Benchmarking Simulations against the ThermoML Database: Neat Liquid Densities and Static Dielectrics

Kyle A. Beauchamp*,[1] Julie M. Behr*,[1] Patrick B. Grinaway,[1] Bas,[1]
Kenneth Kronlein,[2] Michael R. Shirts,[3,*] and John D. Chodera[1,†]

[1]*Memorial Sloan-Kettering Cancer Center, New York, NY, USA*
[2]*NIST*
[3]*Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22094-0471*

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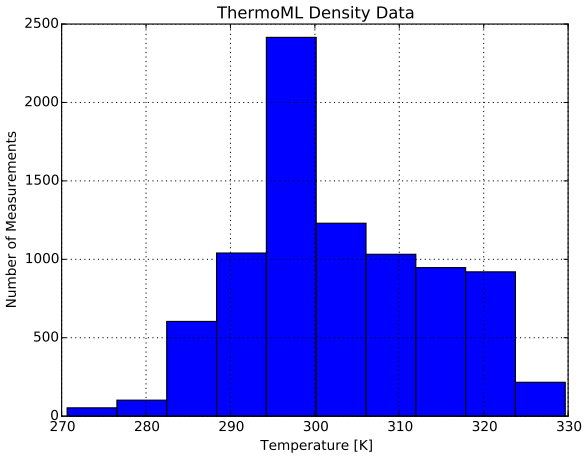
I. ABSTRACT

Useful atomistic simulations require accurate depictions of solvent. Simple experimental observables, such as density and static dielectric constants, offer straightforward targets for evaluating forcefield quality. Here we examine the possibilty of benchmarking atomistic models against the NIST ThermoML database of physicochemical measurements, which curates thousands of density, dielectric, and other measurements. We present a detailed benchmark of the GAFF forcefield against measurements extracted from ThermoML and discuss the extent of available data for neat liquids. We show that empirical polarizability models correct systematic biases inherent in predicting dielectric constants with fixed-charged forcefields. Combining our dataset with the Virtual Chemistry benchmark set provides an extensive benchmark suite for liquid properties.



II. INTRODUCTION

Intro

III. RESULTS

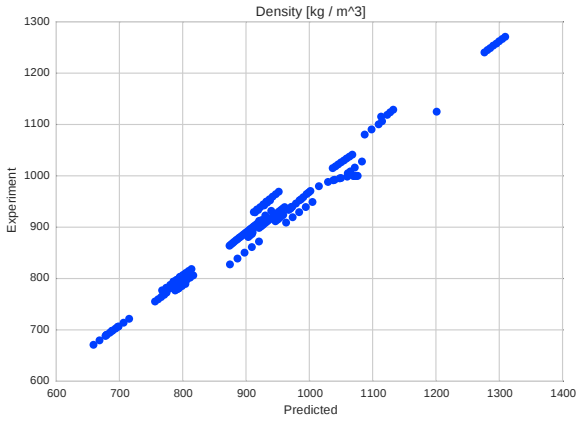
A. Neat Liquid Measurements in ThermoML

To assess the feasibility of benchmarking organic molecule forcefields against ThermoML, we performed a number of queries to summarize the data content of ThermoML.

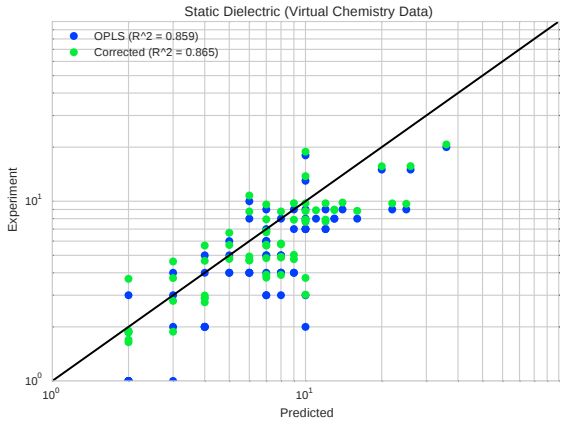
Filter	Mass Density	Static Dielectric
Full	308248	4170
Druglike elements	37944	847
≤ 10 heavy atoms, ≤ 100 atoms	27393	773
Temperature	16529	609
Pressure	8160	399
Aggregate T, P	3443	382

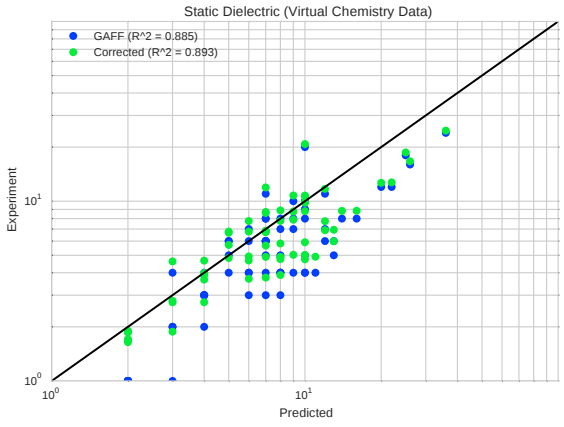
* michael.shirts@virginia.edu
† jchodera@mskcc.org

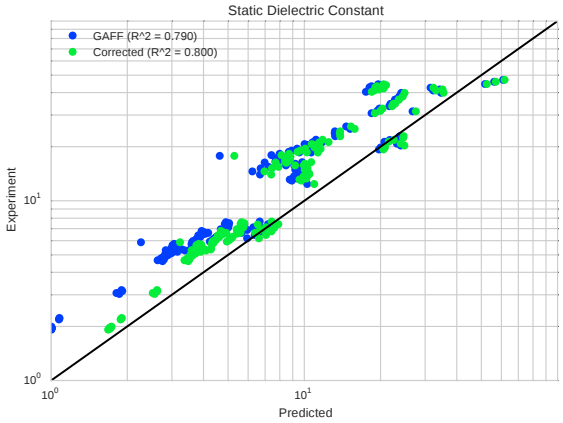
B. Benchmarking GAFF against ThermoML: Mass Density



C. Benchmarking GAFF against ThermoML: Static Dielectric







D. Benchmarking GAFF against ThermoML: Static Dielectric

IV. DISCUSSION

A. Fitting Forcefields to Dielectric Constants

Cite work by Chris Fennell on CCl4. How to get a internally consistent model. Static dielectric constant includes electronic polarization, need to subtract it out. Cite TIP4PEW paper. Could use frequency-dependent dielectric, but empirical polarizability models are highly accurate. Cite LPW CCL4 paper. Use idea of a molecular series CCL0 -¿ CCL1 ... CCL4 as example of internally inconcistent model when directly fitting dielectric constant.