Automated Parameterization of Polarizable Force Fields for Molten Salts via Genetic Algorithms

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1. Introduction

Recent developments on efficient energy conversion, such as those in nuclear reactors or solar power plants, have sparked a renewed interest in using molten salts for heat transfer, energy storage, and nuclear fuel waste pyroprocessing applications [1–3]. To this end, molten salts require excellent thermophysical and transport properties.

Since experiments can be difficult and expensive, one method that can be used to provide insights into molten salt systems is the use of molecular dynamics (MD) simulations [3,4]. Classical MD (CMD) simulations are a powerful simulation methodology that can be used to analyze the motions of atoms and molecules; providing a view of the dynamic "evolution" of the system. However, the accuracy of CMD remains a major hurdle in studying molten salts. To this day, very few CMD force fields, such as those by Salanne et al., exist [3].

Hence for this purpose, we employ the use of genetic algorithms (GAs) to develop force field parameters for the polarizable ion model (PIM) for the popular LiCl, KCl, and LiCl-KCl (58.8% mol LiCl) molten salts [5]. From the results reported herein, it was observed that the GA was very efficient, and once run, the GA automatically determines the optimum parameter set.

2. Methods

2.1 Genetic algorithm

For details regarding the GA methodology, please refer to our previous study, which gives a thorough explanation of the GA protocols [6]. To generate the initial population, we used the parameters from Salanne et al. [3]. At the beginning of the optimization, an initial population is generated by randomly selecting parameters within 10% variance of the Salanne et al. model.

Traditionally atom-wise parameters, for example, Li-Cl, Cl-Cl, or K-Li, are parameterized separately. However, this results in a large number of optimizable parameters. Hence, we optimized the Li-Li, K-K, and Cl-Cl terms and then obtained the force field parameters for the remaining interactions using mixing rules [7,8]. The LiCl, KCl, and LiCl-KCl (58.8% mol LiCl) simulations are then performed in parallel using the same force field parameters. The fitness function employed in this work employed the use of experimental densities for LiCl and KCl, and LiCl-KCl (58.8% mol LiCl) [9], and the diffusion coefficients for LiCl and KCl [10]. The functional form of the fitness function was the same as used in our past work [6].

2.2 Simulation protocols

The system for the CMD simulations consisted of 200 atoms for the LiCl and KCl systems. While the LiCl-KCl (58.8% mol LiCl) system consisted of 60 Li, 42 K, and 102 Cl atoms. Unless stated otherwise, All CMD simulations were performed using the CP2K package at 1400 K and 1 atm (at NPT) [11]. The temperature and pressure were controlled by the Nosé–Hoover thermostat and barostat with relaxation times of 0.1 and 1.0 ps, respectively. Equations of motion were integrated with a time step of 1 fs. The initial simulation box was generated using the Packmol software and was used as the starting structure for each generation [12]. The system was first equilibrated for 500 ps; which was followed by a 1000 ps production run to calculate the physical properties.

First-principles MD (FPMD) calculations were conducted using the hybrid Gaussian and Plane Wave density functional implemented in the CP2K/Quickstep program [11]. The valence electrons were described by the molecularly optimized double-ζ basis set (MOLOPT-DZVP-SR-GTH) and the Perdew–Burke–Ernzerhof functional, whereas the core electrons were treated with the Goedecker–Teter–Hutter (GTH) pseudopotentials. A total of two parallel FPMD runs were conducted for each system and each FPMD run was conducted for 100 ps. Initial configurations for the FPMD simulations were taken from random CMD snapshots using the Salanne et al. model. The number of atoms in the systems were the same as the CMD simulations. FPMD simulations were conducted at 1033, 1212, and 860 K for LiCl, KCl, and LiCl-KCl (58.8% mol LiCl), respectively. The remaining MD protocols were the same as the CMD.

3. Results and Discussion

3.1 Temperature dependence of densities and diffusion coefficients

To evaluate the performance of the GA-derived parameters, we compare the physical properties obtained from the GA-derived parameters and the model developed by Salanne et al. to experimental results Figs. 1-3).

From Figs. 1-3, it can be seen that our GA-derived parameters perform significantly better than the model proposed by Salanne et al. In general when using the GA force field, it is possible to reasonably reproduce both the thermodynamic and dynamic properties in a wide temperature range. This signifies the efficacy of the GA methodology described in this study, which eliminates the need for manually varying the force field parameters to reproduce the experimental measurements.

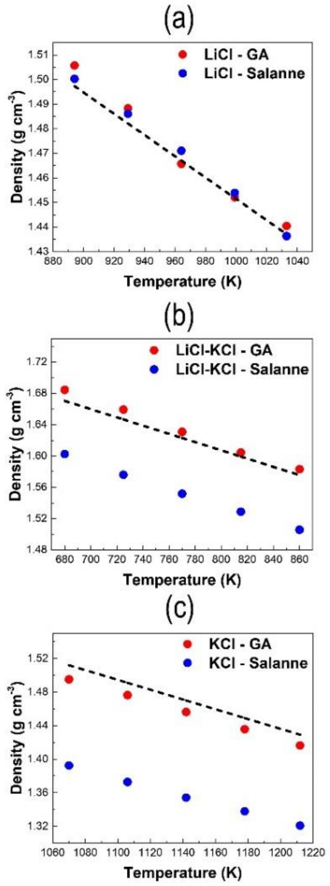

Fig. 1. Density of (a) LiCl, (b) KCl, and (c) LiCl-KCl (58.8% mol LiCl) at different temperatures using the GA-derived parameters and previously developed parameters by Salanne et al. compared to experimental results (black dashed line).

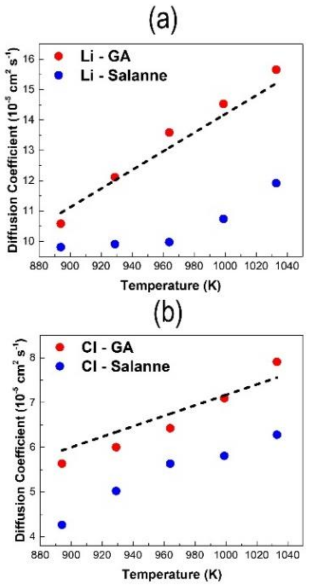

Fig. 2. Diffusion coefficients of (a) Li and (b) Cl in LiCl at different temperatures using the GA-derived parameters and previously developed parameters by Salanne et al. compared to experimental results (black dashed line).

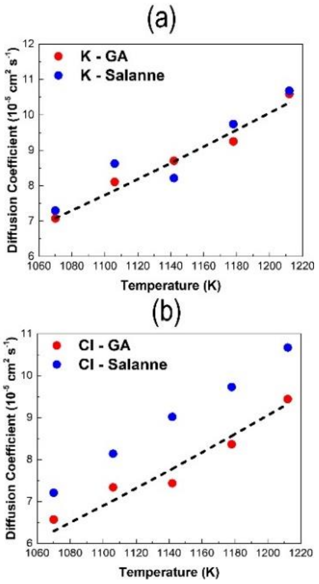

Fig. 3. Diffusion coefficients of (a) K and (b) Cl in KCl at different temperatures using the GA derived parameters and previously developed parameters by Salanne et al. compared to experimental results (black dashed line).

3.2 Radial distribution functions

The GA-derived parameters are further evaluated by analysis of the microstructures present in the system. The most obvious way to study the local organization of any system is the analysis of the radial distribution functions (RDFs). Figs. 4-6 illustrates the RDFs from CMD using the GA-derived parameters and FPMD simulations for molten LiCl, KCl, and LiCl-KCl (58.8% mol LiCl) at 1033, 1212, and 860 K, respectively. From Figs. 4-6, it is evident that the CMD can reproduce the FPMD results to quite a reasonable extent.

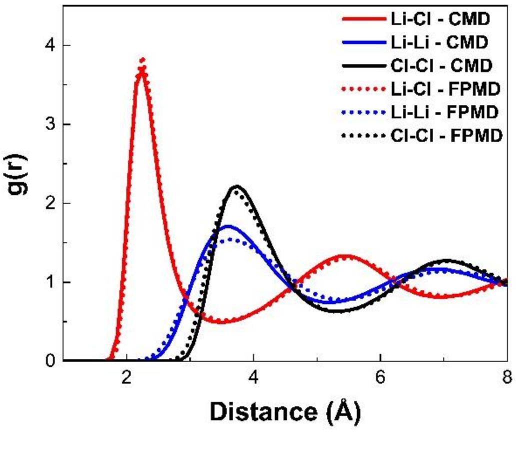

Fig. 4. RDFs for molten LiCl (at 1033 K) from CMD using the GA-derived parameters (solid lines) and FPMD (dotted

lines).

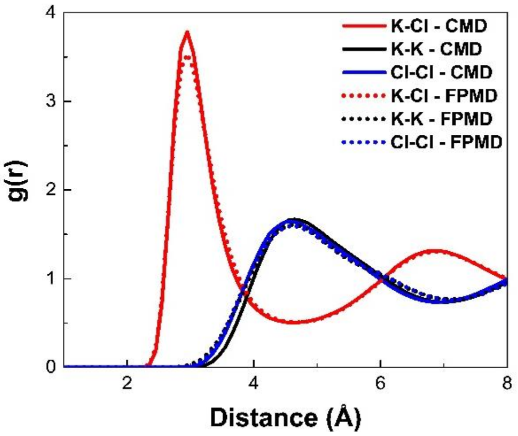

Fig. 5. RDFs for molten KCl (at 1212 K) CMD using the GA-derived parameters (solid lines) and FPMD (dotted lines).

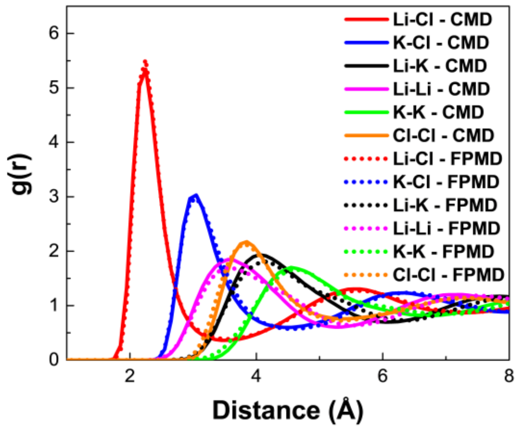

Fig. 6. RDFs for molten LiCl-KCl (58.8% mol LiCl) (at 860 K) CMD using the GA-derived parameters (solid lines) and FPMD (dotted lines).

3. Conclusions

The GA-derived parameters are not only able to reasonably reproduce experimental physical properties over a wide temperature range, but also structural characteristics from first-principles MD. The force field developed herein allows for a promising way to accurately simulate molten salts. Future studies will extend the methodology presented in this work to other molecular systems, opening up new avenues in the development of force fields for molten salts.

REFERENCES

[1] J. Serp, M. Allibert, O. Beneš, S. Delpech, O. Feynberg, V. Ghetta, D. Heuer, D. Holcomb, V. Ignatiev, J.L. Kloosterman, L. Luzzi, E. Merle-Lucotte, J. Uhlíř, R. Yoshioka, D. Zhimin, The molten salt reactor (MSR) in generation IV: Overview and perspectives, Prog. Nucl. Energy. 77 (2014) 308–319.

[2] U. Pelay, L. Luo, Y. Fan, D. Stitou, M. Rood, Thermal energy storage systems for concentrated solar power plants, Renew. Sustain. Energy Rev. 79 (2017) 82–100.

[3] M. Salanne, C. Simon, P. Turq, P.A. Madden, Calculation of activities of ions in molten salts with potential application to the pyroprocessing of nuclear waste, J. Phys. Chem. B. 112 (2008) 1177–1183.

[4] J. Song, S. Shi, X. Li, L. Yan, First-principles molecular dynamics modeling of UCl_3 in LiCl-KCl eutectic, J. Mol. Liq. 234 (2017) 279–286.

[5] J.B. Liu, X. Chen, J.B. Lu, H.Q. Cui, J. Li, Polarizable force field parameterization and theoretical simulations of $ThCl_4$–LiCl molten salts, J. Comput. Chem. 39 (2018) 2432–2438.

[6] A. Bin Faheem, J.Y. Kim, S.E. Bae, K.K. Lee, Efficient parameterization of intermolecular force fields for molecular dynamics simulations via genetic algorithms, J. Mol. Liq. 337 (2021) 116579.

[7] S. Saidi, N. Alharzali, H. Berriche, A combining rule calculation of the ground-state van der Waals potentials of the magnesium rare-gas complexes, Mol. Phys. 115 (2017) 931–941.

[8] K. V. Mirskaya, Combining rules for interatomic potential functions of Buckingham form, Tetrahedron. 29 (1973) 679–682.

[9] G.J. Janz, R.P.T. Tomkins, C.B. Allen, J.R. Downey, G.L. Garner, U. Krebs, S.K. Singer, Molten salts: Volume 4, part 2, chlorides and mixtureselectrical conductance, density, viscosity, and surface tension data, J. Phys. Chem. Ref. Data. 4 (1975) 871–1178.

[10] G.J. Janz, N.P. Bansal, Molten Salts Data: Diffusion Coefficients in Single and Multi Component Salt Systems, J. Phys. Chem. Ref. Data. 11 (1982) 505–693.

[11] T.D. Kühne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R.Z. Khaliullin, O. Schütt, F. Schiffmann, D. Golze, J. Wilhelm, S. Chulkov, M.H. Bani-Hashemian, V. Weber, U. Borštnik, M. Taillefumier, A.S. Jakobovits, A. Lazzaro, H. Pabst, T. Müller, R. Schade, M. Guidon, S. Andermatt, N. Holmberg, G.K. Schenter, A. Hehn, A. Bussy, F. Belleflamme, G. Tabacchi, A. Glöß, M. Lass, I. Bethune, C.J. Mundy, C. Plessl, M. Watkins, J. VandeVondele, M. Krack, J. Hutter, CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations, J. Chem. Phys. 152 (2020) 1–47.

[12] L. Martínez, R. Andrade, E.G. Birgin, J.M. Martínez, PACKMOL: A package for building initial configurations for molecular dynamics simulations, J. Comput. Chem. 30 (2009) 2157–2164.