# Humboldt Research Fellowship

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**ABSTRACT**

Jadran, I have included outlines for two different proposals. The first proposal is to use more realistic nonbonded potentials to improve the high pressure extrapolation. The second proposal is to move beyond the Lorentz-Berthelot combining rules to improve the prediction of mixture properties. I would appreciate your insight regarding which of these is more likely to be funded and which is more important and/or interesting.

## 1 Outline: Developing more accurate nonbonded potentials for EOS development

1. Background to establish need for hybrid data sets
   (a) Design of efficient and reliable chemical processes requires accurate equations of state over a wide range of temperatures and pressures
   (b) The quantity and quality of experimental data is insufficient for most compounds
   (c) Molecular simulation is an ideal approach for overcoming the data deficiency at extreme temperatures and pressures
   (d) Improved EOS are developed by supplementing experimental data with simulation results
2. Reliability of hybrid data set approach depends on accuracy of force field, specifically, how well the model extrapolates to extreme temperatures and pressures
   (a) Recent work has demonstrated that the united-atom Lennard-Jones $n$-6 force field does not extrapolate from vapor-liquid equilibria conditions to elevated pressures
   (b) Improved extrapolation requires a more physically realistic nonbonded potential
   (c) For this reason, we propose the use of an extended Lennard-Jones (ex-LJ, 12-10-8-6) potential
3. The ex-LJ 12-10-8-6 potential is more flexible than the LJ 12-6, and more theoretically justified than the Mie $n$-6
4. Although the ex-LJ was proposed over two decades previously, it has not been tested as extensively as the LJ 12-6, Mie $n$-6, and exponential-6
5. One reason for the lack of popularity is that the higher dimensional parameterization of the ex-LJ is computationally infeasible when implementing traditional iterative force field optimization approaches

(a) Multistate Bennett Acceptance Ratio (MBAR) combined with basis functions (BF) has been shown to greatly accelerate force field parameterization

(b) MBAR reweights configurations sampled with a reference force field to predict thermodynamic properites for a non-simulated force field

(c) Basis functions store the contributions from the $r^{-m}$ terms for the nonbonded energies and forces

6. The methodology proposed in this study is to:

   (a) Develop an EOS over the temperatures and pressures where reliable experimental data exist

   (b) Fit the ex-LJ parameters to EOS derivative Helmholtz energy properties in range where EOS is reliable

   (c) Perform molecular simulations at state points where experimental data are not available

   (d) Iterate:

      i. Refit the EOS to the hybrid data set

      ii. Reoptimize the force field parameters to match EOS (using MBAR so that no additional molecular simulations are required)

7. With this iterative approach, it is possible to ensure that the force field derivative properties are internally consistent with those of the EOS, resulting in better extrapolation for both the EOS and the force field

8. Important to develop new combining rules for cross interactions of ex-LJ

9. Additional binary interaction parameters improve agreement with mixture properties

# 2 Justification for funding

1. Why is this important?

   (a) Reliable estimates of thermophysical properties have signficant practical industrial applications

2. Why me?

   (a) Expertise in force field parameterization and, specifically, the MBAR-BF method

   (b) Expertise in both molecular dynamics and Monte Carlo simulations

3. Novel aspects of this research to expand my expertise:

   (a) Fitting fundamental equations of state

   (b) Residual helmholtz energy derivatives from molecular simulation

   (c) Hybrid data set approach

4. Why Jadran?

   (a) Dr. Vrabec has helped pioneer the FEOS hybrid data set approach

   (b) Substantial computational resources at disposal

   (c) Strong research group and collaborators

   (d) Experience developing molecular simulation software