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Monte Carlo Simulations with LAMMPS

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Motivation: Why Use Monte Carlo in LAMMPS?

Limitations of MD

- Does not allow number of particles to change
- Sampling limited by slow translational dynamics e.g. interdiffusion in metal alloys

Monte Carlo Methods

- Allow unphysical moves that can overcome kinetic barriers
- Allows atoms or molecules to be added or removed
- Allows atoms to switch to a different element
- Faithfully preserves equilibrium Boltzmann probability distribution of atomic configurations, atom counts, molecule counts, etc.

Implementation of MC Methods in LAMMPS

History

- Development begun by Paul Crozier in 2011
- Initially limited to single atom moves
- Later added molecule moves
- Could not handle manybody potentials or electrostatics (no EAM, Tersoff, water)
- Paul overcame this in 2014 by adding full_energy option
- I have taken over maintenance since Paul's departure.
  - Added intra_energy and group keywords
  - Performed validation experiments
  - Fixed several problems with insertions and rotations
  - Added some safeguards against invalid moves

Implementation of MC Methods in LAMMPS

Requirements

- Support particle creation/destruction
- Compute pre- and post-creation/deletion potential energies.
- Work efficiently, and in parallel on multiple processors.
- Written in LAMMPS coding style and include documentation so that it can be shared.
- Allow creation/deletion of molecules.
- Report relevant statistics to users.
- Be compatible with other LAMMPS features (MD, ensembles, force fields, computes, etc.)

Overview: `gcmc` Fix Style

Description

This fix performs grand canonical Monte Carlo (GCMC or muVT) exchanges of atoms or molecules of the given type with an imaginary ideal gas reservoir at the specified temperature and chemical potential.

It also allows NVT Monte Carlo moves i.e. translations and rotations.

Applications

Equilibrate small fluid molecules around a complex substrate or solute (protein, polymer, zeolite)

Accelerate equilibration in slow-diffusing systems

Advantages

Fully integrated into LAMMPS

Allows hybrid MC/MD simulations

Runs in parallel

Supports most LAMMPS potentials

Limitations

Not superfast

No enhanced-sampling Monte Carlo methods, such as CBMC

Overview: `gcmc` Fix Style

fix ID group-ID `gcmc` N X M type seed T mu displace keyword values ...

- ID, group-ID are documented in *fix command*
- `gcmc` = style name of this fix command
- N = invoke this fix every N steps
- X = average number of GCMC exchanges to attempt every N steps
- M = average number of MC moves to attempt every N steps
- type = atom type to assign to inserted atoms (offset for molecule insertion)
- seed = random # seed (positive integer)
- T = temperature of the ideal gas reservoir (temperature units)
- mu = chemical potential of the ideal gas reservoir (energy units)
- displace = maximum Monte Carlo translation distance (length units)

Overview: `gcmc` Fix Style

`mol` value = template-ID
  template-ID = ID of molecule template
`shake` value = fix-ID
  fix-ID = ID of fix shake command
`region` value = region-ID
  region-ID = ID of region where MC moves are allowed
`maxangle` value = maximum molecular rotation angle (degrees)
`pressure` value = pressure of the gas reservoir (pressure units)
`fugacity_coeff` value = fugacity coefficient of the gas reservoi
`full_energy` = compute the entire system energy
`charge` value = charge of inserted atoms (charge units)
`group` value = group-ID
`group-ID` = group-ID for inserted atoms (string)
`grouptype` values = type group-ID
  type = atom type (int)
  group-ID = group-ID for inserted atoms (string)
`intra_energy` value = intramolecular energy (energy units)

Overview: `atom/swap` Fix Style

Description

This fix performs Monte Carlo swaps of pairs of atoms. This can be done according to the canonical (NVT) or semigrand (deltamuVT) ensembles

Applications

Equilibrate close-packed crystal mixtures that diffuse slowly e.g. metal alloys

Advantages

Fully integrated into LAMMPS

Allows hybrid MC/MD simulations

Runs in parallel

Supports most LAMMPS potentials

Limitations

Not very fast

No enhanced-sampling Monte Carlo methods, such as CBMC

Overview: `atom/swap` Fix Style

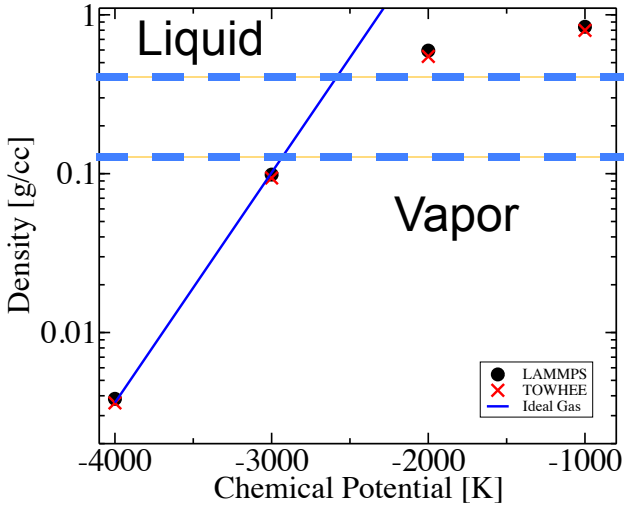
fix ID group-ID `atom/swap` N X seed T keyword values …

- ID, group-ID are documented in fix command
- `atom/swap` = style name of this fix command
- N = invoke this fix every N steps
- X = number of swaps to attempt every N steps
- seed = random # seed (positive integer)
- T = scaling temperature of the MC swaps (temperature units)

`types` values = two or more atom types
`delta_mu` values = number_of_types-1 relative chemical potentials
`ke` value = no or yes
  no = no conservation of kinetic energy after atom swaps
  yes = kinetic energy is conserved after atom swaps
`semi-grand` value = no or yes
  no = particle type counts and fractions conserved
  yes = semi-grand canonical ensemble, particle fractions not conserved
`region` value = region-ID
  region-ID = ID of region to use as an exchange/move volume

Result: Water Vapor Isotherm, no charges

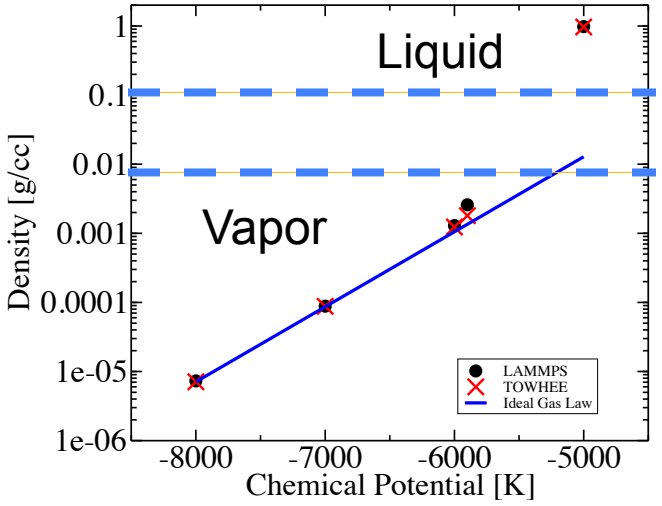
- TIP3P model, but no electrostatics
- Ran GCMC in TOWHEE for 1e6 steps at 300 K
- Chemical potentials spanned both vapor (low density) and liquid (high density) states
- Ran LAMMPS with `fix gcmc`
- Insertions, deletions, translations, rotation
- No dynamics, so all molecules are rigid
- TOWHEE and LAMMPS agree to within 10% at all densities
- Also verified that `intra_energy` keyword works as advertised



- TOWHEE and LAMMPS agree to within 10% at all densities
- Speed:
  - 10^6 moves, ~400 atoms:
  - TOWHEE: 66s
  - LAMMPS: 101s, partial energy
  - LAMMPS: 242s, full energy

Result: Water Vapor Isotherm

- SPC/E water model
- Used Ewald sum for fixed charges
- Ran GCMC in TOWHEE for 1e6 steps at 400 K
- Chemical potentials spanned both vapor (low density) and liquid (high density) states
- Ran LAMMPS with `fix gcmc`
- Insertions, deletions, translations, rotation
- No dynamics, so all molecules are rigid
- TOWHEE and LAMMPS agree to within 10% at all densities
- Long-range electrostatics forced the `full_energy` option



- Good match between TOWHEE and LAMMPS
- Some difference for the saturated vapor and the liquid phase (incomplete sampling?)
- Speed:
  - 10^6 moves, ~150 atoms:
  - TOWHEE: 122s
  - LAMMPS: 415s, full energy

Conclusions

- LAMMPS now has robust general Monte Carlo capabilities
- Canonical (NVT), Grand Canonical (muVT) and Semi-Grand (deltamuVT) ensemble simulations are possible with most potentials
- Coverage includes:
  - long-range electrostatics (kspace)
  - many body pair styles
  - hybrid pair styles
  - eam pair styles
  - energy from other fixes
- GCMC results validated against TOWHEE for both uncharged and charged molecular systems.

BACKUP