Thermodynamic Mixing along the Plagioclase Liquid Join

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Plagioclase feldspar is the most common mineral in the Earth’s crust, with implications for magma generation, ascent, storage, and eruptive processes, as well as the formation of continental and oceanic crust. The mixing properties of molten silicates—plagioclase feldspar (NaAlSi$_3$O$_8$ – CaAl$_2$Si$_2$O$_8$) being an archetypical composition—play a crucial role in the thermodynamics of multicomponent-multiphase systems common to igneous and high-grade metamorphic petrology. Thermodynamic mixing properties have been well studied for liquids in equilibrium with solid (crystal) phases (Ghiorso et al., 1983). However, thermodynamic data for silicate liquids at $T > 2000$ K and $P > 1$ GPa are sparse (Neilson et al., 2016). This commonly leads to the assumption of ideal mixing when dealing with multiphase thermodynamic systems at high temperature ($T$) and pressure ($P$) relevant to the Earth’s interior. How robust is this assumption? Is the mixing across the plagioclase liquid join at extreme conditions ideal?

To accompany the experimental work on thermodynamic properties of liquid silicates, numerical calculations (such as molecular dynamics simulations) have allowed geologists to extend the working knowledge of silicate properties to deeper and hotter conditions. Molecular dynamics (MD) simulations model the atomic interactions of particles based on Newtonian physics, and thermodynamic properties can be derived using statistical mechanics in conjunction with these ensemble calculations. Only computational resources are required to allow one to investigate the whole range of temperature ($T$) and pressure conditions relevant to the Earth’s interior (and beyond). Using a classical MD methodology, we simulated liquid plagioclase with
65,000 particles in the microcanonical ensemble (constant number of particles \([N]\), internal energy \([E]\), and volume \([V]\)). For more details, see (Neilson et al., 2016).

This project was designed to study the effect of compositional changes in liquid plagioclase feldspar on thermodynamic properties such as \(V\) and \(E\). The compositional effect essentially shows the thermodynamic mixing properties of the liquid. To see the variation across the plagioclase liquid join, we targeted six compositions: \(\text{Ab}_{100}, \text{Ab}_{80}\text{An}_{20}, \text{Ab}_{60}\text{An}_{40}, \text{Ab}_{40}\text{An}_{60}, \text{Ab}_{20}\text{An}_{80},\) and \(\text{An}_{100}\). These initial simulations were intended to provide a glimpse into the thermodynamic mixing properties at high \(T\) and \(P\) of the liquid state.

An ideal mixing condition would produce a linear mixing line across the compositional join between the end-members’ thermodynamic property of interest. Our analysis herein includes a visualization of the compositional effect on \(V\) or \(E\). This allows one to quickly identify deviations from ideal mixing. After analyzing the six compositions (in moles of albite, \(X_{\text{Ab}}\)) listed above, we were able to identify regions in \(P\)-\(T\)-\(X_{\text{Ab}}\) space to expand for future investigation.

Four target state points were chosen between 0 and 3 GPa and from 3200 to 4800 K (Fig. 1). We used the six compositions at each state point to provide 24 simulations for this research. At a given state point, all (six) simulations fell within one sigma (one statistical deviation in the ensemble average) of the MD-targeted \(T\) and \(P\). Values of \(T\) and \(P\) reported herein are the averages from the six simulations (of the six compositions) at the targeted conditions. The MD-calculated results include thermodynamic properties such as \(T\), \(P\), \(E\), and \(V\). By plotting these properties versus composition at \(T\) and \(P\), we concluded the following results.
Figure 1. P-T conditions for the simulations of this study. The boxes show the statistical error in P and T around each simulation.

In Figure 1 we show the location of our simulations in P-T space. Resulting conditions for high T and high P were 4845 ± 4 K and 2.95 ± 0.015 GPa; low T and high P were 3280 ± 2 K and 2.89 ± 0.021 GPa; high T and low P were 4846 ± 4 K and 0.12 ± 0.027 GPa; and low T and low P were 3278 ± 3 K and 0.00 ± 0.015 GPa. These conditions will allow us to generally identify the changes associated with T along an isotherm (and nearly with P along an isobar).
Figure 2. Excess energy vs. composition (Ab mol%). The red squares are the results of the simulation, and the red line is the linear mixing line between the shown end-member values. (Note the top right panel only goes to $X_{Ab} = 80$ mol%).

In Figure 2 we show the deviation from ideal mixing of $E$. Excess $E$ is defined as the difference between $E$ (from the MD-results) and $E$ interpolated from ideal mixing (red line). If mixing were ideal across the join, then all data would plot on the zero line in Figure 2. At high $T$ and low $P$, the largest deviation from ideality occurs at $Ab_{40}$, which is 8.3 kJ/mol above the value predicted by linear (ideal) mixing. The largest negative deviation occurs at high $T$ and high $P$, with excess energy near -3.1 kJ/mol.

For 4846 K and 0.12 GPa (high $T$ and low $P$), there is a sharp positive deviation from ideality up to $Ab_{40}$, which is muted at lower $T$ (3278 K and 0.00 GPa). The low $T$ and low $P$ conditions have an asymmetric positive deviation from ideality (for excess $E$) centered at $Ab_{40}$ whereas the higher $P$ (low $T$) shows this asymmetry centered at $Ab_{60}$. At high $P$ and high $T$, an asymmetric negative deviation is centered at $Ab_{60}$. 
Figure 3. Excess volume vs. composition (Ab mol%). The red squares are the results of the simulation, and the red line is the linear mixing line between the shown end-member values. (Note the top right panel only goes to X_{Ab} = 80 mol%).

Figure 3 shows the $V$ of mixing represented as the excess volume (difference from linear [ideal] mixing value) vs. composition. At high $T$ and low $P$, the sharp increase in excess volume with increasing Ab mol% abruptly drops between Ab$_{40}$ and Ab$_{60}$ from about 0.75 to -1.4 cm$^3$/mol. The three other state points shown in Figure 3 have very near-ideal mixing for excess volume along the plagioclase join. The lower $P$ shows more deviation from linearity than the high $P$ values. At low $T$ and low $P$, the excess volume seems to follow an asymmetric cubic function across the join with near-linearity at $X_{Ab} > 60$ mol%.

The general positive and negative deviation trends are consistent between excess energy and excess volume, although $E$ of mixing shows a larger deviation than $V$. It is noteworthy that the high $T$ and low $P$ conditions show the strongest deviation from ideality (Fig. 2 and 3). Perhaps due to the very mobile state of the system at extreme $T$ and low $P$, the material behaves more like a gas than a liquid. For this high $T$ and low $P$ condition, we anticipate completing the
simulation work for the missing composition (Ab$_{80}$An$_{20}$) and performing added MD simulations near the large disparities around Ab$_{30}$ and Ab$_{50}$ at these conditions. Data for those “gaps” in our mixing figures would help confirm the present conclusions, or they may lead to extra questions worth pursuing.

There are large deviations from ideal mixing at low $T$ for the excess energy (and less pronounced for excess volume). The maximum peaks at low $T$ for excess energy may be another area of future focus. Added simulations are also needed to complete the high $T$ and high $P$ compositional join, too.

While more work is required to finish this project, these results provide a base-line sampling of how mixing properties behave at high $T$ and high $P$ for liquid plagioclase feldspar. The positive and negative deviations from linearity mixing in both $E$ and $V$ suggest the assumption of ideal mixing may not be appropriate for these conditions. It remains to be seen if other thermodynamic properties follow similar patterns across the plagioclase mixing join at high $T$ and $P$. 
REFERENCES
