Exploring the State-Dependence of Classical Pair Potentials with Neutron Scattering

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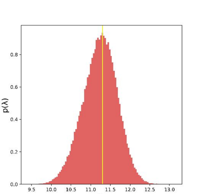
Motivation

The prediction of interaction potentials from pair correlation functions, the so called inverse problem of statistical mechanics, provides a route to develop better force fields for molecular modeling.

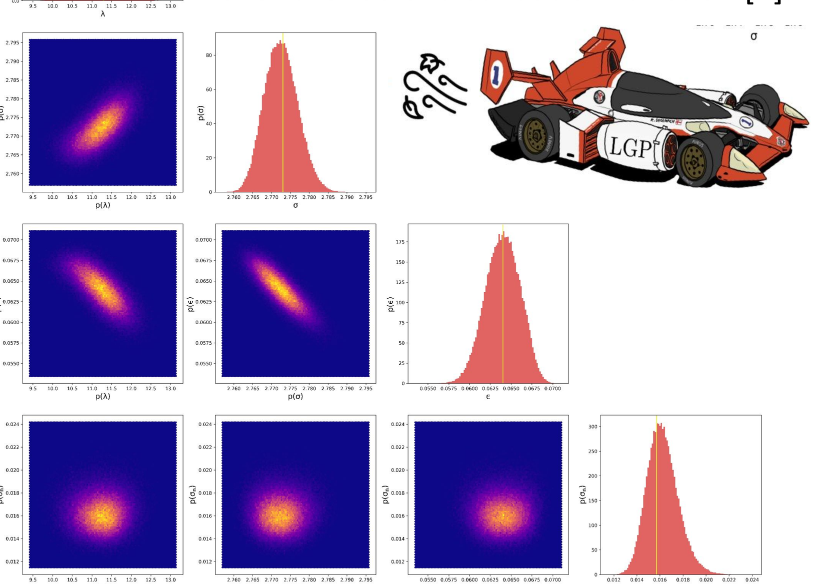
Inverse techniques are widely used for coarse graining, but have not established a foothold in the analysis of experimental data.

Question: Can we extend these inverse techniques to experimental scattering data to improve fluid models?

Pair Potentials are Sensitive to Liquid Structure

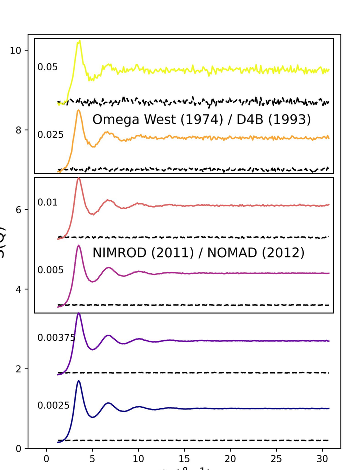


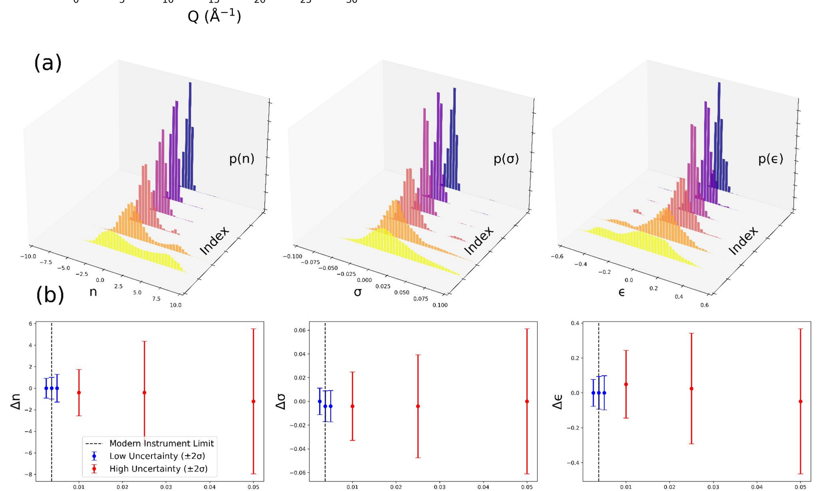
We recently designed a Bayesian UQ method for force fields with local Gaussian process surrogate models over the radial distribution function [1].



Using this model, we tested how sensitive (n-6) Mie parameters are to structure factors at varying degrees of noise.

Bayesian UQ was used to study if neutron scattering data is a good FF benchmark.





We discovered that pair potentials are more sensitive to scattering data than previously believed [2].

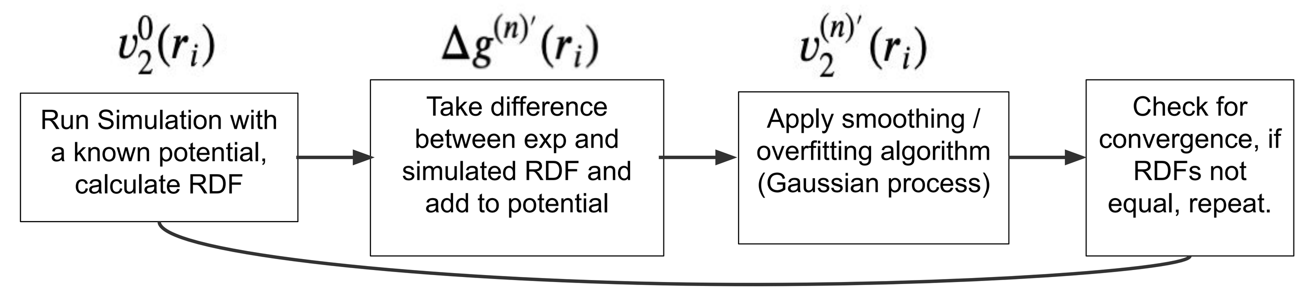
Key Takeaways

- Neutron scattering data is a viable target to train force fields.
- We have created rigorous methods for Bayesian UQ of force fields to complex scattering data.
- **What we can learn from scattering with respect to interatomic interactions?**

Learning Interaction Potentials from Scattering Data and Relations to Quantum Mechanics

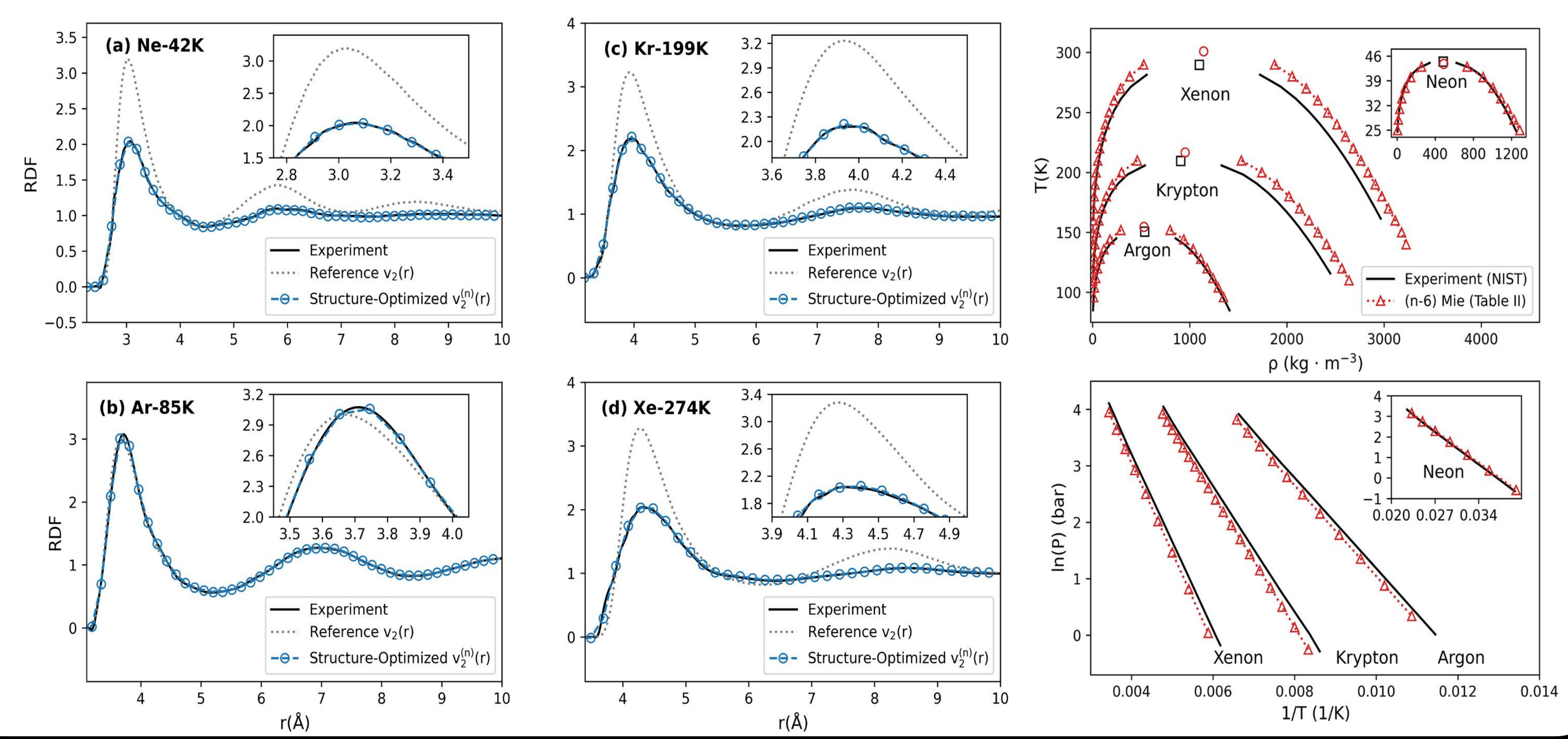
Structure Optimized Potential Refinement (SOPR) [3]

Probabilistic iterative Boltzmann inversion for learning transferable potentials from experimental scattering data.



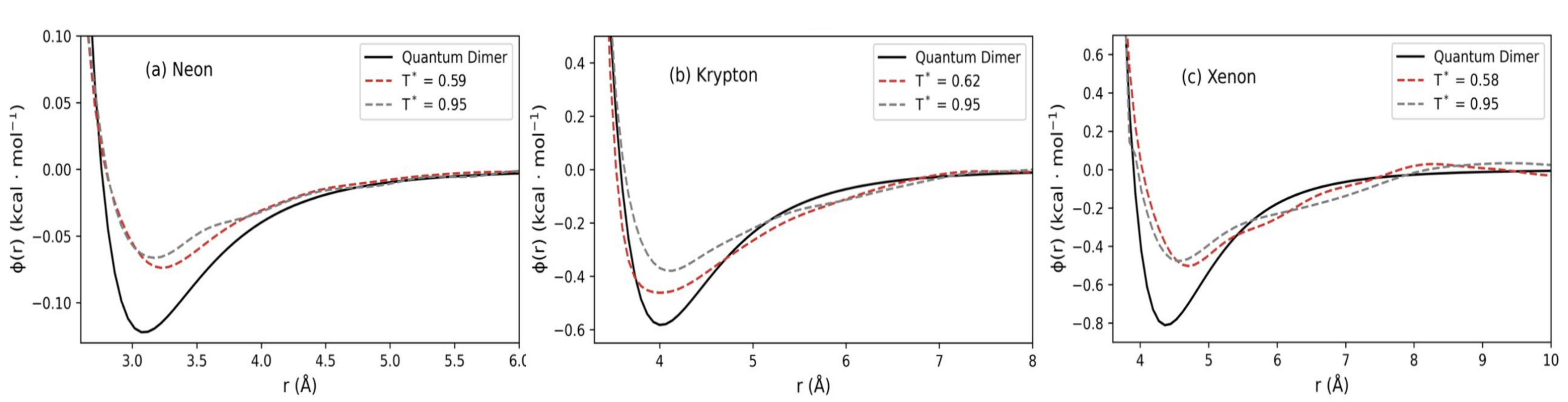
Refinement Equation:

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

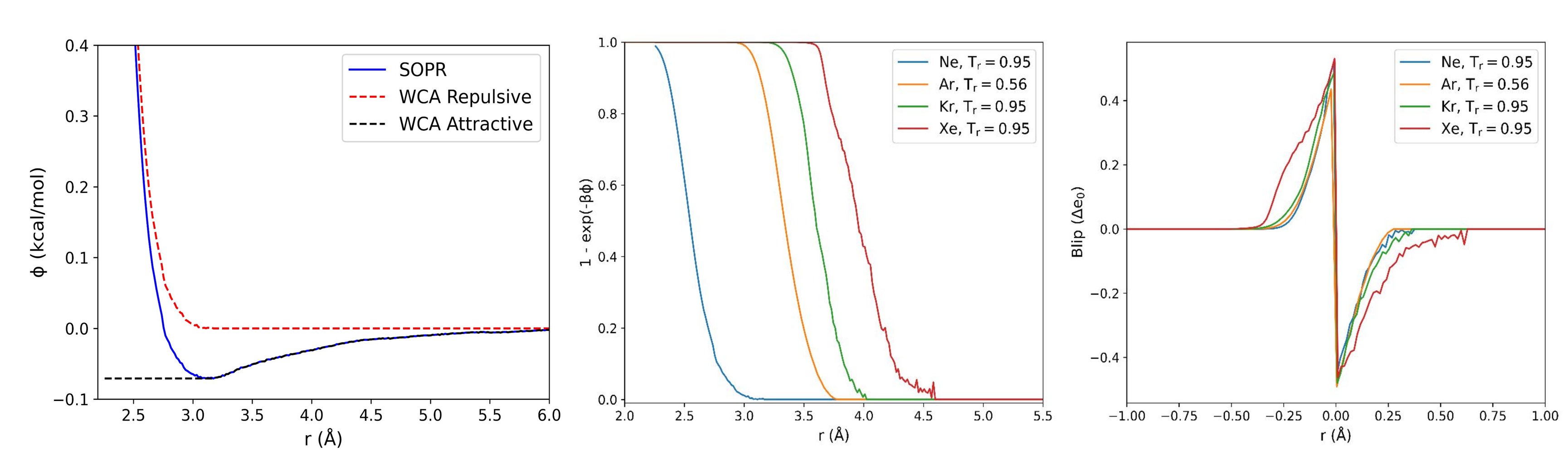


Comparing SOPR and Quantum Pair Potentials

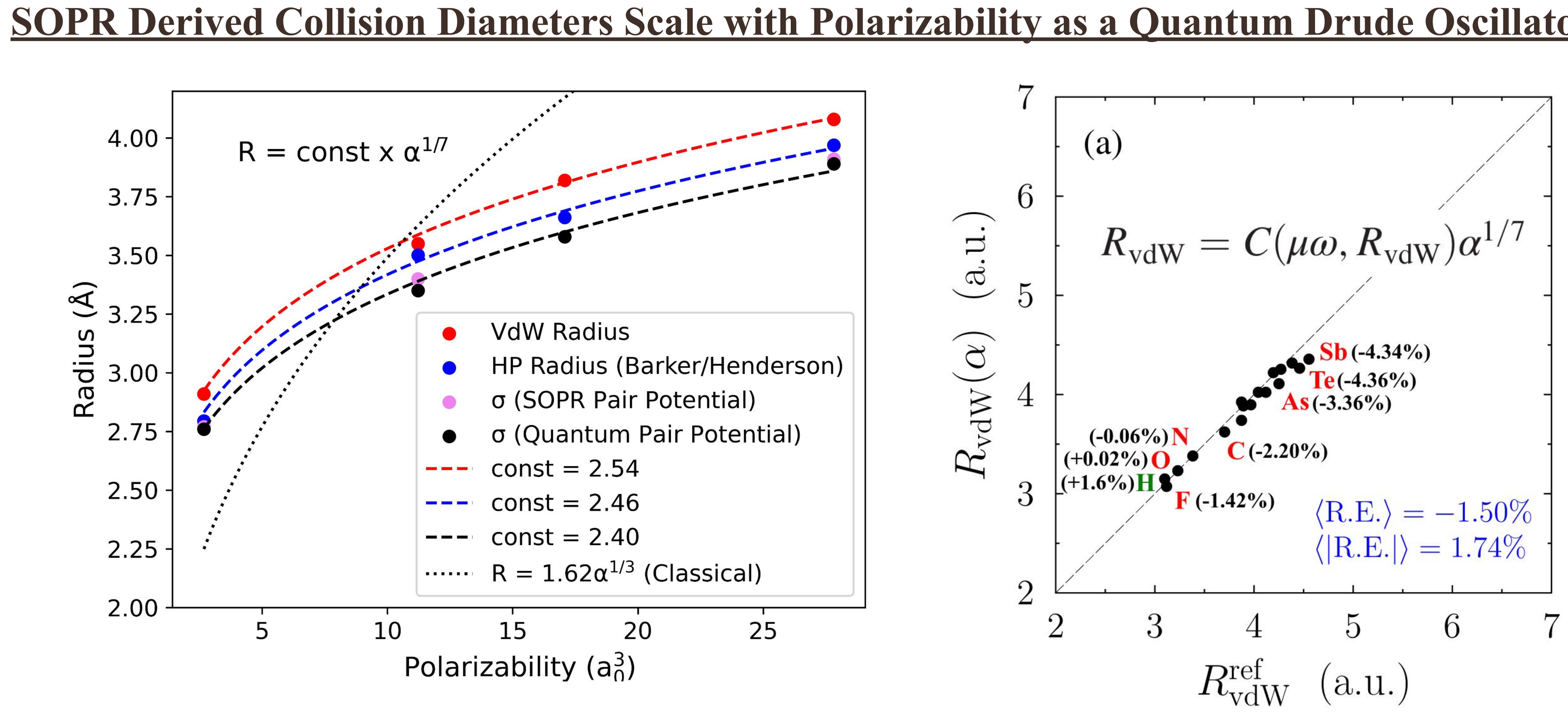
SOPR vs Quantum Potential for Ne, Kr, Xe



Weeks-Chandler-Anderson Decomposition and Computation of Hard Particle Diameter and Blip Function

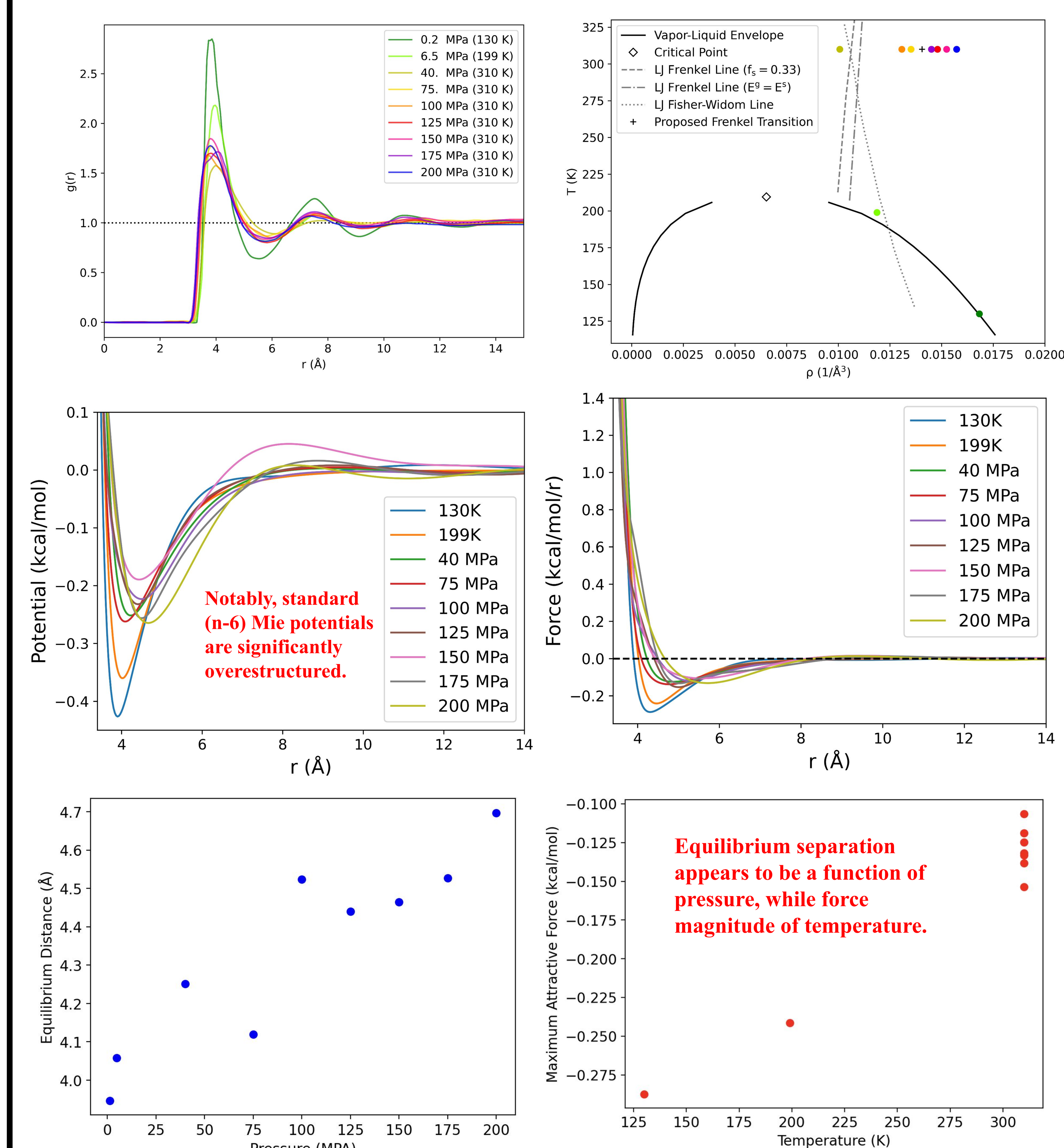


SOPR Derived Collision Diameters Scale with Polarizability as a Quantum Drude Oscillator [4]

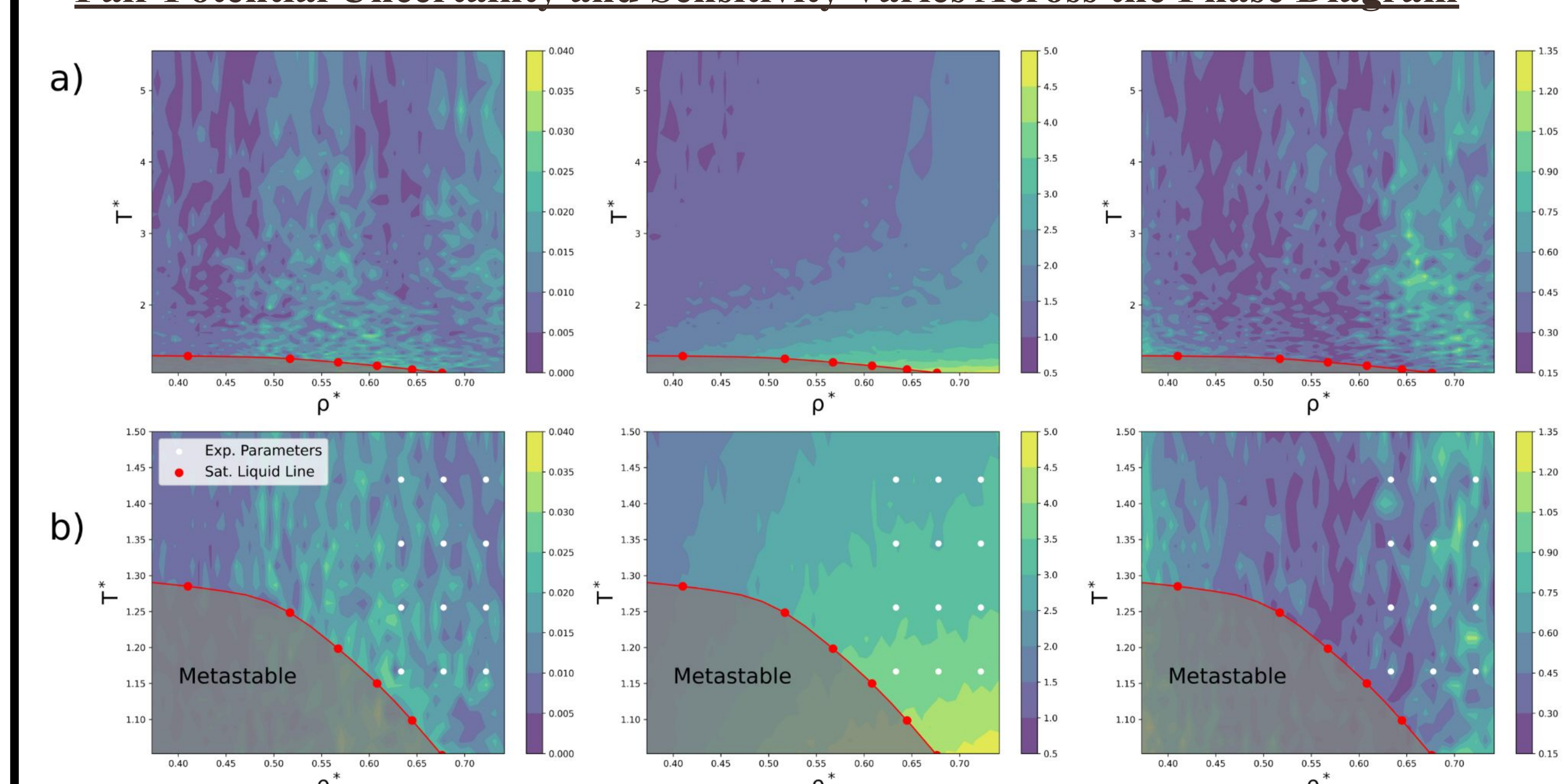


Quantifying State-Dependent Many-Body Contributions to Effective Pair Potentials

SOPR meta-analysis of Krypton Radial Distribution Functions [5,6]



Pair Potential Uncertainty and Sensitivity Varies Across the Phase Diagram



Key Takeaways

- Inferring atomic size from the WCA separation is consistent with the van der Waal radius and provide empirical evidence of a quantum drude oscillator type interaction
- SOPR potentials trained on experimental scattering data show a temperature and pressure dependence that manifests in different features of the potential.
- Sensitivity of the potential to the structure factor in simple liquids is more nuanced than previously reported by Weeks, Chandler and Anderson.

Conclusions

1. Neutron scattering data is a viable target for force field training.
2. Structure inversion is a valuable tool beyond its typical use as a coarse graining method.
3. SOPR potentials can be analyzed to reveal fundamental insight into quantum mechanical behaviors.
4. SOPR potentials are state-dependent and may reveal fundamental insight into how many-body interactions change across the phase diagram.
5. It may be possible to identify supercritical phase transitions from scattering data and SOPR.

Remaining Scientific Questions

1. Are there other quantum mechanical properties that can be inferred from SOPR potentials?
2. How can we rigorously quantify the many-body contribution of the SOPR potential?
3. Why do effective pair potentials have an apparent trend in equilibrium separation as a function of pressure and maximum attractive force as a function of temperature?
4. Do (n-6) Mie potential representations of the potentials exhibit the same trends and how confident are we that these potentials are correct?

References

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Acknowledgments

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