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A Journey towards the Heaven of Chemical Fidelity of Intermolecular Force Fields

Alongside the evolution of density functional theory into a new era led by the dispersion-corrected hybrid density functional theory approaches, formulation of a new generation of intermolecular potentials has also taken the center-stage. The Lennard-Jones potential, one of the popular intermolecular pair potentials for performing large-scale simulations fails to capture some of the intricate features of molecular interactions. Woven around the central theme of anisotropy in the nature of intermolecular interactions, I shall describe our quest for chemical fidelity of empirical potential formulations that include (i) incorporation of the anisotropic nature of exchange-repulsion and dispersion contributions, (ii) multipolar description of the dispersion terms, (iii) damping functions to provide an accurate description of the asymptotes, and (iv) transferability of intermolecular interaction terms. I shall illustrate the nuances of intermolecular force field development in the context of modeling the non-covalent interactions governing the binding of atoms and molecules with carbon and boron nitride nanostructures, as well as interlayer interactions in layered nanostructures. Finally, I shall exemplify the hierarchy of empirical potentials by depicting them on the various rungs of the Jacob's ladder equivalent of density functional theory for the intermolecular force fields.

[1] Stone, A. J. The Theory of Intermolecular Forces, Second ed., Oxford University Press: Oxford. 2013.
[2] Bartolomei, M.; Carmona-Novillo, E.; Hernandez, M. I.; Campos-Martinez, J.; Pirani, F.; Giorgi, G.; Yamashita, K. Penetration of Water through Graphynes' Pores: First-Principles Predictions and Force Field Optimization. J. Phys. Chem. Lett., 2014, 5, 751-755.
[3] Hauser, A. W.; Mitrushchenkov, A. O.; de Lara-Castells, M. P. Quantum Nuclear Motion of Helium and Molecular Nitrogen Clusters in Carbon Nanotubes. J. Phys. Chem. C., 2017, 121, 3807-3821.
[4] Maaravi, T.; Leven, I.; Azuri, I.; Kronik, L.; Hod, O. Interlayer Potential for Homogeneous Graphene and Hexagonal Boron Nitride Systems: Reparametrization for Many-body Dispersion Effects. J. Phys. Chem. C., 2017, 121, 22826-22835.
[5] James, A.; Swathi, R. S. Modeling the Adsorption of Polycyclic Aromatic Hydrocarbons on Graphynes: An Atomistic Potential Formulation [Unpublished, 2021].
[6] Ajay, MK.; James, A.; Megha, R.; Chris, J.; Swathi, R. S. In Pursuit of Accurate Interlayer Potentials for Twisted Bilayer Graphynes [Unpublished, 2021].
[7] Chris, J.; Swathi, R. S. An Anisotropic Dressed Pairwise Potential Model for the Adsorption of Noble Gases on Boron Nitride Sheets [Unpublished, 2021].

R. S. Swathi obtained an integrated B. Sc. Ed degree from Regional Institute of Education, Mysore and an M. Sc. Degree in Chemistry from Indian Institute of Technology, Guwahati. Subsequently, she pursued PhD in theoretical chemistry from Indian Institute of Science, Bangalore working under the supervision of Prof. K. L. Sebastian. Since 2010, Swathi has been working as a faculty member at the School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram and is currently an Associate Professor there. Her multiscale modelling and computation group employs analytical and computational approaches for modeling interesting phenomena involving carbon-based and metal-based nanostructures. Swathi is a recipient of the Young Scientist Awards from Indian National Science Academy, National Academy of Sciences, Kerala State Council for Science, Technology and Environment, and Distinguished Lectureship Award from the Chemical Society of Japan. Swathi was also a young associate of the Indian Academy of Sciences, Bangalore. Swathi is a recipient of the A V Rama Rao Foundation Prize in Chemistry awarded by the JNCASR, Bangalore for the year 2020.