First-principles Monte Carlo simulations of hydrogen-bonding fluids

DOE CSGF Conference

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July 14-16, 2009

Projects

- First principles Monte Carlo simulations
  - Phase equilibria of water
  - Nucleation of super-heated hydrogen fluoride vapor
  - Phase equilibria of methanol
  - Henry's law constant of hydrogen chloride in water
- Monte Carlo simulations with empirical potentials
  - Water confined in nanogaps
  - Crystallization of tetrolic acid
  - Solvation environment of coumarin 102 in acetonitrile/ water mixtures

Phase Equilibria of Water

- Motivation
- Background
  - CP2K/Quickstep
  - Monte Carlo algorithms
- Canonical ensemble simulations
- Isobaric-isothermal ensemble simulations
- Gibbs ensemble simulations

Motivation

- Inexpensive empirical models work well for specific properties or state points

- In principle, quantum mechanical potentials are fully transferable between molecules and provide enough flexibility to describe reactive systems

- Phase equilibria have previously been shown to be extremely sensitive to the interaction potential, and therefore present a good test of a model's accuracy

CP2K/Quickstep

- CP2K is an internationally developed software suite for particle-based simulation

- Quickstep is a near-linear scaling algorithm for computing the energy/forces of a system via Kohn-Sham density functional theory

$$E[\rho] = T_\mathrm{e}[\rho] + V_\mathrm{ne}[\rho] + V_\mathrm{ee}[\rho] + E_\mathrm{xc}[\rho]$$

- Quickstep uses a mixed basis set (atom-centered Gaussians to represent the KS orbitals and plane-waves to expand the electronic density)

http://cp2k.berlios.de

Monte Carlo Algorithms

- Monte Carlo techniques sample the partition function of a specific ensemble

- Metropolis *et al.* [1953] introduced importance sampling

  - Attempt a move (change the system)

  - Accept or reject this move based on the pseudo-Boltzmann weight

Water in the Gibbs Ensemble

- Knowledge of the vapor-liquid coexistence curve (VLCC) is of great importance for molecular simulation

- Only one previous study attempted to compute thermodynamic properties of water

- Phase equilibria provide a sensitive test of the accuracy of density functionals

- One pair of data points for the VLCC took approximately 70 days using 100 processors on Thunder at LLNL

Water in the Gibbs ensemble

V=2411.0   V=2545.6
Cycle= 0.0
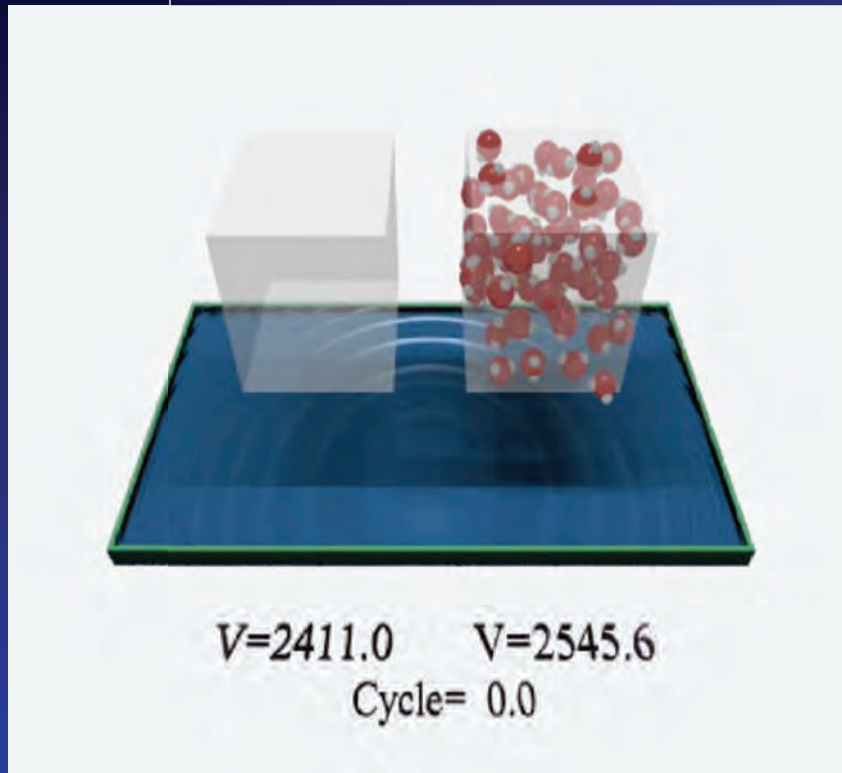
- Translations, rigid-body rotations around the center of mass, conformational changes for thermal equilibrium

- Volume exchanges for mechanical equilibrium
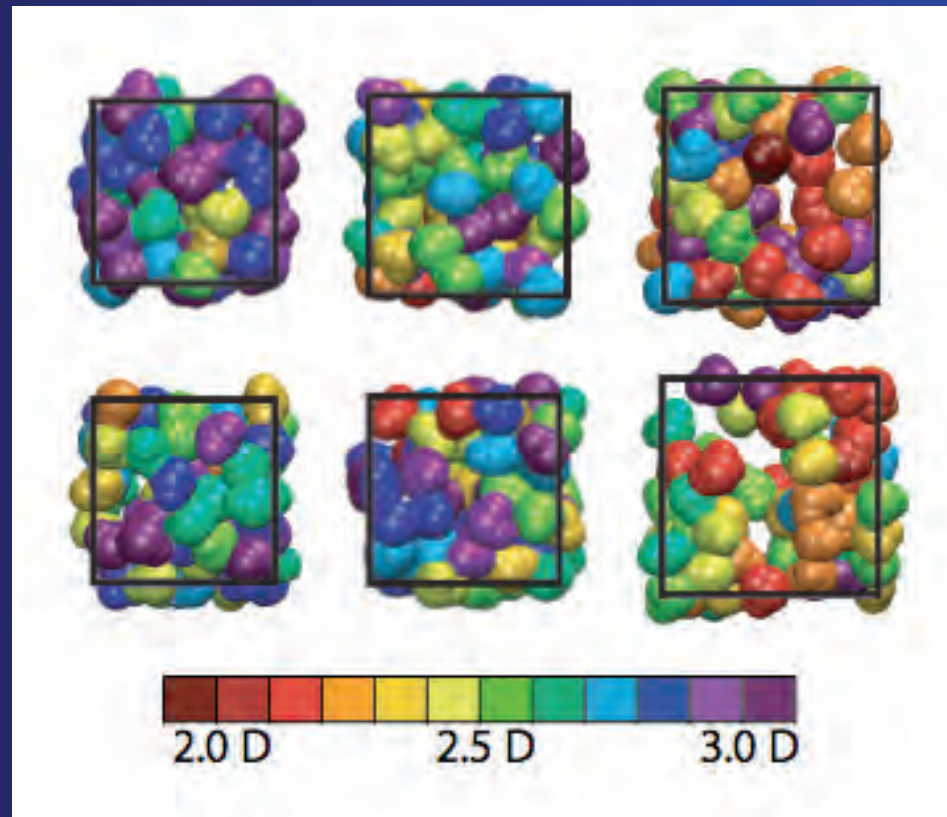
- Molecular swaps for phase equilibrium

Coexistence Curves
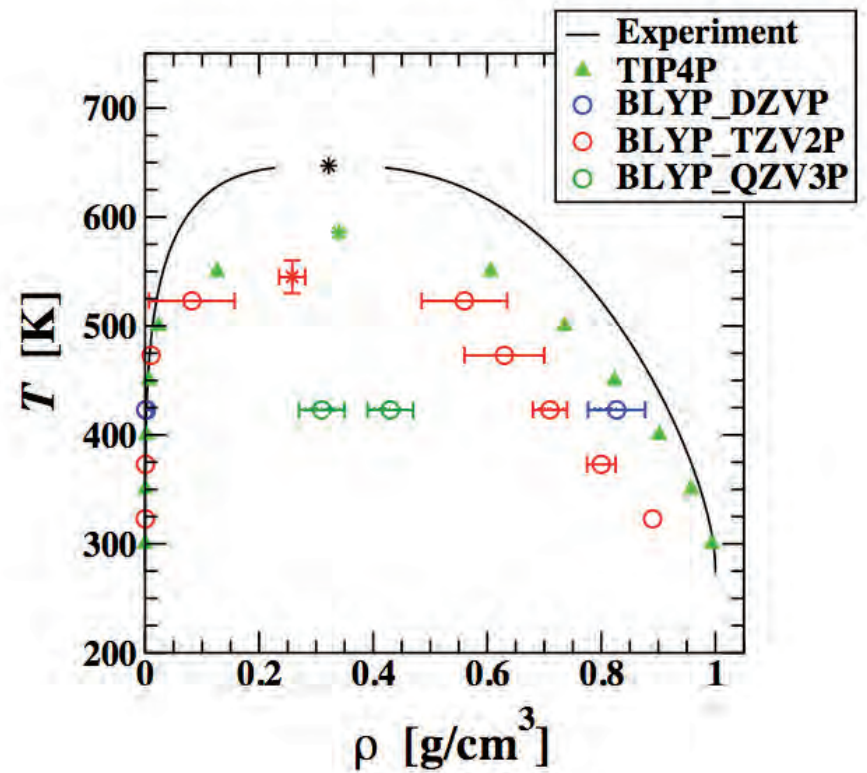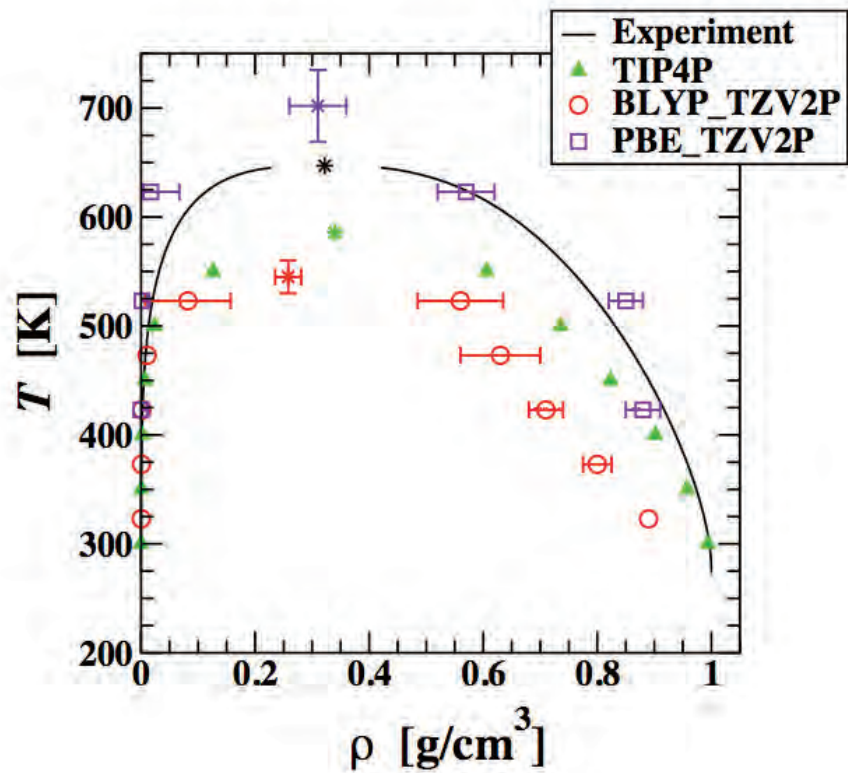
Molecular Dipole Moments

Colored according to molecular dipole in intervals of 0.1 D

# Water in the Gibbs Ensemble - Conclusions

- BLYP-GTH-TZV2P-1200 gives a description of water that is underbound, while PBE-GTH-TZV2P-1200 is overbound

- Phase equilibrium suffers from a significant basis set dependence

- The molecular dipole moments display a high degree of heterogeneity at all temperatures, regardless of the density functional used

Super-heated Hydrogen Fluoride Vapor

- Hydrogen fluoride forms very strong hydrogen bonds
- Extensive aggregation at low temperatures in the vapor phase
- Empirical model simulations show rings and branched clusters, while quantum calculations show only linear aggregates

Aggregation-Volume-Bias Monte Carlo (AVBMC)

- Enhances the sampling of cluster formation and destruction
- Algorithm
  - Select a molecule, i, to be swapped
  - Select a target molecule, j
  - With a probability of P_{bias}, swap i into the bonded region of j (defined as a shell centered on j with inner r_{min} and outer radius r_{max})
  - Move acceptance is determined by energy difference, "in" and "out" volumes, and P_{bias}
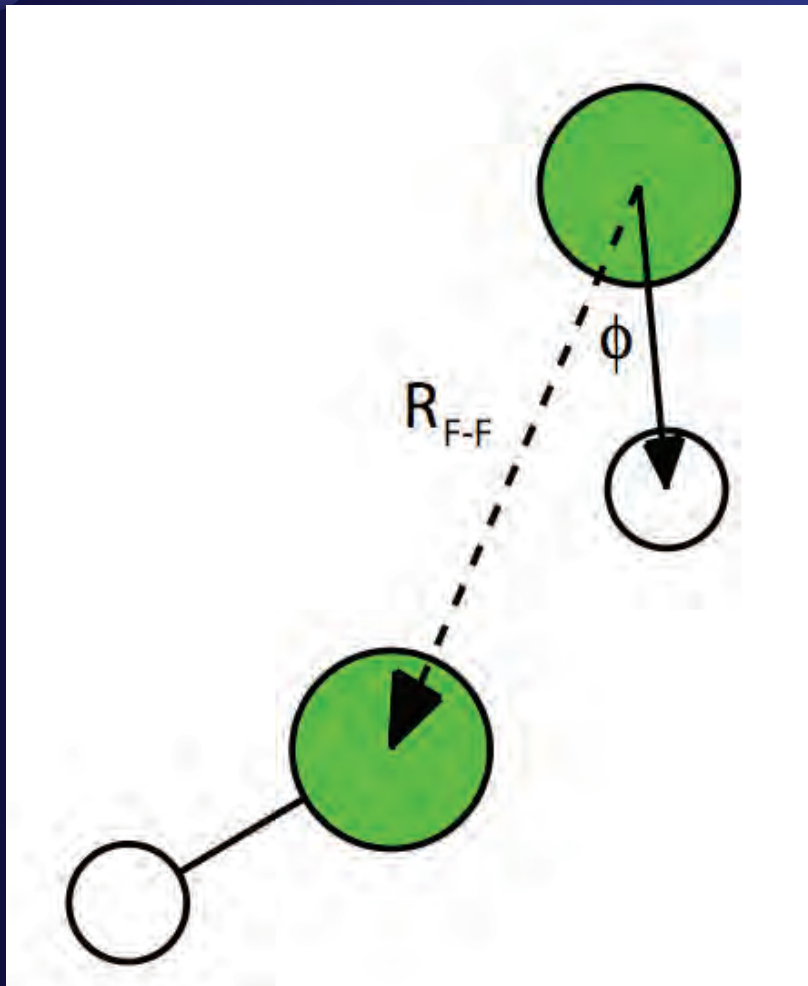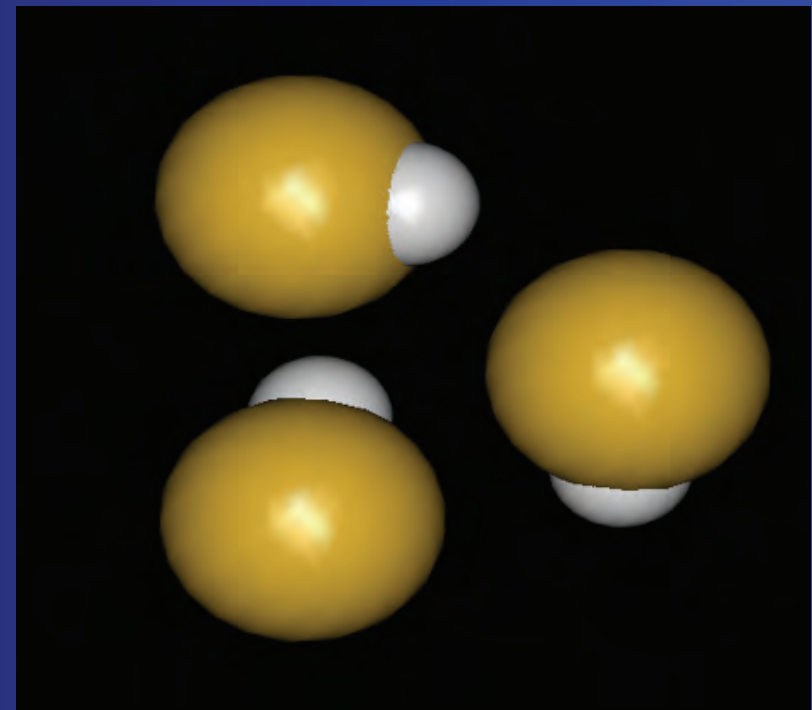- Combine with CBMC to increase efficiency
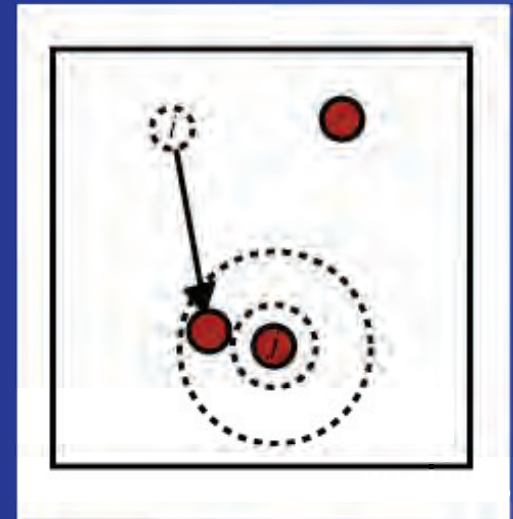
Hydrogen Fluoride
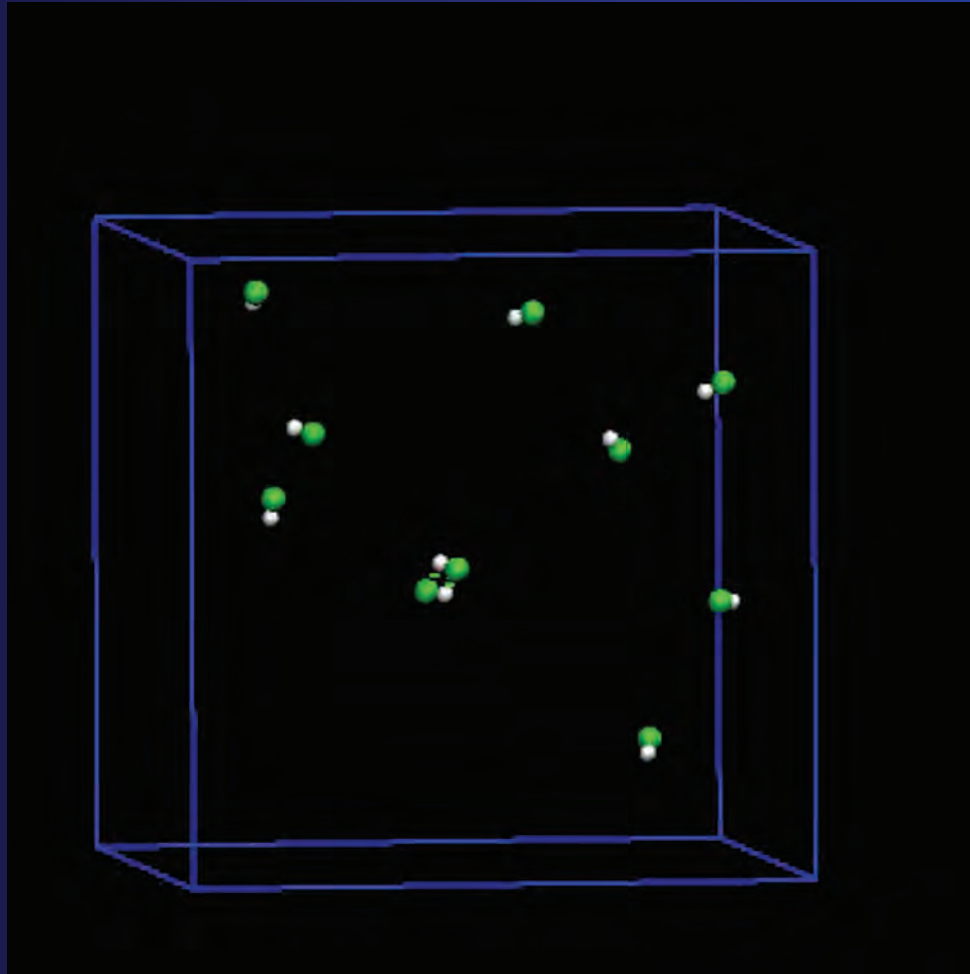
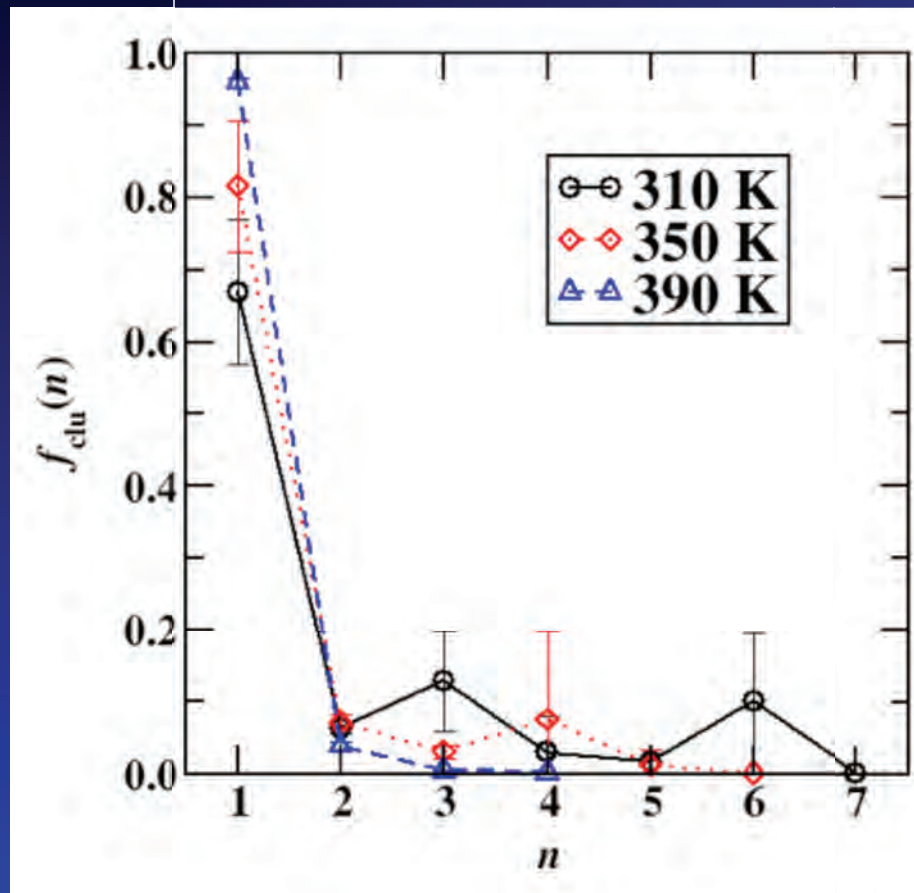

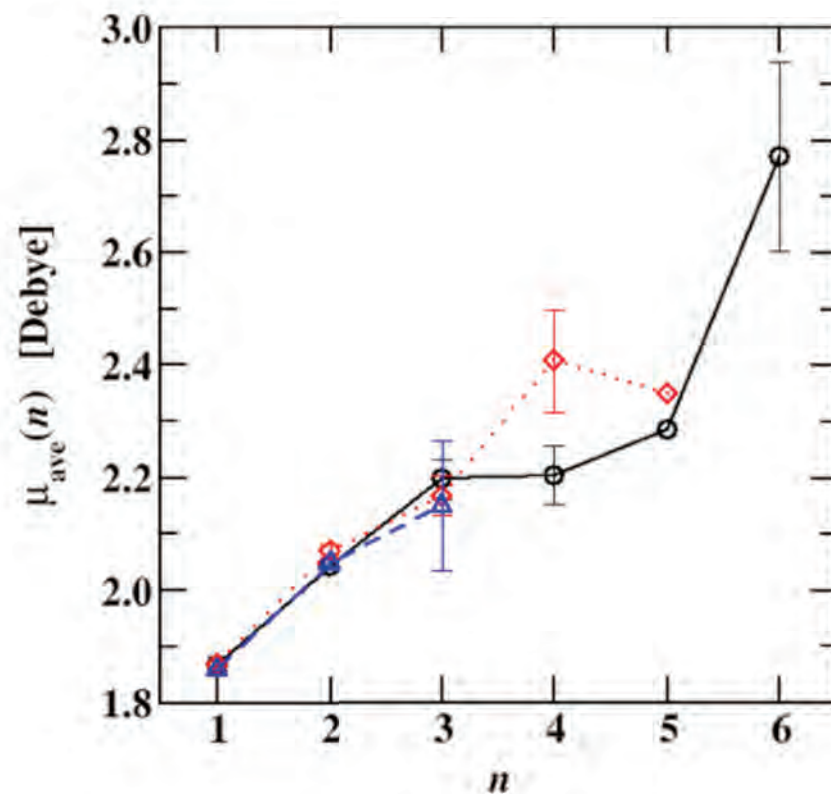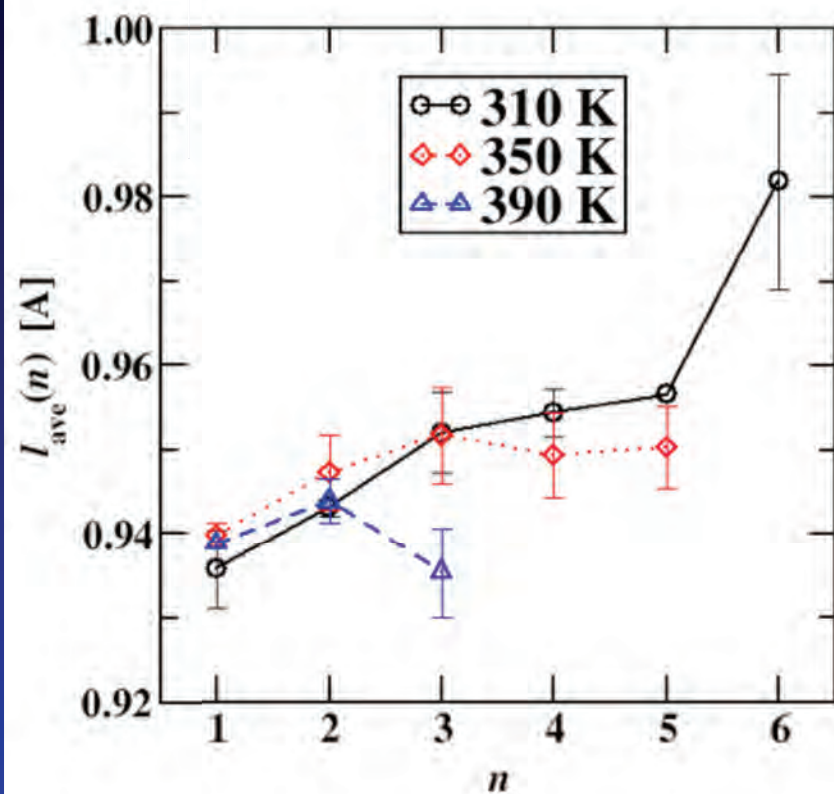T = 350 K

Hydrogen Fluoride - Cluster Definition

- All members of a cluster are connected via a hydrogen bonding network
- A "hydrogen bond" is determined by a combined distance/angle criterion

Hydrogen Fluoride - Cluster Size Distribution

Hydrogen Fluoride - Conclusions

- Plane-wave based simulation codes are not ideal for studying vapor phases
- Increased aggregation is seen at lower temperatures, with clusters up to the septamer
- Density functional theory does produce clusters with non-linear architectures
- Several molecular properties show dependence on the cluster size

Acknowledgements

- J. Ilja Siepmann and the members of the Siepmann group
- Drs. Chris Mundy and Will Kuo, LLNL
- CP2K developers

- 3M Foundation Fellowship
- DOE Computational Science Graduate Fellowship

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Water in the Gibbs Ensemble - System Size Effects

- Normal boiling points:

Size	T_b [K]
32	364 +/- 2
64	364 +/- 2
96	366 +/- 2
128	365 +/- 2
256	364 +/- 1
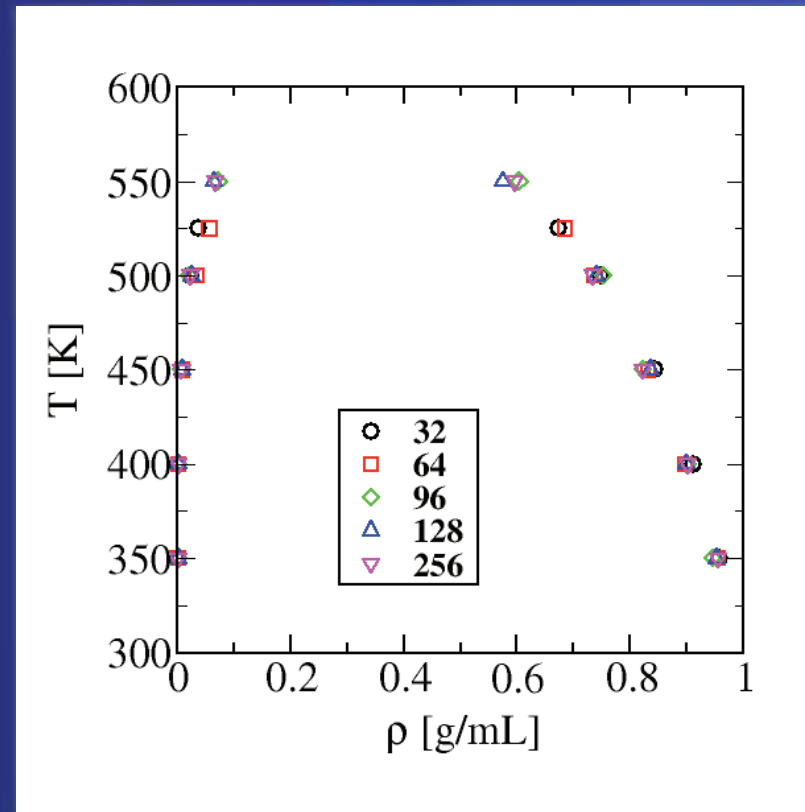
TIP4P force field with LJ tail corrections and Ewald sum