., Ghiorso, M., and Spera, F. (2012) Transport properties and equation of state of 1-bar eutectic melt in the system CaAl$_2$Si$_2$O$_8$-CaMgSi$_2$O$_6$ by molecular dynamics simulation. American Mineralogist, 97, 1155-1164.


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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 $k=1.143 ±0.004$ 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 $P = 0.07 ± 0.16 GPa$ as a function of temperature.

Figure 7: Thermal conductivity of molten Mg$_2$SiO$_4$ as a function of pressure along the $T = 3548 ± 18K$ isotherm.
**Table 1**: NEMD results for liquid and glassy CaMgSi$_2$O$_6$. 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 2: NEMD results for liquid and glassy NaAlSi₃O₈. 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 3**: NEMD results for liquid Mg$_2$SiO$_4$ thermal conductivity values. Temperatures and Pressures in bold are averages used in the Figures. $1\sigma$ fluctuations are reported for T and P of the NEMD run. $1\sigma$ errors for k are found by propagation of error of the computed T gradient and the deviation from linearity in $1/k \text{ versus } 1/L_z$. 

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FIGURES

Figure 1

![Graph showing the relationship between k [W/mK] and Swap Period [fs]]
**Figure 2**

\[ k^{-1} = 0.88 + 4.30L_z^{-1} \]

\[ R^2 = 0.996 \]
Figure 3

![Graph showing thermal conductivity (k) vs. pressure (P) for different temperatures: 2076 K, 2551 K, 3540 K, and 4517 K. The graph includes error bars indicating the uncertainty in the measurements.]
Revision 2

Figure 4

![Graph showing thermal conductivity (k) vs temperature (T) at different pressures (P). The graph includes data points for P=0.19±0.15 GPa and P=10.38±0.23 GPa.](image-url)
Figure 5
Revision 2

**Figure 6**

![Graph showing the relationship between temperature (T [K]) and thermal conductivity (k [W/mK]), with error bars and a note indicating P = 0.07 ± 0.16 GPa.](image)

*Note: This figure illustrates the thermal conductivity (k) of a material as a function of temperature (T), with error bars indicating the uncertainty in the measurements at various pressures. The data points suggest a decrease in thermal conductivity with increasing temperature.*

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Figure 7

![Graph showing varying values of k (W/mK) against P (GPa) with T = 3548 ± 18 K.](image)

- k [W/mK]
- P [GPa]