Molecular Dynamics Studies of MgSiO$_3$ Liquid to 150 GPa: Thermodynamics and Transport Properties

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- Goal is to develop a thermodynamic model for liquids in the system MgO-SiO$_2$ from 0-150 GPa that is consistent with low-P experimental phase equilibrium studies

- Construction of a thermodynamic model using MD results in combination with Rosenfeld-Tarazona theory

- Measures of melt structure and their relation to thermodynamic and transport properties

- Liquid-liquid phase transition

- Plan for future studies
**MgSiO$_3$ Liquid**

Coulomb-Born-Mayer-van der Waals pair potential form and parameters from Oganov (2000) of the form: $U_{ij} = q_i q_j / r_{ij} + A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij}/(r_{ij})^6$

**Simulation constraints**
- 8000 atoms
- 1 fs time step
- simulation duration 50 ps for thermodynamic analysis, 10 ns for calculation of shear viscosity
- Derive P ($\pm 0.3$ GPa)
- E ($\pm 0.5$ kJ/mol), and RDF (CNs)
Thermodynamic Analysis: Internal Energy

Using the theory of Rosenfeld and Tarazona (1998) for the T-dependence of the potential energy and developing the thermodynamic analysis after Saika-Voivod and others (2000)

Potential Energy

\[ U(V,T) = a(V) + b(V)T^{3/5} \]

Internal Energy

\[ E(V,T) = U(V,T) + \frac{3nR}{2M}T \]

\[ E(V,T) = a(V) + b(V)T^{3/5} + \frac{3nRT}{2} \]
Parameterizing the Rosenfeld-Tarazona coefficients

- $a$ and $b$ are $f(V)$ and not $f(T)$
- Polynomial functions are arbitrary
- Will show later that $V = f(\text{CN of O about Si})$, so $a$ and $b$ are really functions of melt structure

\[ a(V) = 126.5 - 3492.1 \, V + 20635 \, V^2 \]
\[ - 59881 \, V^3 + 85463 \, V^4 - 48098 \, V^5 \]

\[ b(V) = -0.3721 + 7.106 \, V - 45.81 \, V^2 \]
\[ + 139.3 \, V^3 - 202.0 \, V^4 + 112.8 \, V^5 \]
Rosenfeld-Tarazona model for the Internal Energy
$C_V$: T-dependence of the Internal Energy

$$C_V = \frac{3}{5} \frac{b(V)}{T^{2/5}} + \frac{3n}{2} R$$
Further thermodynamic analysis...

\[ A(V,T) = \text{Helmholtz Energy} \]

\[ A(V,T) = E(V,T) - TS(V,T) \]

\[ S(V,T) - S(V_0,T_0) = \frac{1}{T_0} \int_{V_0}^{V} \left[ \left( \frac{\partial E}{\partial V} \right)_T + P(V,T_0) \right] dV + \int_{T_0}^{T} \frac{1}{T} \left( \frac{\partial E}{\partial T} \right)_V dT \]

\[ A(V,T) = a(V) + T^{\frac{3}{2}} b(V) + \frac{3n}{2} RT - TS(V_0,T_0) - \frac{3n}{2} TR \ln \left( \frac{T}{T_0} \right) - \frac{T}{T_0} \left[ a(V) + T_0^{\frac{3}{2}} b(V) + \int_{V_0}^{V} P(V,T_0) dV \right] + T^{\frac{3}{2}} \frac{3}{2} \left( 1 - \frac{T}{T_0^{\frac{3}{2}}} \right) b(V) \]

\[ P(V,T) = \text{Equation of state} \]

\[ P = -\left( \frac{\partial A}{\partial V} \right)_T = \left( \frac{T}{T_0} - 1 \right) \frac{da(V)}{dV} + 5 \frac{T^{\frac{3}{2}}}{2} \left( \frac{T}{T_0} \right)^{\frac{3}{2}} \left( 1 - \frac{T}{T_0^{\frac{3}{2}}} \right) \frac{db(V)}{dV} + \frac{T}{T_0} P(V,T_0) \]
Equation of State

Isotherm parameterization with the Universal EOS of (Vinet and others, 1988):

\[ P(T_0, V) = \frac{3K_0(1 - x)e^{\eta(1 - x)}}{x^2} \]

\[ \eta = \frac{3}{2}(K_0'/1 - 1) \]

\[ x = \left( \frac{V}{V_0} \right)^{1/3} \]

\[ P = \left( \frac{T}{T_0} - 1 \right) \frac{d\alpha(V)}{dV} + \frac{5}{2} T^{3/5} \left[ \left( \frac{T}{T_0} \right)^{2/5} - 1 \right] \frac{d\beta(V)}{dV} + \frac{T}{T_0} P(V, T_0) \]
Melt structure: CN of O around Si

~3500 K
Melt structure: CN of O around Mg

~3500 K

Mg-O CN Fraction

P (GPa)
Melt structure: CN of O around O

\[
\begin{array}{c}
\text{P (GPa)} \\
0 & 25 & 50 & 75 & 100 & 125 & 150 \\
\end{array}
\]

\[
\begin{array}{c}
O-O CN Fraction \\
~3500 K \\
\end{array}
\]
Oganov, MgSiO$_3$

- Shift in minima of the RDF
- Effect on second order thermodynamic quantities
- Effect on transport properties
- Is this an artifact of the computation?
Answer to last question is “No”

Rapid decrease in O-O CN is seen in MgSiO$_3$ and in Mg$_2$SiO$_4$ using the Matsui (1994) potential (see Ben Martin’s poster)
O-O transition can be seen in transport properties

Shear viscosity

\[ \log_{10} \eta = -2.3878 \pm 0.0127 + 0.01680 \pm 0.000450 \ P \]

\[ \log_{10} \eta = -2.3620 \pm 0.0205 + 0.014602 \pm 0.000363 \ P \]

\[ \log_{10} \eta = -2.4071 \pm 0.2179 + 0.014763 \pm 0.002369 \ P \]

- Viscosity was computed using the Green-Kubo formulation. Integration of the autocorrelation functions of the three independent off-diagonal stresses leads to an estimate of the shear viscosity (Nevins and Spera, 2006).

- Viscosity increases by a factor of 32 from 0 to 100 GPa and is extrapolated to increase by a factor of 110 at 135 GPa.

- The activation energy for viscous flow is about 1 cm³/mol
Near 0 GPa there is a small region of "anomalous" diffusion for Si and O in which increasing pressure increases the diffusivity. This effect is muted as temperature increases from 3500 K to 5000 K.

Note the cross-over in Mg and O tracer diffusivity at ~2 GPa.

Quasi-"plateaus" around 70 GPa (at ~3500 K) where the rate of decrease of all tracer diffusivities diminishes for ~ 10 GPa. This observation implies that the activation volume for tracer diffusion approaches a minimum at the same P.
Liquid-Liquid phase transition

Stability criterion:

\[
K = -\left( \frac{T}{T_0} - 1 \right) V \frac{d^2a(V)}{dV^2} - \frac{5}{2} T^{\frac{3}{5}} \left[ \left( \frac{T}{T_0} \right)^{\frac{2}{5}} - 1 \right] V \frac{d^2b(V)}{dV^2} - \frac{T}{T_0} V \frac{dP(T_0,V)}{dV} > 0
\]

- Stability criterion defines critical point and spinodal curve for L-L unmixing.
- Coexisting structural states are given by horizontal chords that terminate on a common isotherm.
- For MgSiO$_3$, the critical point is in the deeply supercooled region.

3.008 gm/cm$^3$, 1.514 GPa, 1062.3 K
Conclusions and Future Work

- Thermodynamic analysis based on Rosenfeld-Tarazona theory
- Experimental low pressure $\rho$ and $C_V$ are recovered
- CN statistics reveal O-O transition which also occurs in $\text{Mg}_2\text{SiO}_4$ and is linked to $K$, and transport properties
- Evidence for L-L phase transition