Constructing transferable force fields from neutron scattering measurements with structure optimized potential refinement

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A New Use for Neutron Diffraction?

Calculating potential energy or force field parameters from structure data is called the statistical mechanical inverse problem.

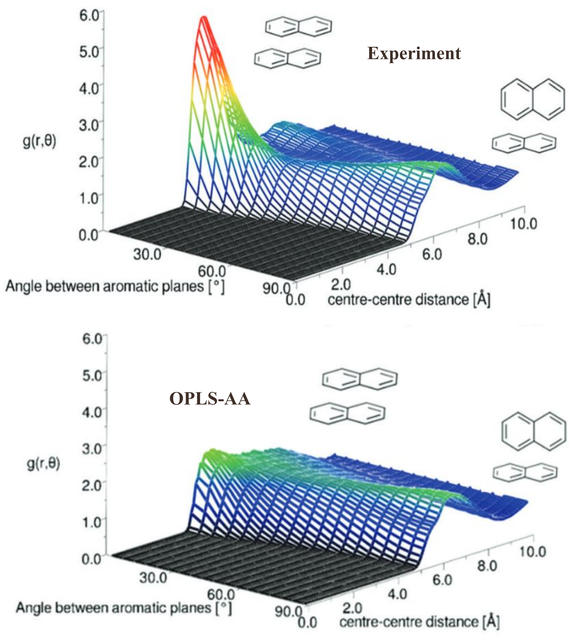
One way to generate accurate structural force fields is by using the inverse problem to find pair potentials that represent the experimental structure.

Inverse methods learn force parameters from experimental data collected at the same length scale as the molecular model (<0.1 Å).

Accurate inverse methods could improve our understanding of self-assembly, fluid structure, and interatomic interactions.

Standard Force Fields Struggle to Predict Structure

Experimental vs OPLS-AA Structure



The angular radial distribution function estimated from simulation is completely different than experiment [1].

Existing Inverse Methods are Poor for Real Data

Ornstein-Zernike: Integral relation from statistical mechanics that relates direct and indirect correlation functions.

Yvon-Born-Green: Integral relation linking pair correlation functions to interatomic potential, generalized to molecules in 2009.

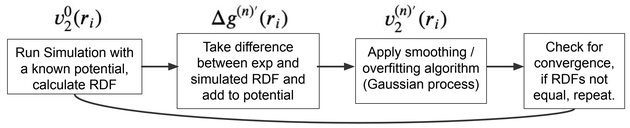
Empirical Potential Structure Refinement: Henderson inverse theorem based approach to iteratively learn interatomic potential from structure.

Relative Entropy Minimization: Minimization of Kullbach-Leibler divergence between free energy diagrams in a statistical ensemble.

Machine Learning: neural networks, Gaussian processes.

Structure Optimized Potential Refinement (SOPR)

SOPR is a numerical Henderson inverse theorem algorithm designed to generate transferable potentials from experimental scattering data.



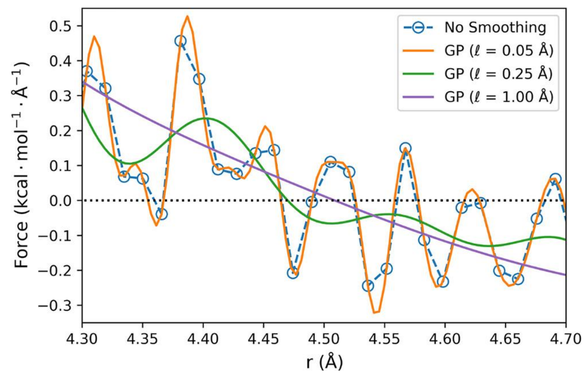
Refinement Equation: $v_2^{(n)'}(r_i) = v_2^0(r_i) + \gamma\beta^{-1}\sum_n \Delta g^{(n)'}(r_i)$

Machine Learning with Gaussian Processes

SOPR uses GPs to probabilistically generate smooth and continuous potentials.

GPs serve to reduce numerical instability and overfitting to uncertain experimental data by acting as a probabilistic function approximator.

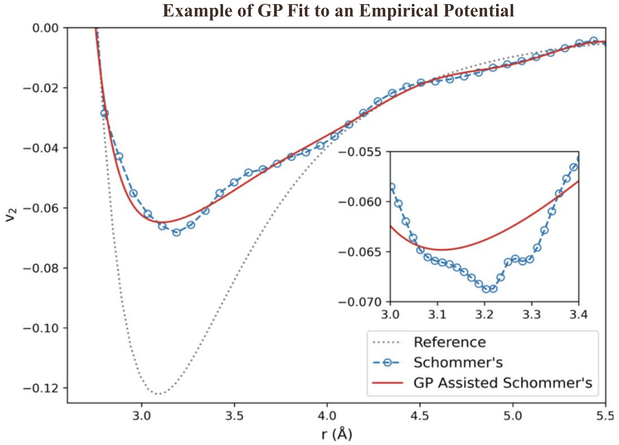
Gaussian process for force stability in SOPR



Different length scale hyperparameters change the features fit by the potential, preventing overfitting and non-physical / numerical errors.

Hyperparameters tuned based on physics-informed prior knowledge.

Example of GP Fit to an Empirical Potential



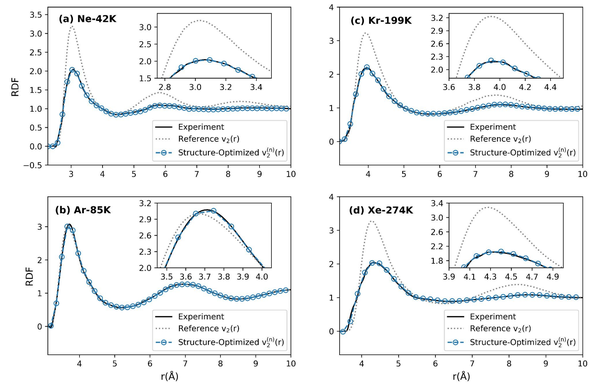
The GP helps stabilize numerical fluctuations in the empirical potential and prevent overfitting to poor experimental data.

SOPR Potentials for the Noble Gas Series

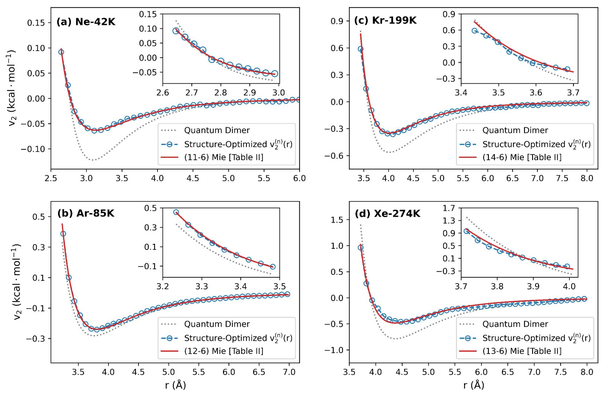
We explore whether structure-optimized potentials can predict fluid structure and other thermodynamic properties simultaneously.

SOPR was tested on the noble gas series Ne, Ar, Kr, and Xe.

Radial Distribution Functions [2]

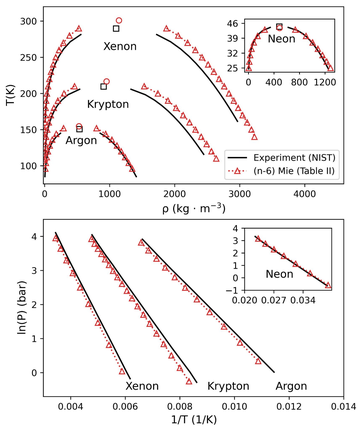


SOPR Potentials + (n-6) Mie Potential Fit



Transferability to Vapor-Liquid Equilibria (VLE)

VLE Predictions from SOPR Potentials



SOPR potentials can predict vapor-liquid phase envelopes and critical points with <5% error.

Repulsive exponents consistent with independent VLE FFs.

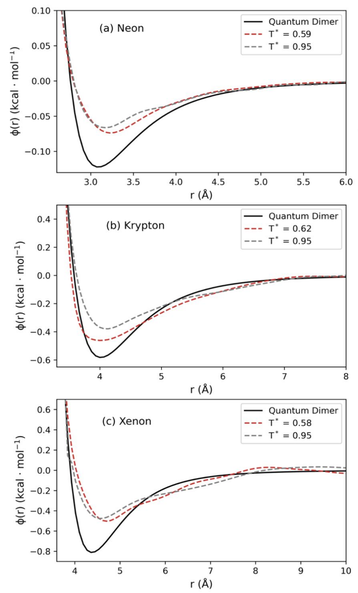
First evidence that Henderson Inverse techniques can be used to build force fields for real fluids.

Ensemble structures are sensitive to details of interatomic force fields.

Motivates continued development of SOPR for molecules/mixtures.

Comparing SOPR and Quantum Pair Potentials

SOPR vs Quantum Potential for Ne, Kr, Xe



SOPR potentials can be decomposed into quantum and many-body pair terms.

SOPR $v_2^{\text{eff}}(\mathbf{r}_{ij};\rho,T) = v_2(\mathbf{r}_{ij}) + v_2^m(\mathbf{r}_{ij};\rho,T)$ **Quantum Many-Body**

The quantum potential represents a two-body atomic potential in a vacuum.

In noble gases, many-body effects appear to be less significant near the triple point (T* = 0.6) compared to the critical point (T* = 1).

SOPR can be used to quantify many-body interactions as a function of thermodynamic state.

SOPR enables us to study the contribution many-body effects in fluid ensembles using neutron diffraction.

General Conclusions

1. **Structure can be used to extract accurate force fields in simple liquids.**
2. SOPR potentials are consistent with other FFs for vapor liquid equilibria.
3. SOPR can be used to quantify many-body interactions in fluid ensembles.

Remaining Scientific Questions

1. Can SOPR be extended to molecular liquids / mixtures?
2. How accurately do SOPR potentials model third and higher order effects?
3. **Can SOPR be used to predict thermodynamic properties for systems in extreme conditions or outside of its calibration range?**
4. What algorithm changes could improve computational stability?

References

1. F. Headen, T., L. Cullen, P., Patel, R., Taylor, A. & T. Skipper, N. The structures of liquid pyridine and naphthalene: the effects of heteroatoms and core size on aromatic interactions. *Phys. Chem. Chem. Phys.* **20**, 2704–2715 (2018).
2. Shanks, B. L., Potoff, J. J. & Hoepfner, M. P. **Transferable Force Fields from Experimental Scattering Data with Machine Learning Assisted Structure Refinement**. *J. Phys. Chem. Lett.* 11512–11520 (2022) doi:10.1021/acs.jpclett.2c03163.

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1. Brennon L. Shanks: Conceptualization, coding, algorithm development, writing, poster preparation and presentation
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