Advances in Monte Carlo Sampling Techniques

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Introduction: What and Why

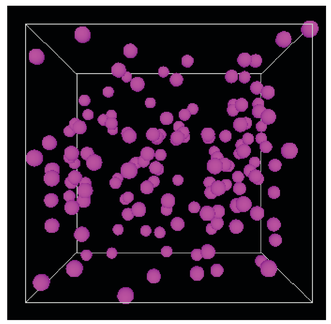
What: We are studying the behavior of a quantum ("light") particle in a fluid.

Why: Knowing how a light particle behaves in a fluid can give us better insight into the composition of materials. For example, if we fill a porous material with gas and insert a positron, eventually the positron and an electron that resides in the fluid will annihilate one another. How long this takes depends on the size and shape of the cavities in the solid and the structure of the gas. Thus, if we know the lifetimes of positrons in differently sized or shaped voids, we can use them as a "probe" to investigate the properties of both the material and of the absorbed fluid.

Definitions

Monte Carlo (MC): A collection of computational methods that simulate complex statistical behaviors.

Metropolis Sampling: A method for accepting or rejecting changes to a simulated system based on the properties of the system.



Above: A simulated fluid

Lennard-Jones Fluid: We simulate a "Lennard-Jones Fluid," which means the fluid obeys the Lennard-Jones pair potential

$$U_{LJ}(r) = 4\varepsilon((\sigma/r)^{12} - (\sigma/r)^{6})$$

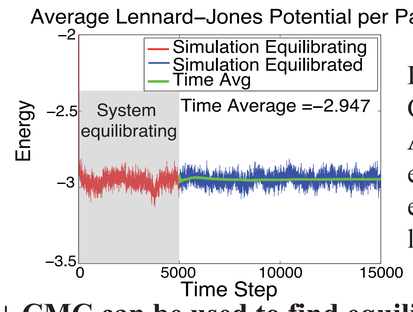
where r is the distance between two atoms and ε and σ are parameters that depend on the particular fluid molecules being modeled.

Light Particle: A particle whose dynamics are accurately described only with quantum mechanics.

Canonical Monte Carlo (CMC)

Canonical ensemble: Fixed volume, temperature, particle number

CMC: Starts in a random configuration and uses Metropolis Sampling to accept or reject moves based on the change in energy.



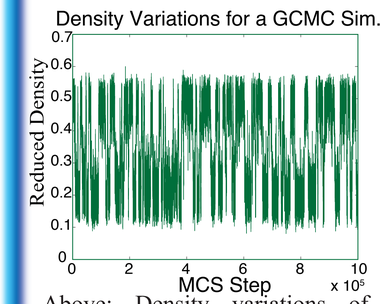
Left: Average energy of a CMC simulation of a fluid. After a time it reaches equilibrium. The time average shown agrees with literature values.

+ CMC can be used to find equilibrium configurations.
- Difficult to use for phase transitions.

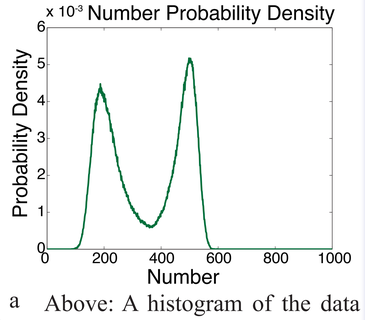
Grand Canonical Monte Carlo (GCMC)

Grand Canonical Ensemble: Fixed temperature, volume, chemical potential; variable particle number.

GCMC: As CMC, except we also attempt to insert and remove particles. Acceptance calculations include chemical potential.



Above: Density variations of a GCMC simulation at a phase coexistence point between vapor and liquid.



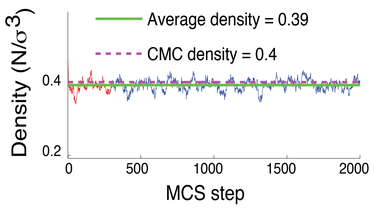
Above: A histogram of the data to the left.

+ GCMC can be used to find phase coexistence points.
- Can't overcome free energy barriers easily.

Widom Method

Widom Method: Finds the chemical potential of a simulated system.

We ran 8 CMC runs at different densities and calculated chemical potential. In 8 ensuing runs at those potentials the difference in density between CMC and GCMC was always less than 4%

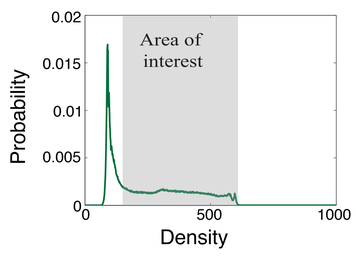


Above: One of 8 graphs comparing CMC and GCMC densities

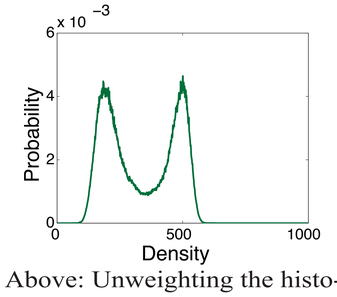
⇒ GCMC and CMC are self-consistent.

Multicanonical Sampling

Multicanonical Sampling: Uses a weighting function to help Metropolis fully explore a system with high free energy barriers.



Above: Simulation weighted by the histogram in GCMC section. We explore all densities equally.



Above: Unweighting the histogram to the left in post processing gives the above histogram.

+ Multicanonical sampling explores space equally.
- Have to find weighting function.

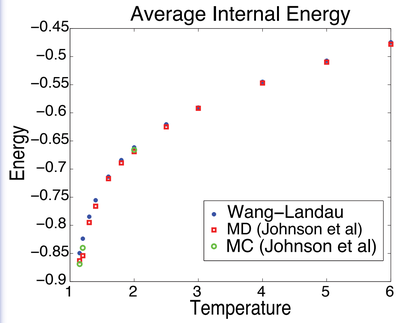
Histogram Reweighting

Histogram Reweighting: Method that takes a histrogram created at energy E_0 and chemical potential μ_0 and "reweights" it to a histogram at energy E_1 and chemical potential μ_1.

⇒ Can find weighting function for multicanonical

Wang-Landau Sampling

Wang-Landau Sampling: Constructs density of energy states, which allows us to find statistical averages at all temperatures.



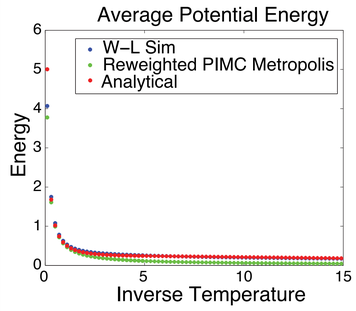
Left: Average internal energy found using one Wang-Landau simulation compared against literature values found using 12 simulations.

+ Wang-Landau is temperature independent.
- Simulations take a long time.

Light Particle Sampling Methods

Path Integral Monte Carlo (PIMC): Treats the light particle as a "polymer" of beads held together by springs.

Path Integral Wang-Landau Sampling: As for classical particles except constructs a two-dimensional density of states for potential and kinetic energy terms.



Left: The average potential energy for a light-particle in a simple harmonic potential. The Wang-Landau simuluation (blue) is more accurate than simply using histogram reweighting on a single Metropolis PIMC simulation (green). The analytical result is shown in red.

⇒ Wang-Landau can be adapted to a light particle.

Conclusions and Future Work

Wang-Landau and multicanonical sampling are best for systems with high free energy barriers. Wang-Landau takes longer than multicanonical but is more useful for systems where it is hard to obtain a weighting function.

In future work we hope to extend these techniques to the combined fluid and light particle system.