Supplemental Information:

Integration of a Structural Coherence Model with a Semi-Universal Machine Learning Interatomic Potential to Predict Molten Salt Thermal Conductivity

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1 Molecular Dynamics Simulations

This section presents the state of the art of existing MD Simulation methods for predicting thermal conductivity. It includes equilibrium MD (Green-Kubo) as well as non-equilibrium MD (NEMD and RNEMD).

1.1 Green-Kubo (EMD)

The Green-Kubo method is an Equilibrium MD method where thermal conductivity is derived by tracking the microscopic fluctuations of heat flux within the space, using a Heat Current Auto-Correlation Function (HCACF). By integrating the HCACF from 0 to infinity, the macroscopic thermal conductivity can be predicted by quantifying

how long microscopic heat flux trajectories survive through the simulation space before dissipating in the melt.

Without a temperature gradient, the simulations can be an order of magnitude smaller than non-equilibrium methods, which require a large enough space for the gradient to develop. A Green-Kubo simulation exhibits negligible difference between 500-6400 atom sized spaces [**?**]. And while deriving an exact analytical solution for the local heat flux was difficult for MLIPs, recent advances in automatic differentiation have improved compatibility between Green-Kubo and MLIPs [**?**].

However, the Green-Kubo method struggles to converge on similar values over multiple trials and therefore requires a large number of trials which are averaged at the end [**? ?**]. Convergence problems occur because the HCACF is slow and noisy to converge, due to the integral accumulating error over the long time-scale and obfuscating the true value [**?**]. The Green-Kubo method's fatal weakness when considering candidates for predicting highly complex salt mixtures is that its derivation becomes much more complicated when applied to multi-component molten salts. This is because the heat current is associated with mass transport, and in order to calculate intrinsic thermal conductivity, the heat transfer from this mass transport must be accounted for, which results in a computationally expensive partial enthalpy addition to each timestep of the simulation [**?**].

1.2 Non-Equilibrium Molecular Dynamics (NEMD)

The NEMD Method consists of two types: Direct and Evans-Gillan (Homogoneous). The Direct method operates by creating a temperature gradient across the simulation space with thermostats, usually Nose-Hoover or Langevin. One boundary condition of the space is set as the hot side, and the other boundary condition as the cold side. Thermal conductivity is derived by measuring the heat flux through the space between the thermostats, and dividing it by the temperature gradient according to Fourier's Law [**?**].

While theoretically straight-forward and analogous to Fourier's Law, the physical damping that occurs at boundary conditions due to the thermostats results in extremely large scaling requirements for predicting bulk properties [**?**]. Evans-Gillan's method (cite gillans and evans) addresses this damping by replacing thermostats with a field that affects each particle throughout the simulation individually, by adjusting the equations of motion. While fixing damping, adjusting the equations of motion is highly complex and requires adjustment to the low level parameters within the MD software. Recent advancements in modern MD packages have made these adjustments significantly easier to integrate [**? ?**].

1.3 Reverse Non-Equilibrium Molecular Dynamics (RNEMD)

The second of the non-equilibrium methods, reverse non-equilibrium molecular dynamics (RNEMD), operates by simulating heat flux and recording change in temperature [**?**]. This is achieved by dividing the simulation space into small slices, or "bins," then creating a temperature gradient by setting cold and hot zones. A bin at one end is set as cold, and the bin in the middle is set as hot. Because periodic

boundary conditions are used, the bin at the other end is also a cold bin because it is as if it adjacent to the other cold end. To simulate the temperature gradient, the cold and hot zones are periodically scanned at a set time interval. The atom with the highest velocity in the cold bin, and the atom with the lowest velocity in the hot bin are identified, then switched instantaneously by replacing their velocity vectors with each other. This allows for momentum and kinetic energy to be conserved, which pairs cleanly with the NVE, microcanonical ensemble [**?**].

Once the temperature gradient is established, the simulated heat flux works against the fluid's intrinsic conductivity, and thermal conductivity can be calculated by integration of Fourier's law. Thermal conductivity, k, is set equal to total kinetic energy moved by the RNEMD velocity swaps, ΔQ, divided by twice the cross sectional area, A, (due to the bi-directional flow of heat with the hot zone placed between cold zones), the total time interval Δt, and the spatial temperature gradient $\frac{\Delta T}{\Delta z}$:

$$k = \frac{\Delta Q}{2A\Delta t(\frac{\Delta T}{\Delta z})} \tag{1}$$

The RNEMD method has a significant advantage over both Green-Kubo and NEMD methods because the simulated heat flux is explicitly known. This eliminates the complexity associated with partial enthalpies and deriving a field that simulates a temperature gradient. By calculating thermal conductivity using only kinetic energy and local temperature, RNMED positions itself as a uniquely compatible candidate for integration with MLIPs that struggle with stress tensors but easily and accurately measure kinetic energy and temperature. This simplicity means that it also converges much more quickly than the Green-Kubo method, with similar accuracy [**?**].

The largest weakness that the RNEMD method has is that of finite-size effects. Because the dominant form of heat transfer in molten salts is vibrational phonons, unless the distance between the hot middle slabs and cold end slabs is much larger than the mean free path of the phonon, boundary slabs truncate the vibrational modes, artificially lowering the simulation's thermal conductivity prediction ([**?** **?** **?**]. As well as accounting for finite-size effects, the RNEMD requires careful accounting of the velocity swapping rate. If the rate is too high, impossibly high temperature gradients will result in non-linear responses that disqualify Fourier's law as an accurate approximation [**?** **?**].

Despite the difficulties of finite-size effects and velocity swapping rates associated with RNEMD, it is widely used and extremely robust due to its simplicity. While previously limited to AIMD and computationally cheaper empirical models like PIM, RIM, and BMHTF, the advent of MLIP models that achieve near DFT-level accuracy at a fraction of the computational cost allows for the scale RNEMD requires to avoid phonon scattering effects.

Although with a large enough supercomputer cluster it is theoretically possible, the large simulation size of the RNEMD method is restrictive in the context of predicting thermal conductivity for the nearly 800 molten salts listed in ORNL's MSTDB without recorded predictions [**?**]. As a result, Kinetic Theory Models have also been

investigated as potentially computationally light methods for predicting a wider range of molten salt mixtures [**?**].

2 SOFT Reactor 10th Year

To investigate high entropy salts, two 8-component salts were formulated to mimic ORNL's SOFT reactor's molten salt composition after 10 years of operation, with a key limitation being the cations available in the SuperSalt machine learning interatomic potential (MLIP). The composition is recorded for the 1st, 10th and 30th year of operation [**?**]. In order to simulate fission products, certain cations were replaced with cations from the SuperSalt potential.

Using the SOFT reactor data in Table 4 of ORNL's "Roadmap for thermal property measurements of Molten Salt Reactor systems" [**?**], the 10th year composition was selected and imitated by replacing actinides, lanthanides, refractories, and transition metals with ions available from the SuperSalt potential. The SOFT reactor data consisted of NaCl, UCl_3, $PuCl_3$ as the fuel, and Xe, Mo, Zr, Cs, Ru, Nd, Pd, Ce, Ba, Rh, Tc, La, Pr, Sm, Sr, Te as fission products. According to the original report by Taube et al. [**?**], the reactor was run at 650 $C°$, so the MD simulations of the ISM model were performed at 923 K. The overall molar composition of the salt after 10 years of operation is shown in Table 1

Table 1: SOFT Composition at 10th year of operation

Constituent	**Mol %**	**Type**	**Constituent**	**Mol %**	**Type**
NaCl	50.25	Fuel	$CeCl_3$	0.27	Waste
UCl_3	39.76	Fuel	$BaCl_2$	0.16	Waste
$PuCl_3$	5.39	Fuel	$RhCl_3$	0.16	Waste
Xe	0.57	Waste	$TcCl_4$	0.14	Waste
$MoCl_3$	0.55	Waste	$LaCl_3$	0.14	Waste
CsCl	0.50	Waste	$PrCl_3$	0.13	Waste
$ZrCl_4$	0.49	Waste	$SmCl_3$	0.10	Waste
$RuCl_3$	0.47	Waste	$SrCl_2$	0.09	Waste
$NdCl_3$	0.41	Waste	$TeCl_4$	0.07	Waste
$PdCl_2$	0.36	Waste			

Two strategies were used to simulate the SOFT reactor salt. The difference between the methods was in the imitation of actinides and lanthanides. Both methods replaced transition metals (Ru, Pd, Rh) with Zn in order to mimic covalent bonding and tetrahedral complexes. Refractory metals and metalloids (Mo, Tc, Te) were replaced with Zr. Xe as a noble gas could not be replaced.

2.1 Method 1: Mg^{2+} and Ca^{2+} Substitution:

Method 1 replaces actinides with Mg to match high charge density, and lanthanides with Ca to match ionic radius. Mg's low v_s also drops the thermal conductivity, which mimics actinides' effect in salt mixtures [**?**]. Although this method successfully drops

the thermal conductivity, the substitution of actinides with oxidation numbers of +3 with divalent cations results in fewer chloride ions in the melt, which changes the composition. The resulting composition of this substitution method is shown in Table *make table*

Table 2: Molar percent composition and component classification of the Mg simulated surrogate molten salt mixture.

Compound	Mol %	Type
NaCl	50.54	Fuel / Carrier Salt
$MgCl_2$	45.41	Fuel (Actinide Surrogate)
$ZrCl_4$	1.27	Fuel (Metalloid & Refractory Surrogate)
$CaCl_2$	1.07	Waste (Lanthanide Surrogate)
$ZnCl_2$	0.98	Waste (Transition Metal Surrogate)
CsCl	0.49	Waste (Fission Product)
$BaCl_2$	0.15	Waste (Fission Product)
$SrCl_2$	0.10	Waste (Fission Product)

2.2 Method 2: Mg^{2+}-Zn^{+4} and Ca^{2+}-Zn^{+4} Substitution:

The second method replaces actinides and lanthanides with $MgCl_2$-$ZrCl_4$ and $CaCl_2$-$ZrCl_4$. By replacing two actinide or lanthanide ions with a Zr^{+4} and divalent cation (+2), the average charge (+3) is matched, allowing for a closer overall match in composition to the original salt. Zr has been used as a surrogate to represent actinides in the +4 oxidation state [**?**] and contributes to the formation of networks which is an observed characteristic of actinide-bearing molten salts [**?**]. The resulting composition of this substitution method is shown in Table 3.

Table 3: Molar percent composition and component classification of the Mg-Zr simulated surrogate molten salt mixture.

Compound	Mol %	Type
NaCl	50.54	Fuel / Carrier Salt
$ZrCl_4$	24.51	Fuel (Actinide Surrogate)
$MgCl_2$	22.71	Fuel (Actinide Surrogate)
$ZnCl_2$	0.98	Waste (Transition Metal Surrogate)
$CaCl_2$	0.54	Waste (Lanthanide Surrogate)
CsCl	0.49	Waste (Fission Product)
$BaCl_2$	0.15	Waste (Fission Product)
$SrCl_2$	0.10	Waste (Fission Product)

References

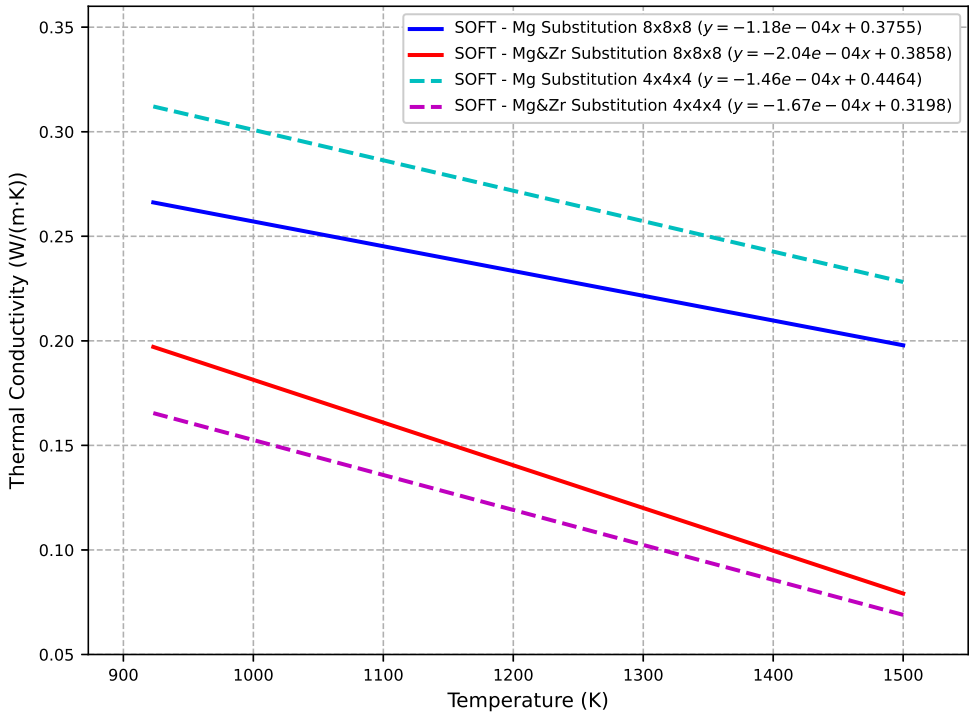

Fig. S1: SOFT reactor 10th year salt predictions, with a 4x4x4 system compared to a 8x8x8 system. The increase in size appears to have a significant effect on the results, indicating that for highly complex salts with trace elements such as Ba, Sr, and Cs, scaling the simulation size to include them is necessary.