Equation of State Calculations by Fast Computing Machines

Dario Sergo

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Objective of Monte Carlo Method

Objective of Stat. Physics

Computing integrals like:

$$\langle O \rangle = \frac{\int_{R^{6N}} d\vec{x}^N \omega(\vec{x}) O(\vec{x})}{\int_{R^{6N}} d\vec{x}^N \omega(\vec{x})}$$

Where O is a generic observable. ω is (usually) the canonical weight $\omega \propto e^{-\beta H(\vec{x})}$

By virtue of the central limit theorem:

Fundamental property of Monte Carlo Integration

$$\langle O \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{x_i \sim \omega(x_i)/Z} O(x_i)$$

Where $Z = \int \omega(x)$ is the partition function.

Naive way to proceed, before this article came out

Evidently, I can write:

$$\langle O \rangle = \lim_{N\to\infty} \frac{1}{N} \sum_{x_i \sim Uniform} \frac{\omega(x_i)}{Z} O(x_i)$$

"Weight" Method:

1. Generate $x_i \sim Uniform$
2. Compute the canonical factor $\omega(x_i) = e^{-E\beta}$
3. Sum over all the $O(x_i)\omega(x_i)$

Problems:

- I still must compute the partition function (another integral to compute)
- The energy is usually sparse, meaning that the majority of configurations have low values (below computer precision) of $\omega(x_i)$. $\implies$ Many samples needed.

The new method: the Metropolis Hasting Algorithm

This article proposes a new method The Metropolis (Hasting) Algorithm.

Advantages:

1. No need to compute the partition function
2. Sample efficiently from phase space according, to the correct probability distribution $\omega(x)/Z$.

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The Metropolis Hasting Algorithm

Suppose that we have a system of particles with P.B.C in 2D. Calling (x_i, y_i) the position of particle i. In Metropolis Hasting the state is updated as follows:

0. Given a starting configuration $\vec{x}$, select (x_i, y_i).
1. Updated position according to

$$x_i' = x_i + \alpha\xi_x$$

$$y_i' = y_i + \alpha\xi_y$$

   α is the "box size", ξ are random uniform variables
2. Evaluate ($\vec{x}'$ is the updated configuration): $r = \frac{\omega(\vec{x}')}{\omega(x)}$
3.

$$\begin{cases} \text{Case 1: If } r \geq 1\text{, the new configuration } \vec{x}' \text{ is ACCEPTED} \\ \text{Case 2: If } r < 1\text{, generate } \eta \sim U(0,1). \\ \quad \text{If } r < \eta\text{, configuration } \vec{x'} \text{ REJECTED} \\ \quad \text{If } r \geq \eta\text{, configuration } \vec{x'} \text{ ACCEPTED} \end{cases}$$

The Metropolis Hasting Algorithm

Important Considerations:

- $r = e^{-\beta\left(E(\vec{x'}) - E(\vec{x})\right)}$ Depends only on energy difference: fast to compute (for Fast-Decaying potentials)
- α: size of boxes $\Longrightarrow$ Hyperparameter. Set so that: #Accept $\approx$ #Reject

Extremely useful property of Metropolis Hasting:

No need to compute $Z = \int \omega$

Only ratio r to be computed!

How to use Metropolis Hasting

After N_s (s for "samples") steps of the algorithm I end up with: $\{\vec{x}_i\}_{i=1}^{N_s}$ random variables.
I compute:

$$\langle O \rangle = \frac{1}{N_s - M} \sum_{i=M}^{N_s} O(\vec{x}_i)$$

(trowing away the first part of the samples).

This is an example of Monte Carlo Markov Chain, indeed

$$P(\{\vec{x}_i\}_{i=1}^{N_s}) = \prod_{i=1}^{N_s-1} P(x_{i+1}|x_i) \times P(x_1)$$

Question: Why should the samples x_i be canonically distributed?

Historical Proof of Metropolis Algorithm

We are initializing a lot of INDEPENDENT SYSTEMS (i.e, realizations of MH). Define:

- State S and state R, with $E_R > E_S$
- ν_R, ν_S: number of "points" (systems) is state S and state R
- $T_{S \to R} = T_{R \to S}$ "trial move" (the cubic displacement).

What we would like to prove:

$$\nu_R \propto e^{-\beta E_R}$$

Historical Proof of Metropolis Algorithm

Number of systems moving from R to S: $\nu_R T_{S\to R}$
Number of systems moving from S to R: $\nu_S T_{S\to R} \times e^{-\beta(E_R - E_S)}$

Metropolis noticed that this Markov Chain is ergodic, so each point in phase space is reachable (because we do not remove systems when we do a rejection).

Net number of system going from $S \longrightarrow R$:

$$T_{S\to R}(\nu_S \times e^{-\beta(E_R - E_S)} - \nu_R)$$

Therefore, at the steady state we must have:

$$\nu_R \propto e^{-\beta E_R} \qquad \nu_S \propto e^{-\beta E_S}$$

otherwise we would have a net flux of particles going from $S \longrightarrow R$, meaning that the systems would "drain" (incompatible with ergodicity).

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The rigid sphere problem

DEFINITION

- Spheres confined in 2D, with P.B.C, on a surface of area $A = 1$
- Initially placed as in the figure, at distance $d = 1/14$
- Diameter of spheres $d_0 = d(1 - 2^{\nu - 8})$

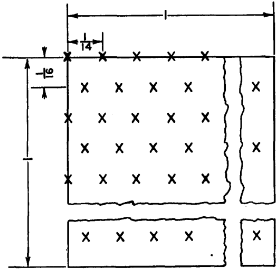

Figure: Initial disposition of rigid spheres

The problem of interest

Question to investigate:

I would like to study the state equation of the rigid sphere problem, as a function of d_0

Goal:

Recast the problem to make it amenable to Metropolis Hasting.

The equation of state of the rigid spheres:

The Virial Theorem states:

Virial Theorem:

$$\langle \sum_i \vec{X}_i^{TOT} \cdot \vec{r}_i \rangle = 2E_{kin}$$

$X_i^{\vec{TOT}} = \vec{X}_i^{int} + \vec{X}_i^{ext}$

- $X_i^{\vec{TOT}}$: total force on particle i.
- $\vec{X}_{int}$ force due to collisions with other particles
- $\vec{X}_i^{ext}$ external "confining" force.

It is easy to see that (P being the pressure acting on the particles):

$$2E_{kin} = 2PA + \langle \sum_i \vec{X}_i^{int} \cdot \vec{r}_i \rangle$$

The equation of state of the rigid spheres:

Defining $\bar{n}$ the number density at distance d_0 from a particle I can show that:

$$\langle \sum_i \vec{X}_i^{int} \cdot \vec{r}_i \rangle = (-Nv^2 m/2)\pi d_0^2 \bar{n} \quad (1)$$

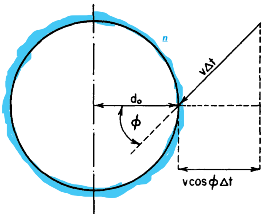

Fig. 1. Collisions of rigid spheres.

Figure: Position at which $\bar{n}$ is computed

The equation of state:

Then, recognizing the kinetic energy $E_{kin} = Nk_bT$:

Equation of State

$$PA = Nk_bT(1 + \pi d_0^2 \bar{n}/2)$$

We just need to compute $\bar{n}$ now (doable with Metropolis Hasting)

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Metropolis Hasting of the Rigid sphere problem

The interparticle potential is of type "hard sphere":

$$\phi(r_{ij}) = \begin{cases} 0 & if \quad r_{ij} > d \\ +\infty & if \quad r_{ij} < d \end{cases} \tag{2}$$

Therefore Metropolis Hasting simplifies:

Metropolis Hasting for Hard spheres

0. Given a starting configuration $\vec{x}$, select (x_i, y_i).
1. Updated position according to

$$x_i' = x_i + \alpha\xi_x$$

$$y_i' = y_i + \alpha\xi_y$$

   α is the "box size", ξ are random uniform variables
2. if $\exists j | \sqrt{(x_i' - x_j)^2 + (y_i' - y_j)} < d_0$ then REJECT trial move and return $\vec{x}$.
3. if $\forall j | \sqrt{(x_i' - x_j)^2 + (y_i' - y_j)} > d_0$ then ACCEPT trial move and return $\vec{x'}$.

Computation of $\bar{n}$ with Metropolis Hasting

I need to compute the number density $\bar{n}$, at distance d_0 from a particle.

Steps:

1. I use Metropolis Hasting to generate many configurations of particles (which are canonically distributed).
2. I define a circular ring of radius Kd_0 and d_0 (centered on a particle). I section it in 64 concentrical annuli of area $\Delta A = (K^2 - 1)\pi d_0^2/64$.
3. I count how many particles N_m ($m \in \{1, ..., 64\}$) are within each annulus (for each configuration) and average over all the configurations.
4. I plot N_m and fit it to obtain $N_{1/2}$. Then $\bar{n} = \frac{N_{1/2} \times N}{\Delta A}$.

Computation of with Metropolis Hasting

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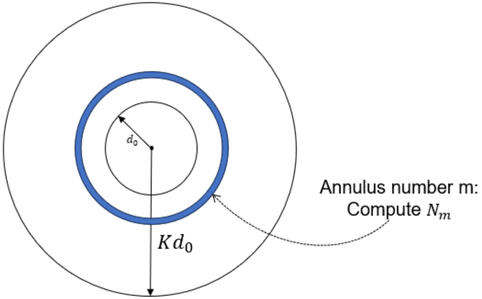

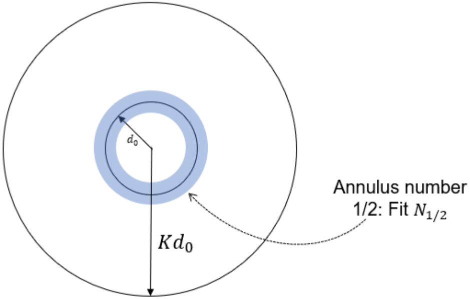

Results from the article

Example curve of number density N_m ($m \in \{1, ...64\}$) for a particular $d_0 = d(1 - 2^{8-\nu})$

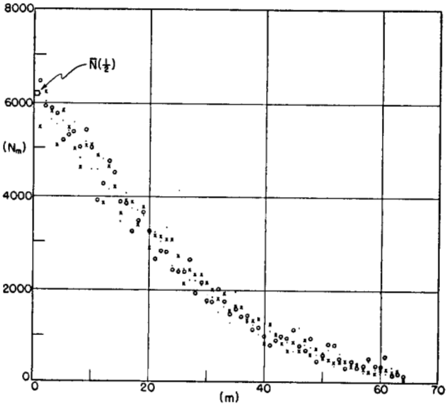

FIG. 5. The radial distribution function N_m for $\nu = 5$, $(A/A_0) = 1.31966$, $K = 1.5$. The average of the extrapolated values of $N_{\frac{1}{2}}$ in $\bar{N}_{\frac{1}{2}} = 6301$. The resultant value of $(PA/NkT) - 1$ is $64\bar{N}_{\frac{1}{2}}/N^2(K^2 - 1)$ or 6.43. Values after 16 cycles, ●; after 32, ×; and after 48, ○.

Equation of state from Metropolis Hasting

Equation of state $\frac{PA}{Nk_bT} - 1 = \pi d_0^2 \bar{n}/2, \qquad A_0 = \frac{\sqrt{3}}{2} d_0^2 N$

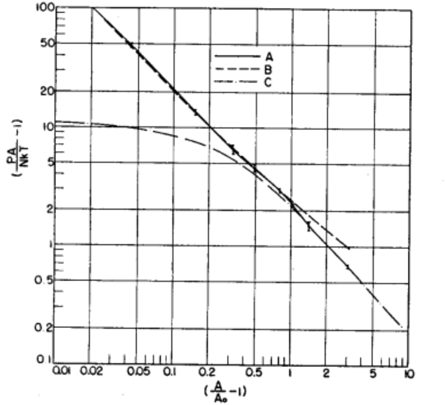

FIG. 4. A plot of $(PA/NkT)-1$ *versus* $(A/A_0)-1$. Curve A (solid line) gives the results of this paper. Curves B and C (dashed and dot-dashed lines) give the results of the free volume theory and of the first four virial coefficients, respectively.

- A curve: prediction with M-H
- B curve: density functional theory
- C curve: Virial expansion (coefficients from MANIAC)

Concluding Remarks

Some remarks on the results:

- M-H produces results which are well aligned with density functional theory, up to $A/A_0 \approx 1.8$
- At large values of A/A_0 the results of density functional theory are not in good accordance with M-H. Curve C and A on the other hand show good accordance at large A/A_0.

What we learned today

- What are the Monte Carlo Methods
- How the Metropolis Hasting MCMC was originally defined and its advantage over "Von-Neuman" sampling
- We saw the historical proof of the Metropolis Hasting algorithm
- We saw the first application of this algorithm to a simple problem

Reference:
N. Metropolis ed Altri "Equation of State Calculations by Fast Computing Machines"