MANY-BODY MOLECULAR DYNAMICS SIMULATIONS OF IONIC SYSTEMS: FROM CLUSTERS TO BULK AND INTERFACES

Paesani, Francesco
UNIVERSITY OF CALIFORNIA, SAN DIEGO
9500 GILMAN DR
LA JOLLA, CA, 92093
USA

08/04/2021
Final Technical Report

Air Force Research Laboratory
Air Force Office of Scientific Research
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

1. REPORT DATE (DD-MM-YYYY) 04-08-2021	2. REPORT TYPE Final	3. DATES COVERED (From - To) 15 Aug 2016 - 14 Aug 2020

4. TITLE AND SUBTITLE MANY-BODY MOLECULAR DYNAMICS SIMULATIONS OF IONIC SYSTEMS: FROM CLUSTERS TO BULK AND INTERFACES	5a. CONTRACT NUMBER
	5b. GRANT NUMBER FA9550-16-1-0327
	5c. PROGRAM ELEMENT NUMBER 61102F
6. AUTHOR(S) Francesco Paesani	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF CALIFORNIA, SAN DIEGO 9500 GILMAN DR LA JOLLA, CA 92093 USA	8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203	10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR RTB2
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2021-0089

12. DISTRIBUTION/AVAILABILITY STATEMENT
A Distribution Unlimited: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The overarching goal of this research project was to develop an novel theoretical/computational methodology, rigorously derived from a many-body formalism, for modeling ionic systems from the gas to the condensed phase. We achieved this goal by combining data-driven representations of many-body short-range quantum mechanical interactions, which arise from the overlap of the electron densities of individual molecules, with physics-based representations of many-body polarization and long-range interactions. We demonstrated that the resulting many-body potential energy functions display chemical accuracy for each term of the many-body expansion of the interaction energies between ions and water, thus enabling molecular-level computer simulations of ionic systems with unprecedented accuracy and predictive power, from the gas to the condensed phase.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON MICHAEL BERMAN
a. REPORT	b. ABSTRACT	c. THIS PAGE			
U	U	U	UU	2	19b. TELEPHONE NUMBER (Include area code) 426-7781

Many-Body Molecular Dynamics Simulations of Ionic Systems:
From Clusters to Bulk and Interfaces
AFOSR award number: FA9550-16-1-0327
Principal Investigator: Francesco Paesani

The overarching goal of this research project was to further develop our many-body molecular dynamics (MB-MD) methodology to enable modeling of ionic systems from the gas to the condensed phase. MB-MD combines data-driven many-body (MB) representations of molecular interactions rigorously derived from "first principles" with classical and quantum molecular dynamics (MD) methods to characterize structural, thermodynamic, dynamical, and spectroscopic properties across phases.

Our MB-MD methodology enables the development of accurate multidimensional potential energy functions (PEFs) that are rigorously derived from the many-body expansion (MBE) of the energy. These many-body PEFs (MB-PEFs) adopt a hybrid data-driven/physics-based scheme, where a data-driven model, which captures many-body (short-range) quantum-mechanical interactions arising from the overlap of the electron densities of individual molecules (e.g., Pauli repulsion, and charge transfer and penetration), is integrated with a physics-based model of many-body interactions, which are generally represented by classical many-body electrostatics. By construction, our MB-PEFs are, therefore, fully transferable from the gas to the condensed phase.

As part of this research project, we focus on three aspects of our many-body formalism:

1. Development of a rigorous theoretical framework for interpreting the various components of our MB-PEFs.

2. Application of our MB-PEFs to characterizing structural, thermodynamic, and dynamical properties of different ionic systems.

3. Development of an integrated computational infrastructure for the automated generation of MB-PEFs.

1) In two papers (*J. Chem. Theory Comput. 2019, 15, 2983* and *J. Chem. Theory Comput. 2020, 16, 3055*], we investigated the nature of the interactions between halide and alkali-metal ions and water using various many-body models and density functionals across Jacob's ladder of DFT approximations. Our analyses demonstrate that our MB-PEFs correctly capture short-range quantum-mechanical effects, such as charge transfer, and charge transfer and penetration, which cannot be represented by classical expressions employed in common force fields. At the same time, our analyses of interaction energies carried out with the absolutely localized molecular orbital energy decomposition analysis (ALMO-EDA) method also shows that, while all density functionals are able to correctly reproduce permanent electrostatics and induction, they show significant variance for charge transfer energies. In particular, since density functionals developed within the generalized gradient approximation (GGA) and hybrid functionals predict the most and least attractive charge transfer energies, respectively, we argued that the large variance is likely due to the delocalization error. This observation was key to informing further developments of our MB-PEFs.

2) In a series of papers (J. Phys. Chem. A 2018, 122, 5811, Nat. Chem. 2019, 11, 367, J. Phys. Chem. Lett. 2019, 10, 2823, J. Phys. Chem. A 2019, 123, 2843), we characterized the structure and hydrogen-bonding dynamics of small ion-water clusters. In particular, we used quantum molecular dynamics simulations based on the path-integral formalism to unravel specific ion effects on the dynamics of ion-water and water-water hydrogen bonds in halide-dihydrate complexes. Our analyses show that We found that the halide−water hydrogen-bond strength decreases going from $Cl^-(H_2O)_2$ to $I^-(H_2O)_2$, the opposite trend is observed in the strength of the water−water hydrogen-bond. Our results indicate that nontrivial many-body effects may also be at play in the hydration shells of halide ions in solution, especially in frustrated systems (e.g., interfaces) where the water molecules can have dangling OH bonds. These findings stimulated new research projects aimed at characterizing nuclear quantum effects in the hydrogen-bond dynamics of ionic solutions, both in the bulk and at air/liquid interfaces.

We also characterized the structure and vibrational spectra of relatively larger ion–water clusters. In the case of the halide ions, we found that all four halides have high propensity for the surface of the clusters. For fluoride–water clusters, our results are in contrast to previous reports suggesting that fluoride prefers to be fully hydrated in the interior of small clusters. We believe that these differences are likely due to inaccuracies in previous models of ion-water interactions and highlight the importance of a correct representation of many-body effects for a quantitative description of ion hydration.

3) In a more technical paper (J. Chem. Phys. 2019, 151, 194111) by one of our postdocs (Sandra Brown), who was supported by this AFOSR grant, we characterized the numerical aspects of the fitting problem associated with the development of MB-PEFs, addressing questions which are of both practical and fundamental importance. These include concrete illustrations of the non-convexity of the problem, the ill-conditionedness of the linear system to be solved and possible need for regularization, the sensitivity of the solutions to the characteristics of the training set, and limitations of the approach with respect to accuracy and the types of molecules that can be treated. The specific focus of this study was on describing the functional form of our MB-PEFs along with a discussion of permutationally invariant polynomials, fitting procedure, and training set generation.

This study effectively provided a detailed description of our software infrastructure for the development of MB-PEFs for arbitrary (small) molecules, which we are planning to release this summer.