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MedeA Gibbs : Thermodynamics of fluids and adsorption

When J.W. Gibbs introduced the concept of chemical potential and free energy in the late 19th century, the structure of matter at the nanoscale was still poorly known. Scientists and engineers had to parametrize the Gibbs free energy solely using experimental data in order to model fluid phase equilibria and adsorption in industrial adsorbents. Advances in statistical mechanics and improved knowledge of intermolecular forces enable simulations at the molecular level for many systems of industrial relevance. MedeA Gibbs applies Monte Carlo techniques in simulations to understand fluid structures at the molecular level and obtain properties such as fluid phase equilibria for pure compounds and mixtures, near-critical behavior, adsorption isotherms and selectivity.

Properties from Gibbs:

- *Phase properties:*

  Volumetric (density, molar volume), virial pressure, cohesive energy, chemical potential (or fugacity), residual heat capacity, compressibility, thermal expansivity, Joule-Thomson coefficient
- *Phase equilibria of pure compounds:*

  Vapor pressure, vaporization enthalpy
- *Phase equilibria of binary and multicomponent systems:*

  Phase compositions, phase densities, cohesive energy
- *Adsorption:*

  Amount adsorbed of each species, guest-host energy, integral heat of adsorption

Simulation conditions available from Gibbs:

- *Single phase fluid calculations (NVT, NPT statistical ensembles)*
- *Two-phase and three-phase fluid equilibria (Gibbs Ensemble Monte Carlo)*
  - *At imposed global volume (pure compounds, binary and multicomponent systems)*
  - *At imposed pressure (binary and multi-component systems)*
- *Simulation of adsorption in microporous crystalline solids (Grand canonical ensemble)*

Key benefits of Gibbs:

- *Explicit account of molecular shape, flexibility, and polarity to compute thermodynamic properties from first principles*
- *Use of well-tested forcefields*
- *High extrapolation capacity in temperature and pressure*
- *Simulation of pure component properties (toxic, unstable,…) from molecular structure only*
- *Simulation of multicomponent fluid properties without empirical coefficients for mixing rules*
- *Understanding of fluid adsorption behavior as a result of the microstructure of the adsorbent and fluid composition*
- *Calculation of liquid-vapor critical points without classical pitfalls*
- *Contribution of the various forms of energy to fluid properties*

Required MedeA modules:

- *Core MedeA environment*
- *JobServer and TaskServers*
- *Forcefields*

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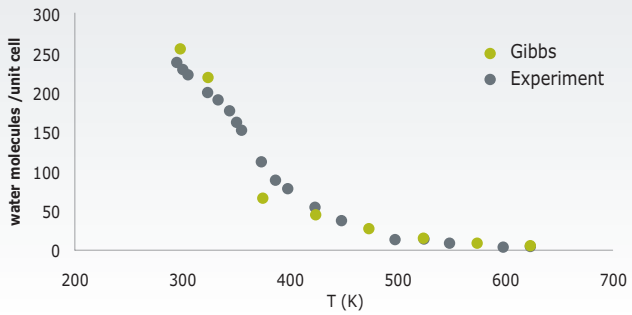
Computational characteristics:

- *Two methods for long range corrections to electrostatic energy (reaction field, Ewald summation)*
- *Allows rigid molecules, flexible molecules (linear, branched, cyclic) with electrostatic charges*
- *Adsorption :*
  - *Edition of microporous crystalline solids of various space groups from databases (ICSD, Pearson, Pauling) through MedeA visual builder*
  - *Cubic, orthorhombic and non-orthogonal simulation boxes*
  - *Pre-calculation of energy grids for high computational efficiency*
- *Featuring major force fields for fluid properties: OPLS-UA, TraPPE, AUA*
- *14 different Monte Carlo moves for the efficient sampling of internal and intermolecular configurations (configurational bias, rotational bias, etc.)*
- *Runs either locally or on remote server through JobServer + TaskServer MedeA architecture*
- *Parallelization of energy calculations by Open-MP*

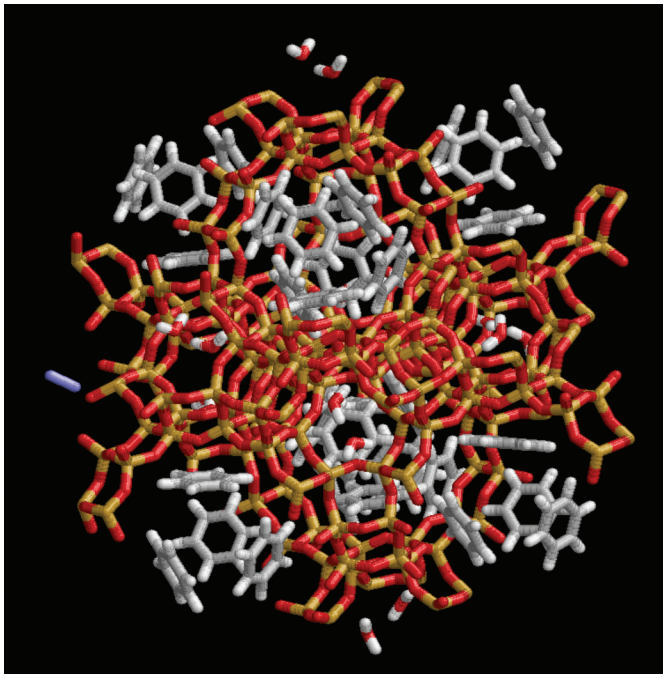
Validation Test: Water desorption in faujasite

Na56Y at constant pressure (1690 Pa)



Example configuration of adsorption of a multicomponent gas mixture in NaY faujasite at 323K and 1 bar:

85% methane, 10% ethane, 3% propane, 0.1% n-heptane, 0.01% benzene, 2% CO_2, 0.006% H_2O



The aluminosilicate framework appears in yellow and red. Benzene is the most adsorbed species (approximately 4 molecules per supercage, in approximate tetrahedral symmetry). Water (white-red-white) is present in the smaller alpha-cages only (0 to 4 molecules per cages).

Saturated hydrocarbons are almost absent (in this snapshot there is just one ethane molecule, appearing in purple on the left). The most adsorbed components are neither the most abundant (methane) nor the higher molecular weight (n-heptane), due to the importance of electrostatic forces in this cation-exchanged zeolite.

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