Using LAMMPS to Simulate Vapor-Liquid Equilibrium

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Introduction

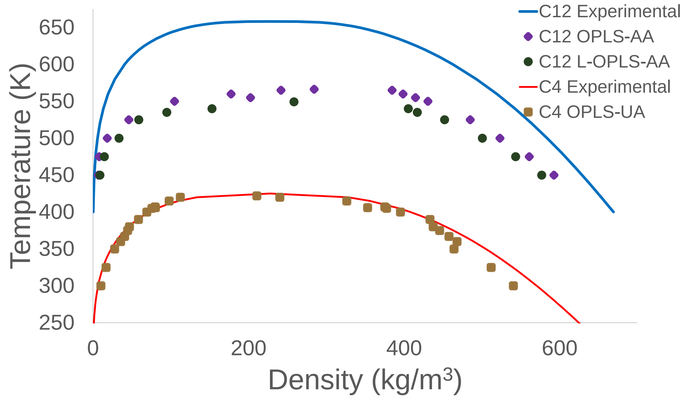
- Rocket engines operate in regions near the critical point of pure component and mixtures
- Understanding the physio-chemical properties of fluids in the near critical region is essential for modeling and understanding of the combustion chamber
- Unfortunately mean field theories (ie: equations of states (EOSs)) fail in the near critical region
  - Due to the correlation length being infinite at the critical point
- New theories need to be applied in order to understand the near critical behavior
- MD allows us to probe the near critical region in order to develop these new theories

Calculation Details

- All simulations were performed within LAMMPS using the OPLS potential (all and united atom)
- VLE determined by performing a Voronoi analysis and a series of two- and one-phase simulation
- Law of rectilinear diameters and density scaling law used to determine the critical point

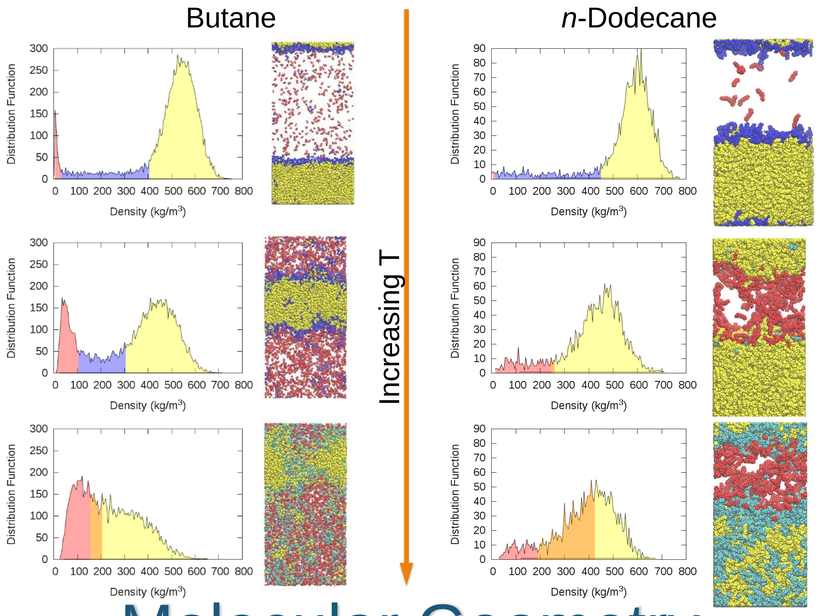
Vapor Liquid Equilibrium

- Butane and *n*-Dodecane chosen as probe molecules
- Used the OPLS potential
  - United atom for butane
  - All atom for *n*-dodecane
- Able to simulate temperatures within 1% of the calculated critical point
- The same class of potentials, can yield drastically different critical points for hydrocarbons when compared to experimental data



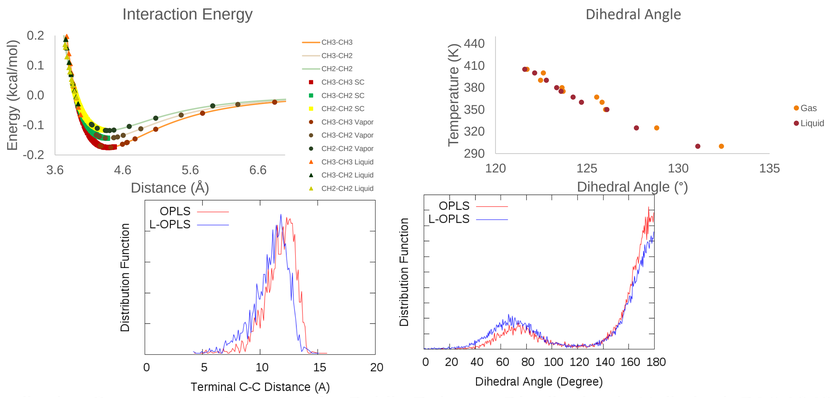
Phase Identification

- Phases determined by Voronoi analysis
- As temperature increases,
  - Interface becomes less smooth
  - More molecules move into the vapor phase
  - Near the critical point, some molecules are considered both vapor and liquid
    - Supercritical molecules



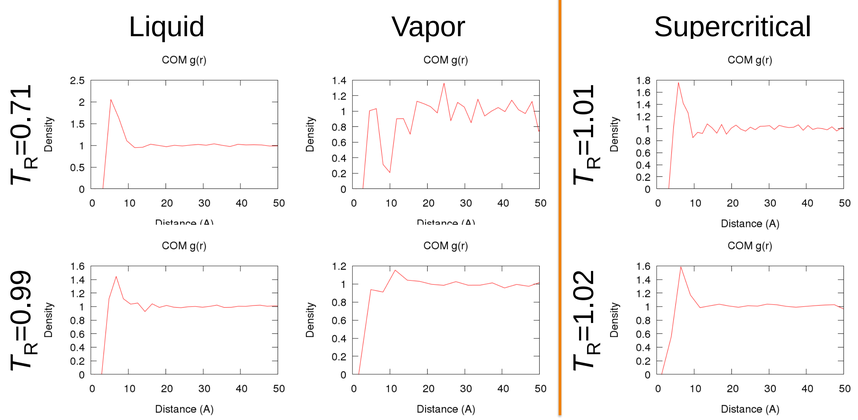
Molecular Geometry

- Different phases sample different regions of potential
  - Liquids sample repulsive wall
  - Vapors sample attractive tail
  - Supercritical fluids sample potential well
- As the temperature increases, more *gauche* dihedrals appear
- Different potentials yield slightly different geometries



Radial Distribution Function

- Decay of radial distribution function (RDF) is the correlation length
- The correlation length increases as the critical point is approached
- First solvation shell for liquid contains more molecules than vapor
- Supercritical fluid RDF has longer correlation lengths compared to liquid and vapor



Conclusions

- The same class of potentials can give different predictions of the critical point for different hydrocarbons
- MD allows for simulations within 1% of the calculated critical temperature
- As the critical point is approached
  - Interface becomes more ragged
  - Molecules can be considered supercritical close to the critical point
  - The correlation length increases
- Different phases sample different regions of the potential
- The correlation length is the greatest in the supercritical phase and increases as the critical point is approached

Acknowledgements

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