Molten salt reactors (MSRs) are a promising nuclear reactor concept that are of increasing interest to reactor vendor companies. These reactor concepts, in which fuel and/or fertile material are dissolved directly into a halide salt coolant, have several significant benefits over traditional light water reactor (LWR) concepts that are in operation today. For example, MSRs are capable of producing medical radioisotopes and electricity simultaneously in large amounts. In addition, molten salt thorium-fueled reactors can be designed to prevent proliferation of weaponizable material, are inherently safe and thus eliminate the risk of events such as meltdown accidents, and can be designed to avoid producing long-lived transuranic nuclear waste.

Molten salt thorium-fueled reactors are not new, and the concept has already been validated through a test reactor at Oak Ridge National Laboratory [2]. The Molten Salt Reactor Experiment (MSRE) operated from 1965 to 1969, with a dual focus of proving the feasibility of the concept and the potential for fuel breeding. This experiment effectively validated both concepts [2, 3], though no effort was made to extract medical and research isotopes. For many years, little work was done to evaluate isotope generation or even chemical processing of MSR fuel salts. In the recent past, growing interest in MSR technology has revived efforts to look at fuel salt processing. For example, one study investigated the potential of reprocessing fission products (FP) from the MSR coolant [11]. The focus was on reprocessing the fuel salt to facilitate an improved core for the molten salt breeder reactor (MSBR). Though some follow-up work explored the potential for MSR coolant salt reprocessing [12], substantial work is still required to fully understand the challenges of fission product separation.

Recent studies have indicated that one of the most significant fundamental topics that must be established prior to the licensing of a commercial MSR is the structure and speciation in the molten salt coolant with and without fission products [13], as this information plays a key role in developing transport and thermodynamic models. This challenging research focus is exacerbated by the fact that in a molten salt reactor there are over 50 elements dissolved (fission products, fuel, and transuranic elements) in the coolant at any given moment [13]. Due to the sheer volume of ion-ion interactions present in such a mixture, it is essential that a method for determining the local structure of halide salts with and without the presence of fission products be developed. Further, gaining insight into the speciation and complexation of the ions in the melt will provide a basis for understanding numerous basic properties such as viscosity, thermal conductivity, activity coefficients, and more, supporting the goal of developing reliable theoretical simulation models used for optimizing MSR systems.

In this work, we present pair distribution function techniques, corrosion potential, ion-ion interaction potentials and subsequent impacts on thermophysical properties of the coolant, and the structure and speciation of the fission products in the salt.

The Structure of Molten FLiNaK

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A high-pure and chemically isolated sample of FLiNaK was produced for the neutron scattering experiment using the following method. Individual components of LiF, NaF, and KF in a 46.5:11.5:42 mol% composition were dried in a vacuum oven for 6 hr at roughly 300 °C. The individual components were then passed into an anaerobic, anhydrous argon-filled glovebox where they were combined and melted at roughly 600 °C in a nickel crucible. This melt was then transported to the beamline using a vacuum furnace to access temperatures below and above the melting point were collected for a total integrated proton charge of 4 C and 1000 °C. A 1.63 g sample of FLiNaK was crushed into a powder in an argon glove box near the beamline and loaded into a standard vanadium sample can. The sample was then transported to the beamline in a vacuum jar and loaded into the furnace chamber, which was subsequently evacuated. The total duration of the exposure of the sample can to air was less than 30 s. The total scattering structure function \( S(Q) \) was obtained from the neutron time-of-flight data at various temperatures following standard data reduction protocols, including absolute normalization using a vanadium rod for reference. Scattering patterns obtained at temperatures below and above the melting point were collected for a total integrated proton charge of 4 C and 12 C, respectively (approximately 1 and 3 hours, respectively). The suppression of the scattered intensity at low momentum transfer \( Q \) due to the large neutron absorption cross section of natural Li (arising from the \(^6\)Li isotope) was corrected empirically using a hydrogen-type Placzek correction fitted to the scattering pattern in the range of \( 1 < Q < 20 \) Å\(^{-1}\).

![Density of FLiNaK determined from the AIMD simulations in the present work (blue circles, with the solid turquoise line showing a linear fit) compared to experimentally estimated values (dashed lines) from An et. al \cite{21} and Powers et. al \cite{22}.](image)

The experimental pair distribution function (PDF) \( g(r) \) was generated for each total scattering pattern according to the relationship \cite{19}:

\[
g(r) = 1 + \frac{1}{2\pi^2 \rho_0} \int_0^{Q_{\text{max}}} Q[S(Q) - 1] \sin(Qr) dQ, \tag{1}
\]

where \( \rho_0 \) is the number of atoms per unit volume and \( Q_{\text{max}} = 15 \) Å\(^{-1}\), estimated to be the largest value of \( Q \) for which meaningful scattering signal in the molten state remained larger than statistical noise in the data. For scattering patterns collected at temperatures below the melting point, the reduced PDF \( G(r) = 4\pi r \rho_0 [g(r) - 1] \) was also generated with \( Q_{\text{max}} = 20 \) Å\(^{-1}\). Fits to \( G(r) \) were performed using the program PDFgui \cite{20}.

AIMD simulations based on density functional theory (DFT) were performed using the CP2K software package \cite{24}. Calculations utilized the Perdew-Burke-Ernzhof (PBE) exchange-correlation functional \cite{25}, a form of general gradient approximation (GGA). The Gaussian and plane waves method (GPW) was used, in which wave functions are represented by atom-centered Gaussian orbitals and the electron density is represented by plane waves \cite{26}. Within this framework, all atoms were modeled using DZVP-MOLOPT-SR-GTH basis sets \cite{27} with core electrons treated with Goedecker-Teter-Hutter pseudopotentials \cite{24} \cite{27}.

Simulations were performed in the NPT ensemble, with pressure held at atmospheric pressure through the method of Martyna et al. \cite{28} and temperature held constant through the Nose-Hoover thermostat \cite{29}. All simulations had a time step of 0.5 fs. As the NPT ensemble allows density to fluctuate, density was here used to define equilibration, with the simulation cell considered equilibrated if the average density over a period of 5 ps (10,000 steps) is within 2% of the average density of the next 5 ps. The NPT ensemble is sensitive to relatively small errors in calculated energy, and so

![FIG. 1. Density of FLiNaK determined from the AIMD simulations in the present work (blue circles, with the solid turquoise line showing a linear fit) compared to experimentally estimated values (dashed lines) from An et. al \cite{21} and Powers et. al \cite{22}.](image)
high energy cutoffs were required for predicted densities to converge: 2000 Ry for the plane-wave energy cutoff, and 120 Ry for the relative cutoff, which in the GPW method corresponds to the planewave cutoff of a reference grid on which Gaussians are mapped. AIMD simulations in the NPT with high energy cutoffs are computationally expensive, but in this case were found to predict densities remarkably close to experiment. Fig. 1 shows density versus temperature determined from MD simulations (each data point representing an equilibrated simulation cell containing 50 FLiNaK atoms) and compared to experimental correlations from the literature \[21–23\]. The agreement is particularly good for the two most recent experimental studies \[21, 23\].

Notably, this agreement with experiment was achieved without including corrections for Van der Waals dispersion. When a cell containing 100 atoms of FLiNaK was simulated at 667 °C without dispersion corrections, the equilibrated density was found to be within 0.2% of the expected value at that temperature from experimental correlation reported by Chrenková et al \[21\] (well within the 2% margin of error of that correlation). When non-local Van der Waals corrections were included, the predicted density differed from the experimental correlation by 4%. Given that molten salts are dominated by relatively strong ionic forces, it is reasonable that Van der Waals corrections would not be strictly necessary to model molten salt behavior. That these corrections appear to significantly reduce accuracy may indicate that, when sufficiently high energy cutoffs are used while simulating molten salts, non-local Van der Waals corrections introduce artefacts making DFT calculations less accurate; however, further study is required to determine the extent of this effect. Regardless, dispersion corrections were not used in this study. The 100 atom FLiNaK simulation cell described here was also used to calculate radial distribution functions for comparison with neutron diffraction results.

We now present the results of our combined neutron total scattering and AIMD studies. In Fig. 2 we display the total scattering structure function \(S(Q)\) for molten FLiNaK at 467 °C (just above the melting point) and 980 °C (the highest temperature attained during the experiment). The scattering patterns are offset vertically for clarity. The patterns are typical for liquids. Since no long-range order is present in the molten state, there are no sharp Bragg peaks in the pattern. However, there are very clear diffuse features in \(S(Q)\) out to approximately 12 - 15 Å\(^{-1}\), which arise from well-defined short-range ionic correlations that persist in the molten state. The features in the scattering pattern become increasingly broad and weak as the temperature increases from 467 °C to 980 °C, indicating that the short-range correlations become less well-defined at higher temperatures. At lower temperature in the solid state (data not shown), sharp peaks are present, indicating crystalline order.

A more intuitive view of the structure of FLiNaK in both the solid and molten states can be gained by examining the real-space PDF patterns. Peaks in the PDF correspond to ion-ion pairs separated by the value of \(r\) at which the peak is found, with the sign and size of the peak determined by the number of ion pairs separated by that distance and the product of the neutron scattering lengths of the corresponding ions. To examine the evolution of the structure through the melting point, we plot the PDF \(g(r)\) at several temperatures in Fig. 3. At 25 °C, well-defined features in the PDF persist over the entire displayed range, as expected for the long-range order in the solid state. The first peak in \(g(r)\) at 25 °C is negative and centered around \(r = 2.0\) Å, corresponding to the first nearest neighbor Li-F peak. Li has a negative scattering length and F has a positive scattering length.
so all Li-F peaks are negative. The nearest-neighbor Na-F and K-F peaks are both positive due to the positive scattering lengths of Na and K, but they are less clearly visible in the pattern. From fits to the reduced PDF \( G(r) \) at 25 °C (not shown), the nearest-neighbor Na-F peak is expected to occur at 2.32 Å. There is indeed a small feature in \( g(r) \) at this position, but the low concentration of NaF greatly reduces its magnitude. The nearest-neighbor K-F peak is centered around 2.67 Å, resulting in significant overlap with the first Li-Li and F-F peaks at 2.85 Å from the LiF component. As the temperature is raised from 25 °C to 433 °C, the peaks in the PDF patterns become increasingly broad due to thermal vibration, but well-defined features persist over the full \( r \) range.

The PDF patterns change dramatically in the molten state, as seen in Fig. 3 for the data collected at 467 °C and above. A strong negative peak is still clearly visible at low \( r \), indicating that the Li-F nearest neighbors are still well correlated. Interestingly, this first negative peak shifts from 2.0 Å in the solid state to 1.8 Å in the molten state, demonstrating that the strong attraction between Li\(^+\) and F\(^-\) results in a shorter average ionic bond in the molten state than in the solid state. A similar effect has been observed in other molten salts such as NaCl \([30]\). On the basis of the AIMD simulations to be described later, we associate this shortening of the Li-F bond to a reduction of the coordination number from 6 in the solid state to 4 in the molten state. The nearest-neighbor Na-F and K-F peaks are included in the broad positive peak observed between approximately 2 Å and 3.5 Å, along with contributions from various other ion pairs. Two additional weak and broad peaks centered around 5.5 Å and 8 Å can also be observed in Fig. 3 for the data collected at 467 °C, 500 °C, and 600 °C, but beyond approximately 9 Å, any remaining features in the PDF are comparable to the noise level. At 980 °C, the broad peak centered on 8 Å is not clearly resolvable, indicating that the non-random correlations on this length scale have been significantly weakened with increasing temperature.

We now turn to the AIMD simulations to extract more detailed information about the local structure and interactions in molten FLiNaK. After a given simulation converges, the ionic configurations can be averaged over a suitable period of time (40 ps in this case) and used to calculate the partial PDFs for each distinct type of ion-ion pair. These partial PDFs can then be summed together using the concentrations and scattering lengths as weights to generate the total PDF for comparison with the experimental PDF. Ideally, one could obtain the partial PDFs directly from the experimental data by conducting equivalent measurements on several different samples with different levels of isotopic enrichment \([10,17]\), but this is an expensive procedure that is beyond the scope of the present work. Fortunately, the negative scattering length of Li is useful for distinguishing Li correlations from others, which partially compensates for the lack of isotope-dependent data.

The calculated PDF determined from the AIMD simulation of FLiNaK at 667 °C, a typical nuclear reactor operating temperature, is compared to the experimental PDF measured at 600 °C in Fig. 4(a). The experimental data and calculated PDF are shown as the black symbols and red curve, respectively. As seen in the figure, the calculated PDF provides an excellent match to the data over the first 8.35 Å, confirming that the AIMD simulations provide an accurate picture of the structure of molten FLiNaK. (b) The partial PDFs \( g_{\alpha\beta} \) extracted from the AIMD simulations, displayed over the first 5 Å. Note that these partial PDFs have not been weighted by the concentrations or scattering lengths of the ions.

FIG. 4. (a) Observed PDF and calculated PDF determined from AIMD simulations of FLiNaK. The excellent agreement demonstrates that the simulations provide an accurate picture of the structure of molten FLiNaK. (b) The partial PDFs \( g_{\alpha\beta} \) extracted from the AIMD simulations, displayed over the first 5 Å. Note that these partial PDFs have not been weighted by the concentrations or scattering lengths of the ions.
shifted to shorter $r$ most significantly. This is consistent with the observed shift in the negative Li–F peak across the melting point in Fig. 3(b), demonstrating that the simulations accurately capture this effect. Subsequent partial PDFs are significantly broader, indicating that the corresponding correlations are more widely distributed in real space.

Nearest-neighbor (NN) peak distances and coordination numbers extracted from the AIMD simulations are shown for the most important ion pairs in Table I along with the results from an earlier x-ray scattering experiment [31]. The NN peak distances are in excellent quantitative agreement between the two studies. On the other hand, the coordination numbers show the same qualitative trend, but significant quantitative discrepancies exist. We note that the earlier x-ray study had much more limited sensitivity to the light elements in FLiNaK than the present neutron study, and that their method of determining the coordination numbers considered only the NN correlations of the three unlike-ion pairs and $F^––F^–$ and $K^––K^–$, ignoring all others. For these reasons, we consider the coordination numbers extracted from the present AIMD simulations to be more reliable.

The results presented here provide a crucial contact point between theory and experiment. The success of the AIMD simulations in describing the experimental PDF data demonstrates that we have an appropriate model for FLiNaK, which until now has been lacking a sound experimental basis. Detailed structural information from the simulations can therefore be extracted and used confidently for further theoretical and experimental work. Specifically, this work sets the stage for future studies that use the AIMD-predicted structure to explore solution chemistry and the solution complexes that form around fission products, providing direct insight into the behavior of the system under operating conditions in a molten salt reactor.

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### Table I

| NN peak (Å) | Coordination Number |
|-------------|---------------------|
| AIMD Exp. | AIMD Exp. |
| Li$^+$–F$^–$ | 1.84 | 1.83 | 4.00 | 3.3 |
| Na$^+$–F$^–$ | 2.20 | 2.18 | 5.42 | 3.8 |
| K$^+$–F$^–$ | 2.60 | 2.59 | 7.12 | 4.0 |
| F$^–$–F$^–$ | 3.10 | 3.05 | 11.2 | 8.9 |

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