

Review

Research Progress on the Application of FPMD in Molten Salt Electrolysis

Yilin Wang, Yanhong Jia, Benlin Yao , Yiqun Xiao and Hui He *

Department of Radiochemistry, China Institute of Atomic Energy, Beijing 102413, China; wangyilin0716@126.com (Y.W.); jiayanhong66@126.com (Y.J.); yaobenlin0855@126.com (B.Y.); xiaoyiqun@cnnmail.cn (Y.X.)

* Correspondence: hehui@cnnmail.cn

Abstract

The pyrometallurgical reprocessing of spent fuel developed by the United States is currently one of the most promising nuclear fuel reprocessing methods. The electroreduction, electrolytic refining, and electrodeposition processes involve electrochemical research in high-temperature molten chloride systems. In recent years, much progress has been made in simulating and studying molten-salt systems from a microscopic perspective using the first-principles molecular dynamics (FPMD) simulation technique. Using this method for simulation calculations is more conducive to analyzing the microscopic action mechanism and microscopic mechanism in the system from the atomic level and explaining the internal reasons for various electrochemical behaviors and phenomena. This opens up a new path for the study of molten-salt electrochemical systems. However, there are still a few systematic reviews of simulating work in first-principles computation. Therefore, this work summarizes the theoretical calculation work on molten-salt electrochemical systems of recent years, focusing on the research progress in computational aspects such as coordination properties, physical properties, and electrode behavior, which has good guiding value for the application of FPMD in molten-salt electrochemistry.

Keywords: first-principles molecular dynamics; coordination properties; molten-salt electrochemistry; chloride molten salts

1. Introduction

First-principles computation is a theoretical and computational chemistry method used to investigate and predict the properties of molecules and materials without relying on empirical or experimental input parameters. The method is grounded in the fundamental principles of quantum mechanics. Solving the Schrödinger equation describes the behavior of electrons in atoms, molecules, and condensed-phase materials. Using specific equations of motion, computers can calculate the trajectories of particles within the system, obtain their dynamic evolution paths, and analyze the transport and structural characteristics of individual components. The application of first-principles methods enables researchers to model experimental phenomena from a microscopic perspective, interpret complex electrochemical behaviors, and predict properties under extreme conditions [1–4]. Such methods are particularly suitable for molten-salt electrochemical studies involved in nuclear fuel pyroprocessing [5]. In typical chloride molten-salt systems, the operating temperature is maintained above 500 °C. Under such high-temperature environments, experimental measurements of fundamental physical and chemical parameters, including redox potentials



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of key elements, become extremely difficult due to technical limitations and radiological constraints [6,7].

First-principles computation, in contrast, allows investigations at the atomic level and can effectively compensate for the lack of experimental data. It helps researchers gain deeper insight into molten-salt systems and establish more comprehensive and integrated understandings [8]. Moreover, simulation calculations can be used to predict electrochemical behaviors of various components in high-temperature molten-salt electrolytes, rapidly generate large quantities of parameter data, and avoid complex radioactive operations. This review aims to summarize and provide an outlook on the latest developments and trends in computational studies of molten-salt systems, offering a comprehensive understanding of the field's history and achievements, and providing insights for further in-depth exploration and explanation of the electrochemistry of molten-salt systems.

2. Methodology of First-Principles Computation

As shown in Figure 1, since the 1950s, the number of studies on molten-salt electrorefining and its underlying mechanisms has increased steadily. Meanwhile, many key technologies related to molecular simulation calculations have developed rapidly and have been widely applied in this field. Based on the intrinsic differences in the descriptions of interparticle interactions, molecular dynamics methods can be mainly divided into two categories: *ab initio* molecular dynamics (AIMD) and classical molecular dynamics (CMD). AIMD is often referred to as first-principles molecular dynamics (FPMD). In CMD, the interactions between particles are described by empirical force fields, while in FPMD, interatomic forces are directly derived from quantum mechanical calculations, typically using density functional theory [9].

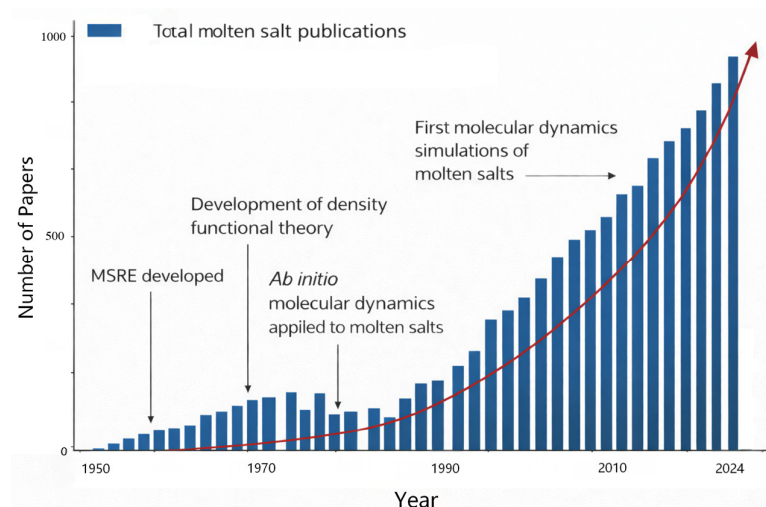


Figure 1. Schematic diagram showing the year-over-year increase in the number of papers published on molten-salt chemistry.

The theoretical foundation of first-principles computation dates back to 1926, when the Schrödinger equation was proposed, marking the beginning of quantum mechanics. The general form of the Schrödinger equation is as follows:

$$H\Psi = E\Psi, \quad (1)$$

where H is the Hamiltonian operator of the system, Ψ is the wave function, and E represents the total energy. Solving this equation yields the electronic structure and energy distribution of the system [10].

In the 1950s, the Hartree–Fock method initiated the era of quantum chemistry by providing approximate solutions to many-electron systems [11]. In the 1960s, Kohn and Hohenberg proposed the density functional theory (DFT), and the Kohn–Sham equations were developed to simplify complex many-electron problems into single-electron forms [12]. This greatly expanded the computational capability and applicability of first-principles methods.

With the rapid increase in computational resources after 2000, first-principles methods began to be applied to larger and more complicated systems such as nanomaterials, biomolecules, and functional materials. Widely used computational software packages—including VASP 6.0, Quantum Espresso 3.2, Gaussian 16, and ABINIT 10.0—have provided powerful tools for these studies [13–16].

Around 2020, machine learning techniques began to be integrated with first-principles calculations, forming a new interdisciplinary trend. The combination of machine learning potentials with molecular dynamics simulations has been demonstrated to be particularly useful for optimizing molten-salt compositions and predicting ideal mixtures for reactors. This emerging approach is expected to further enhance the safety and efficiency of molten-salt reactor systems and represents a highly promising research field [17–19].

3. Microscopic Structure Analysis of Molten Salts via First-Principles Methods

Among the structural information obtainable from FPMD simulations, the radial distribution function (RDF) is the most important. RDF describes the probability of finding another atom at a distance r from a selected reference atom under the assumption of uniform spatial distribution. From RDF curves, the local atomic arrangement and coordination structures in molten salts can be quantitatively analyzed [20].

Song et al. used classical molecular dynamics and FPMD to simulate molten-salt mixtures and predicted the differences in various properties of different elements in molten LiCl–KCl eutectic [21]. The simulated structure of molten LiCl–KCl–MCl_n mixture is shown in Figure 2. The structure was analyzed to obtain its RDF and compared with the literature values extracted from the experimental study, and many valuable results were obtained. For example, the positions of the first peaks of Ag⁺–Cl[−] and Cu⁺–Cl[−] obtained by neutron diffraction experiments of pure molten salt were 2.62 Å (773 K) and 2.34 Å (778 K), which are consistent with the FPMD simulation values of 2.572 Å and 2.167 Å [22,23]. Furthermore, the first peak positions of La³⁺–Cl[−], Ce³⁺–Cl[−], and U³⁺–Cl[−] in the X-ray diffraction of molten chloride are 2.85 Å (1150 K), 2.81 Å (1173 K), and 2.85 Å (1200 K), respectively, which are in good agreement with the corresponding FPMD simulation values of 2.812 Å, 2.770 Å, and 2.689 Å [24–26], as shown in Table 1. In addition, the first peak position of molten PuCl₃ was simulated to be 2.687 Å, which is also consistent with the literature value of 2.80 Å [27].

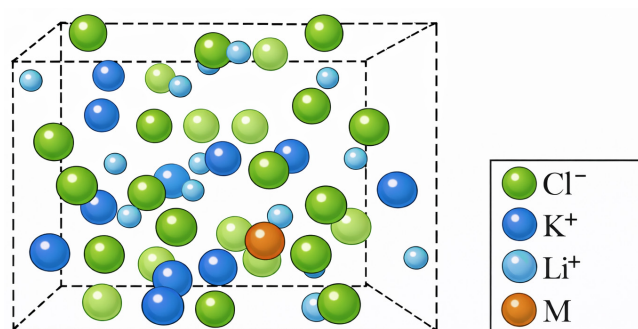


Figure 2. Schematic diagram illustrating the modeling of LiCl–KCl–MCl_n molten-salt mixture (M = La, Ce, U, or Pu).

Table 1. First peak positions of $M^{n+}-Cl^{-}$ in molten $LiCl-KCl-MCl_n$ eutectic.

Species of Molten Salts	FPMD Simulation Values	Experimental Values
LiCl-KCl-AgCl	2.572	2.62
LiCl-KCl-CuCl	2.167	2.34
LiCl-KCl-LaCl ₃	2.812	2.85
LiCl-KCl-CeCl ₃	2.770	2.81
LiCl-KCl-UCl ₃	2.689	2.85

Similarly, RDF peak positions for trivalent actinide and lanthanide chlorides such as $La^{3+}-Cl^{-}$, $Ce^{3+}-Cl^{-}$, and $U^{3+}-Cl^{-}$ obtained from X-ray diffraction experiments are highly consistent with corresponding FPMD results. These comparisons confirm that FPMD methods can reliably reproduce short-range structures in high-temperature molten-salt systems [28].

Zhang et al. further investigated the structural characteristics of actinide elements (Th, Pa, U, and Np) in molten LiCl-KCl eutectic using FPMD simulations [29]. The results show that with increasing atomic number, the An-Cl first peak distance decreases, following the well-known actinide contraction trend. As shown in Table 2, the predicted coordination numbers and bond distances also exhibit good agreement with EXAFS and XRD measurements [30–32].

Table 2. First peak positions R_{An-Cl} (Å) and coordination numbers CNs for $AnCl_4$ in molten.

Species of Molten Salts	R_{An-Cl} (Å)		CNs
	FPMD Simulation Values	Experimental Values	FPMD Simulation Values
LiCl-KCl-ThCl ₄	2.724	2.718/2.903 ^a	7.315
LiCl-KCl-PaCl ₄	2.705	2.644/2.955 ^a	6.931
LiCl-KCl-UCl ₄	2.602	2.65 ^b	6.194
LiCl-KCl-NpCl ₄	2.581	2.604/2.936 ^a	6.254

^a XRD data for the crystalline phase. ^b EXAFS data for UCl₄ in molten LiCl at 1023 K.

Overall, RDF and coordination number analyses are the most widely adopted computational strategies in molten-salt microscopic studies. These methods provide essential theoretical support for understanding local structures and solute speciation behaviors in reprocessing-related molten salts.

4. Calculation of Physical Properties Using First-Principles Methods

4.1. Viscosity

Viscosity measurements are extremely important for molten-salt electrochemical systems because viscosity directly reflects the fluidity of the electrolyte and strongly influences ion diffusion and migration. Experimentally, viscosity can be measured by shear cell, capillary, neutron scattering, or electrochemical methods [33–37]. However, such measurements become challenging at temperatures above 800 K or in systems containing radioactive elements.

First-principles methods provide alternative computational routes. Based on the Stokes–Einstein–Sutherland relation [38], viscosity η can be correlated with the self-diffusion coefficient D as follows:

$$\eta = \frac{Tk_b}{6\pi RD'} \quad (2)$$

where T is the absolute temperature, k_b is the Boltzmann constant, and R is the hydrodynamic radius, often approximated as half of the first coordination distance.

Various methods have been proposed in the literature for predicting the viscosity of molten salts based on microscopic structural parameters. Duemmler suggested during

data processing that the solvent kinetic radius can be approximated as half of the first coordination distance [39]. This approximation is typically implemented by defining the kinetic radius R as half of the distance corresponding to the first peak position on the RDF curve, followed by calculation of viscosity using the Stokes–Einstein–Sutherland relationship. However, this method relies on a series of idealized assumptions, and systematic deviations between predicted and experimental results are frequently observed. As shown in Figure 3, viscosities calculated using this relationship are generally lower than the experimental values reported by Janz [40]. It should be noted that the data from Janz were obtained for a system containing 40% mol KCl, whereas the work of Kim et al. focused on eutectic compositions [41]; such compositional differences may represent a major factor limiting direct comparison. A similar trend has also been found for LiCl: the viscosities derived from theoretical calculations are significantly lower than the experimental results reported by Tasidou, Janz, and the measurements of Brockner et al. [39,42–44]. Nevertheless, in the case of pure KCl, the prediction method exhibits relatively high reliability, with calculated values in good agreement with experimental data. However, for LiCl–KCl mixtures, the predicted viscosities remain consistently lower than experimental measurements. Overall, the applicability of Stokes–Einstein-type relationships appears to be inconsistent between single-component and mixed molten-salt systems, indicating that existing models still require further improvement for the quantitative prediction of viscosity in molten-salt mixtures.

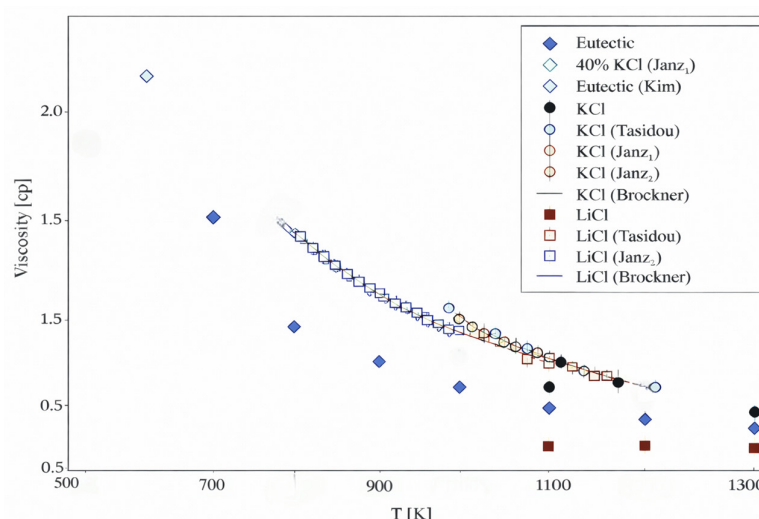


Figure 3. The relationship between viscosity and temperature for the LiCl–KCl eutectic mixture, KCl, and LiCl. Solid markers represent FPMD calculation results, and hollow markers represent experimental data.

Unlike Duemmler’s group, Yan [21] chose the first coordination distance as an approximation of the solvent kinetic radius; the calculated viscosity of the molten-salt mixture is also summarized in Table 3. For the molten LiCl–KCl–UCl₃ mixture, the calculated viscosity is consistent with the dynamic viscosity value of $2.44 \times 10^{-3} \text{ N}\cdot\text{s}\cdot\text{m}^{-2}$ studied by Choi between 750 and 800 K [45].

Table 3. Transport properties derived from FPMD simulations, including self-diffusion coefficients, ionic conductivities, and viscosities (NVT ensemble, 723 K).

Species of Molten Salts	$\kappa \text{ (S}\cdot\text{cm}^{-1}\text{)}$	$D \text{ (}10^{-5} \text{ cm}^2\cdot\text{s}^{-1}\text{)}$	$\eta \text{ (}10^{-3} \text{ N}\cdot\text{s}\cdot\text{m}^{-2}\text{)}$
LiCl–KCl	1.514 (1.557 ^a , 1.547 ^b)		
LiCl–KCl–AgCl	1.464 (1.636 ^b)	1.995 (2.279 ^c)	1.032

Table 3. Cont.

Species of Molten Salts	κ (S·cm ^{−1})	D (10 ^{−5} cm ² ·s ^{−1})	η (10 ^{−3} N·s·m ^{−2})
LiCl–KCl–CuCl	1.445 (1.525 ^b)	2.153 (2.535 ^d)	1.135
LiCl–KCl–TlCl	1.255 (1.530 ^b)	2.609 (3.446 ^d)	0.660
LiCl–KCl–AuCl	1.945	1.437 (1.388 ^c)	1.604
LiCl–KCl–LaCl ₃	1.893 (1.547 ^b)	1.239 (1.466 ^e)	1.520
LiCl–KCl–CeCl ₃	1.284 (1.525 ^b)	0.997 (1.079 ^e)	1.918
LiCl–KCl–UCl ₃	1.674 (1.537 ^b)	0.635 (0.668 ^c)	2.896 (2.44 at 773 K ^f)
LiCl–KCl–PuCl ₃	1.508	0.597 (0.794 ^e)	3.301

^a Experimental measurements were performed using a capillary conductivity cell [46]. ^b Based on the ion-independent assumption, the ionic conductivity of molten KCl–LiCl eutectic and molten pure MCl was estimated using the method described by Janz, G. J., and Okamoto, Y. et al. [47,48]. ^c Experimental measurements were performed using the capillary method [49]. ^d Experimental data were obtained [50]. ^e Experimental data were organized and reanalyzed [51]. ^f Data values used by Choi, S. [45].

The Dewan research group at MIT adopted a different strategy for viscosity calculation, employing an integration method based on the stress tensor autocorrelation function to simulate the viscosity of molten-salt systems [52]. The corresponding formula is expressed as follows:

$$\eta = \frac{1}{k_B TV} \int_0^\infty [\sigma_{\alpha\beta}(0)\sigma_{\alpha\beta}(\tau)]d\tau, \quad (3)$$

where $\sigma_{\alpha\beta}$ represents the independent components of the stress tensor. In the calculation, the stress autocorrelation function is obtained by averaging five independent components (σ_{xy} , σ_{xz} , σ_{yz} , σ_{xx-yy} , and $\sigma_{zz-xx-yy}$), and this averaged autocorrelation function is integrated over time. The viscosity of the system is determined from the plateau value of the running integral after it reaches a stable state. At present, only a limited amount of experimental data describing the viscosity of LiF–ThF₄ mixtures is available for validating these simulation results. Benes, Konings, and Chervinskii [53,54] reported that the viscosity of a molten salt with a composition of 78 mol% LiF–22 mol% ThF₄ at 1273 K is 3.13 Pa·s. In comparison, the simulation results of Dewan et al. indicate a predicted viscosity of 3.49 Pa·s at the same temperature, which is in reasonable agreement with the experimental measurements. This suggests that the integration method based on stress tensor autocorrelation functions is capable of providing a relatively reliable description of the viscosity characteristics of LiF–ThF₄ mixed molten salts.

In summary, viscosity is an important parameter that reflects the transport properties of molten-salt systems, and the corresponding calculation methods have been extensively investigated in this research field. At the present stage, simulation of viscosity mainly relies on the Stokes–Einstein–Sutherland equation. Under the specified theoretical conditions and parameter ranges, the predicted results generally exhibit a reasonable degree of agreement with experimental values. However, for certain molten-salt compositions, discrepancies between simulated and experimentally measured viscosities still remain, with maximum deviations of up to approximately 0.5 N·s·m^{−2}.

The discrepancy between viscosities predicted by FPMD simulations and experimental measurements for molten salts can be attributed to several factors. First, viscosity is a collective transport property that depends on long-time stress autocorrelation functions. Due to the high computational cost of FPMD, simulations are typically restricted to relatively small system sizes and short simulation times, resulting in finite-size effects and limited statistical sampling, which undoubtedly leads to deviations in the results [39]. Second, the accuracy of FPMD simulations is fundamentally limited by the approximate nature of exchange–correlation functionals employed in density functional theory. Commonly used generalized gradient approximation (GGA) functionals, such as PBE, may inadequately

describe short-range repulsion and long-range dispersion interactions, which can lead to an underestimation of ionic correlations and, consequently, an overestimation of ionic mobility and an underprediction of viscosity [17,55]. In addition, experimental viscosity data for molten salts are themselves subject to considerable uncertainties arising from high-temperature measurement conditions, impurity effects, container–melt interactions, and differences in experimental techniques [56]. As a result, reported experimental viscosities often exhibit significant scatter, making direct quantitative comparison with simulation results challenging.

Nevertheless, viscosity simulations are capable of providing valuable insights into the transport behavior and kinetic characteristics of different elements in molten salts, and they serve as a useful approach for correlating microscopic structural features with macroscopic transport properties. Therefore, these research outcomes possess significant relevance and practical importance for mechanistic studies and process optimization in molten-salt electrochemical systems.

4.2. Self-Diffusion Coefficient

The diffusion coefficient is a key parameter for characterizing mass transport behavior in molten-salt electrochemical systems, and its investigation is of great importance for a comprehensive understanding of transport mechanisms. The diffusion rate of ions or molecules in the electrolyte directly affects the performance and operational stability of batteries, electrolyzers, and other electrochemical devices. Accurate knowledge of ionic diffusion coefficients in electrolytes contributes to a deeper understanding of electrode reaction kinetics, thereby providing a theoretical basis for the optimization of electrode materials and the regulation of reaction conditions [57–60].

Besides experimental methods, the diffusion coefficient of a liquid can also be obtained through molecular dynamics simulations. The principle is summarized as follows: By statistically calculating the trajectories of particle motion, and based on the Einstein–Smoluchowski equation [61],

$$MSD = \frac{1}{N \cdot n_t} \sum_{i=0}^N \sum_{j=0}^{n_t} (r_i(t_j + dt) - r_i(t_j))^2, \quad (4)$$

The mean square displacement (*MSD*) as a function of time can be obtained using this equation, where $r_i(t_j)$ is the position of atom i at time t [62]. Therefore, according to the equation,

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} (MSD), \quad (5)$$

Based on the *MSD* curves of all particles, the ionic self-diffusion coefficient D of the molten-salt system can be calculated. It can also be expressed in the following form:

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^N [|r_i(t) - r_i(0)|^2], \quad (6)$$

Bu et al. calculated the self-diffusion coefficients of Ca^{2+} , K^+ , and Cl^- ions in KCl – CaCl_2 molten salts with different CaCl_2 mole fractions at 1100 K and analyzed the results in terms of steric hindrance effects (Figure 4) [63]. The self-diffusion coefficients exhibit clear composition-dependent trends. As the CaCl_2 mole fraction increases from 20 to 80 mol%, the self-diffusion coefficient of K^+ decreases from 3.910×10^{-9} to $3.116 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$. This behavior is mainly attributed to the gradual replacement of K^+ by Ca^{2+} ions and the formation of network structures through Ca^{2+} – Cl^- bridging, which enhances steric hindrance and restricts K^+ mobility. For Ca^{2+} and Cl^- ions, their self-diffusion coefficients

decrease as the CaCl_2 mole fraction increases from 20 to 40 mol%, while the rate of decrease becomes smaller upon further increase to 60 mol%. At higher CaCl_2 contents (up to 80 mol%), a slight increase in the self-diffusion coefficients of Ca^{2+} and Cl^- is observed. These results indicate a competition between the strengthening steric hindrance associated with network formation and the enhanced ionic mobility arising from increasingly dynamic Ca^{2+} coordination environments, which together govern the diffusion behavior of the system.

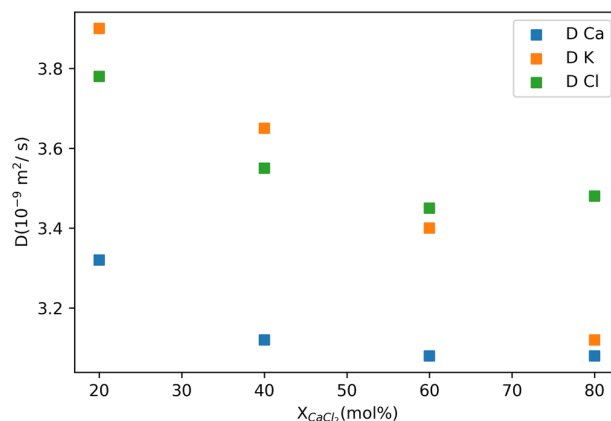


Figure 4. Effect of CaCl_2 mole fraction on the self-diffusion of Ca^{2+} , K^+ , and Cl^- ions in KCl – CaCl_2 molten salts at 1100 K.

4.3. Density

Density measurements play an important role in molten-salt electrochemical research, as density is one of the fundamental physical properties of molten-salt systems and directly influences electrochemical reactions, transport properties, and material performance. Density data can be used to determine the concentration and composition of individual components in molten salts, which is essential for understanding the concentration and solubility of dissolved species. These factors, in turn, affect the rate and equilibrium of electrochemical reactions. Moreover, variations in density with temperature or composition can provide valuable insights into electrochemical reaction mechanisms. Therefore, systematic investigation of density variations is beneficial for achieving a deeper understanding of reaction mechanisms in molten-salt systems [64].

Song et al. performed molecular dynamics simulations to evaluate the density of molten-salt mixtures and found that the temperature dependence of density can be well described by a linear relationship [65]. As shown in Figure 5, when the temperature increases from 858 K to 1019 K, the density of molten LiCl – KCl mixtures decreases from 1.630 to 1.497 $\text{g}\cdot\text{cm}^{-3}$. In comparison, experimental data reported by van Artsdalen and Yaffe show a decrease in density from 1.575 to 1.486 $\text{g}\cdot\text{cm}^{-3}$ over the same temperature range [46]. Compared with the experimental values, densities obtained from FPMD simulations are slightly higher, with relative deviations ranging from 0.33% to 3.13%. Overall, the temperature dependence of density for this system can be accurately fitted using a linear function, as expressed below.

$$\rho = a - bT, \quad (7)$$

The experimental results for a and b are 2.029 $\text{g}\cdot\text{cm}^{-3}$ and $5.274 \times 10^{-4} \text{ g}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$, respectively, while the calculated results are 2.217 $\text{g}\cdot\text{cm}^{-3}$ and $6.892 \times 10^{-4} \text{ g}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$.

Numerous simulations show that the density of molten salt has a clear linear relationship with the temperature of the system, which can undoubtedly play a good predictive and guiding role in density measurement in high-temperature molten-salt system experiments [66–71].

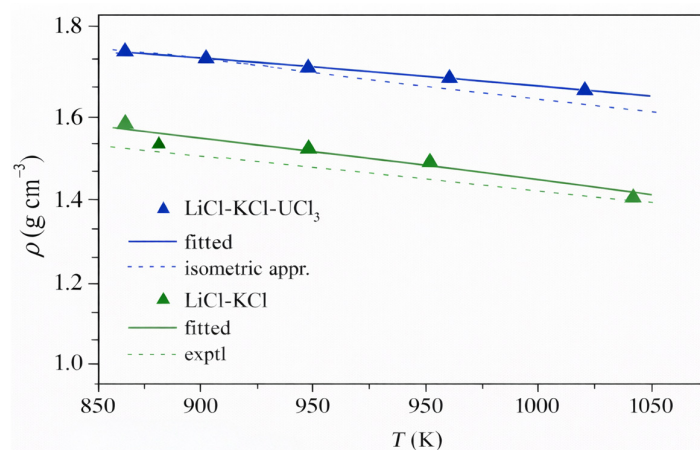


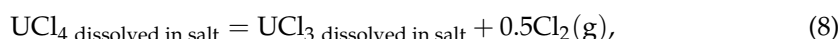
Figure 5. Temperature dependence of the density of LiCl-KCl and LiCl-KCl-UCl₃ molten salts and their fitting curves.

5. Calculation of Electrochemical Properties Using First-Principles Methods

5.1. Redox Potentials

Redox potential is a critical parameter in molten-salt electrochemistry because it determines the thermodynamic feasibility of electrode reactions. Measuring redox potentials experimentally in high-temperature radioactive molten salts is complicated and sometimes infeasible [72].

Nam et al. employed FPMD-based ensemble averaging to calculate the redox potential of the U⁴⁺/U³⁺ couple in LiCl-KCl eutectic. The electrode reaction can be expressed as follows [73]:



The corresponding computational formula for redox potential is as follows:

$$[V_{\text{redox}}]_{\text{UCl}_4/\text{UCl}_3}(\text{vs. Cl}_2/\text{Cl}^-) = - \frac{\{[E(\text{UCl}_3 + \text{MS})] + 0.5 \cdot G(\text{Cl}_2) - [E(\text{UCl}_4 + \text{MS})] + C^S\}}{1 \cdot e}, \quad (9)$$

where M represents the molten salt, E is the ensemble average of the total energy calculated by FPMD, e is the absolute value of the electron charge, $G(\text{Cl}_2)$ is the Gibbs free energy of chlorine gas, and C^S represents entropy corrections. The redox potentials of several redox couples in molten LiCl-KCl salt at 773 K, calculated by FPMD simulation, were compared with the experimentally measured redox potentials (Cl_2/Cl^- as a reference). Table 4 summarizes the calculated redox potentials and their contributions to the mean standard error, experimental measurements, and entropy correction term, and predicts the potentials of other redox couples [74–85].

Table 4. Comparison of calculated redox potentials of several redox couples in molten LiCl-KCl at 773 K (vs. Cl_2/Cl^-) with thermodynamic database predictions.

Redox Couples	Prediction from HSC	FPMD Value (V)	$C^S/n e$ (V)	Experimental Redox (V)
Li(I)/Li(0)	−3.574	−3.445	0.378	−3.606 ± 0.062
Sr(II)/Sr(0)	−3.663	−3.266	0.441	−
La(III)/La(0)	−3.043	−3.091	0.415	−3.125 ± 0.048
Nd(III)/Nd(0)	−2.946	−2.967	0.417	−3.089 ± 0.046
Ce(III)/Ce(0)	−2.983	−3.029	0.415	−3.116 ± 0.124
Zr(IV)/Zr(0)	−1.946	−2.494	0.472	−2.173 ± 0.360

By deriving theoretical expressions for the standard redox potentials of solute species in molten salts, it is possible to predict the redox potentials of a wide range of species in the LiCl–KCl molten-salt system. The calculated values generally show good agreement with experimental data, with deviations typically within 0.5 V. The remaining discrepancies may arise from unavoidable experimental uncertainties as well as other factors such as differences in measurement techniques and reference electrode selection. Overall, current models are capable of reasonably describing redox behavior in molten-salt systems; however, there remains considerable potential for improving predictive accuracy. Consequently, further optimization of experimental measurements and refinement of simulation and calculation methods continue to be of significant research interest and practical importance.

5.2. Electrical Conductivity

Electrical conductivity is one of the main indicators for evaluating electrolyte performance. By measuring conductivity, the ionic conductivity of an electrolyte system can be determined. High conductivity usually means better ion transport and higher reaction rates [86].

Deng conducted a systematic simulation study on the electrical conductivity of various molten-salt mixtures [87]. Specifically, simulated conductivities for LiCl–KCl eutectic systems containing UCl_3 are presented in Figure 6, together with experimental conductivity data for LiCl–KCl eutectic melts containing U^{3+} . Overall, a good agreement between simulation results and experimental measurements is observed. Both simulation and experimental results indicate that, at the same temperature and UCl_3 mole fraction, the electrical conductivities of LiCl–KCl– UCl_3 systems are nearly identical. This behavior suggests that, in the high-viscosity region associated with network formation, U^{3+} cations are strongly constrained by the molten-salt network, and their direct contribution to the total electrical conductivity can be considered negligible. Consequently, the overall conductivity is dominated by Li^+ and K^+ ions, whose contributions are nearly the same due to their similar mobilities in the different molten-salt systems. In the dilute regime (UCl_3 content below approximately 10 mol%), the electrical conductivity decreases almost linearly with increasing UCl_3 concentration. Experimental observations report a similar trend, showing that when the trivalent cation concentration is below approximately 12 mol%, the conductivity is nearly a linear function of trivalent ion content in LiCl–KCl– UCl_3 systems. In contrast, in the viscous regime (UCl_3 content above approximately 10 mol%), the electrical conductivity exhibits an approximately exponential decrease with increasing UCl_3 concentration. The distinct trends observed between the dilute and viscous regimes are fundamentally attributed to concentration-induced structural transformations in the molten-salt network [88–90].

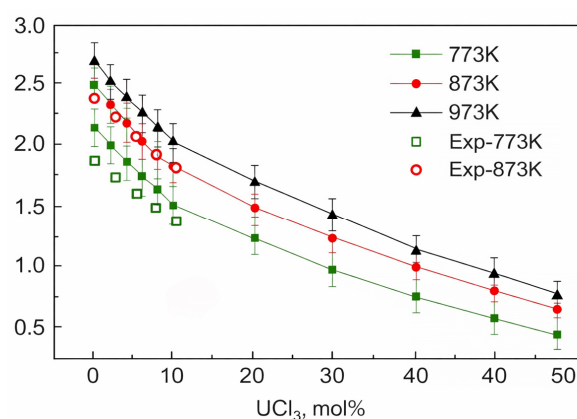


Figure 6. Electrical conductivity of different trivalent cations in LiCl–KCl mixture, including a comparison of FPMD calculations and experimental values.

Overall, the simulated electrical conductivities are in close agreement with experimental data, and the nearly identical conductivity values obtained for systems containing different trivalent cations demonstrate the high accuracy and reliability of the simulation approach in describing charge transport in LiCl–KCl–MCl₃ molten-salt systems.

5.3. Electrochemical Interfaces

With the continuous deepening of research into the electrochemical mechanisms of molten-salt electrolytic refining, first-principles calculations will undoubtedly demonstrate increasing application value in this field [91–94]. The study of electrochemical interfaces is essential for achieving a deeper understanding of electrochemical behavior in materials, including charge transfer, ionic diffusion, and interfacial reactions. Such knowledge not only helps elucidate interfacial mechanisms but also provides theoretical guidance for the selection and optimization of electrode materials, as well as for the systematic evaluation of electrochemical properties in experimental systems [95].

Kwon et al. investigated the thermodynamic stability of uranium electrodeposition on a Mo(110) surface in LiCl–KCl–UCl₃ molten-salt mixtures by means of simulation, and determined the ground-state structures of the Cl/U/Mo(110) surface as a function of adsorbate (U, Cl) coverage [96,97]. However, the constructed model system does not fully account for the influence of the LiCl–KCl molten-salt environment, as it neglects the electrical double-layer structure at the electrode/electrolyte interface. In this sense, the model effectively describes gas-phase adsorption on a metallic solid surface rather than a realistic electrode–molten-salt interface. To date, studies that comprehensively incorporate electrode/molten-salt interfacial effects remain relatively limited.

To address this limitation, Yang et al. examined the interfacial properties between metal electrodes and molten LiCl–KCl–UCl₃ mixtures, with particular emphasis on the distribution and dynamics of U³⁺ ions in the interfacial region [98]. In their work, a constant-charge model was employed to represent the electrodes in order to reduce computational cost. Figure 7 illustrates a periodic simulation snapshot of the molten mixture confined between two planar interfaces along the *z* direction. To characterize ionic distributions at the interface and their response to electrode charge, Yang et al. studied the variation curves of ion number density with distance from the electrode under different surface charge conditions. The results show that a single ionic layer composed of Li⁺, K⁺, and Cl[−] consistently exists between U³⁺ ions and the electrode surface. This interfacial layer may hinder electron transfer from the electrode into the molten mixture, thereby slowing interfacial charge-transfer kinetics. Compared with a neutral electrode, the density maximum of U³⁺ shifts closer to positively charged electrodes and farther away from negatively charged electrodes. This behavior arises from the combined effects of electrostatic screening and Coulomb interactions: excess anions in the first layer near the anode exert an attractive force on U³⁺, whereas excess cations near the cathode induce Coulombic repulsion. When the surface charge density $\sigma_s = 0$, K⁺ ions are more enriched near the electrode than Li⁺. Calculations of the interaction energies in the first ionic layer show that Li⁺–Cl[−] interactions (−5.63 eV·atom^{−1}) are significantly stronger than K⁺ interactions (−2.96 eV·atom^{−1}), which restricts the migration of Li⁺ toward the interface and renders K⁺ more mobile. Consequently, as the magnitude of electrode surface charge increases, the concentration of K⁺ near the anode decreases markedly, while that near the cathode increases.

Although FPMD has been successfully applied to investigate the bulk structure of LiCl–KCl molten salts and the coordination behavior of selected metal ions, its application to electrochemical processes at liquid metal cathode/molten salt interfaces remains highly limited. From a mechanistic standpoint, future FPMD studies should move beyond static structural characterization toward a detailed understanding of potential-dependent separa-

tion and transport mechanisms [99–101]. In LiCl–KCl systems coupled with liquid Bi, Cd, or Pb cathodes, systematic investigations are needed to clarify how applied potential affects the interfacial enrichment, desolvation behavior, and transfer thermodynamics of fission product ions such as Cs and Nd. On the other hand, in terms of engineering relevance and multiscale modeling, the role of FPMD is expected to evolve from a direct predictive tool toward a high-fidelity data generator. Interfacial structures, charge distributions, and reaction free energies obtained from FPMD can be used to train machine-learning interatomic potentials (MLIPs), enabling simulations of liquid metal cathode/molten salt interfaces at larger spatial and temporal scales [102–104]. Such a hierarchical FPMD–ML–continuum modeling framework would provide key parameters for macroscopic electrochemical models, including interfacial transport coefficients, separation selectivity trends, and cathode degradation mechanisms, thereby enhancing the practical value of atomistic simulations for pyroprocessing system design. Future studies may increasingly account for the complexity of realistic cathode conditions, such as variations in liquid metal composition, competitive dissolution of multiple species, the presence of impurities (e.g., oxygen or moisture), and the dynamic evolution of the cathode–salt interface. Incorporating these factors into FPMD models will not only improve agreement with experimental observations but also facilitate the transition of atomistic simulations from mechanistic interpretation toward process optimization in electrochemical pyroprocessing.

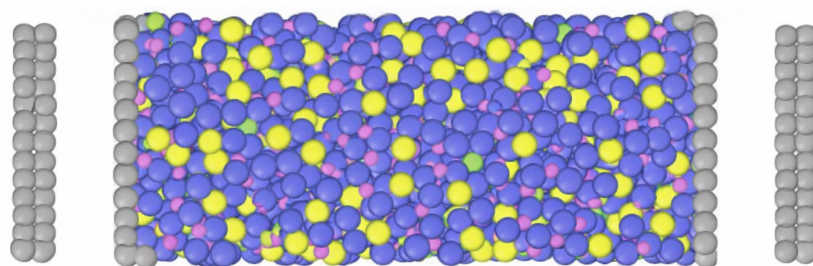


Figure 7. Representative periodic snapshot of the molten mixture confined between two planar interfaces along the *z* direction.

6. Conclusions

First-principles calculations originated from fundamental concepts in theoretical physics and have undergone several key stages of development, gradually becoming indispensable tools in modern scientific and engineering research. Numerous studies have demonstrated that FPMD can be effectively employed to simulate the structural, dynamic, and thermodynamic behavior of solute species in molten-salt systems. With a favorable balance between accuracy and computational cost, FPMD offers a powerful approach for exploring and developing new molten-salt systems.

For high-temperature molten salts such as LiCl–KCl and LiF–KF, first-principles calculations, through appropriate parameter selection and the combined use of advanced computational software, can yield a wide range of key properties, including microscopic structural information, transport characteristics, and electrochemical properties. These insights are of significant value for advancing molten-salt electrochemistry research. A comprehensive review of previous studies indicates that computational results generally exhibit good agreement with experimental validations in terms of overall trends and demonstrate high reliability for most systems, although noticeable deviations remain for certain properties, such as viscosity. With continued advances in computational methodologies and experimental measurement techniques, these limitations are expected to be progressively overcome.

First-principles molecular dynamics still holds significant potential for development in molten-salt electrochemistry research. In the future, machine learning potential functions, multiscale simulations, and coupling methods of first-principles and classical molecular

dynamics can be used to overcome limitations in computational scale and time scale, and to improve the accuracy of predicting key physical properties such as viscosity and conductivity. Further application of this method to complex multicomponent molten salts and interface reactions in engineering-related problems is expected to drive the transformation of first-principles calculations from mechanistic research to material design and performance prediction, playing a more crucial role in molten-salt electrochemistry and related high-temperature technologies. As a powerful theoretical tool, first-principles calculations are poised to play an increasingly important role in promoting the development and practical implementation of molten-salt electrochemical technologies, thereby contributing to the advancement of pyroprocessing technologies.

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