

## ICCP Project 2 - Advanced Monte Carlo Methods

### Choose one of the three options below

#### Introduction

In statistical physics Monte Carlo methods are considered to have started in the Manhattan project (1940's) during which J. von Neumann, S. Ulam, N. Metropolis and R. Feynman used random numbers to estimate neutron scattering and absorption rates in materials. The Metropolis method originated in the paper: "Equation of state calculations by very fast computing machines", by N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, M. Teller and E. Teller, J. Chem. Phys. 21. 1087 (1953). A recent retrospective "Marshall Rosenbluth and the Metropolis algorithm", Physics of Plasmas 12, 57303 (2005) describes some of the history and makes it clear that Metropolis actually had little to do with the development of what is now called the Metropolis method. The credit should really go to Rosenbluth and Teller.

The Metropolis method is the most widely used Monte Carlo method. Monte Carlo methods can be considered to be improvements or variations on other random sampling methods such as importance sampling, which have a longer history. A few examples of the use of Monte Carlo methods in physics are:

- (i) Thermodynamic quantities in statistical and many body physics
- (ii) Multiple integrals in mathematics and analysis
- (iii) Reaction-diffusion problems in chemical engineering and geophysics
- (iv) Polymer or protein conformations
- (v) Particle showers in Nuclear and HEP

Note that MC methods do not replace a theoretical understanding of the problem. Instead a deep theoretical understanding is required before the correct MC simulation can be set up. Actually the literature is full of incorrect simulations, due to either poor input physics or poor quality data analysis. MC methods could take up an entire course in any one of the areas listed above and there are a large number of special purpose MC codes. The mathematics of the method has also attracted a lot of effort where the Metropolis method is often called Markov chain MC.

Monte Carlo methods can be used to find the average properties of classical or quantum mechanical many body systems. In quantum mechanics, the average value of an operator  $\hat{O}$  is found

using

$$\langle \hat{O} \rangle = \frac{\text{tr}(\hat{O}e^{-\beta\hat{H}})}{\text{tr}(e^{-\beta\hat{H}})} \quad (1)$$

where  $\hat{H}$  is the Hamiltonian and  $\beta = 1/(k_B T)$  with  $k_B$  Boltzmann's constant and  $T$  the temperature. In classical physics, the operator is diagonal and the trace (tr) reduces to a sum over the energies or eigenvalues of the system leading to the classical expression,

$$\langle O \rangle = \frac{\sum_c O_c e^{-\beta H(c)}}{\sum_c e^{-\beta H(c)}} \quad (2)$$

where  $c$  labels a configuration or eigenfunction of the system.

ICCP project 2 has three options covering different advanced MC methods. These options are outlined below. You (and your Dutch collaborators) can choose any one of the following three Monte Carlo projects. Moreover for each project there are two possible algorithms. The MSU participant could do one algorithm while the dutch group could do the other. It would be good to compare the results and algorithms for each project. Problem (i) Classical Monte Carlo simulation of a coarse grained polymer chain model. For this project the two algorithms are: (a) Rosenbluth/PERM algorithm; (b) Pivot algorithm. You will calculate the radius of gyration and end-to-end distance of the chain as a function of the number of monomers in the chain ( $N$ ), and as a function of temperature ( $T$ ). At low temperatures the chain is a globule while at high temperatures it is a coil. It is also possible to use MD for this problem so one person could extend their MD code to this problem and compare with the MC results. Problem (ii) Classical Cluster Monte Carlo simulation of the phase transition in spin half ferromagnetic Ising models. For this project the two algorithms are: (a) Swendsen-Wang algorithm; (b) Wolff algorithm. You will calculate the magnetization, susceptibility and specific heat as a function of temperature and compare to the results of the simple Metropolis approach. You can extract the critical exponent for the magnetization near the phase transition for Ising models on square and cubic lattices. Problem (iii) Quantum Monte Carlo simulation of the Helium atom and/or Hydrogen molecule. The two algorithmic approaches used here are: (a) The variational method (Hydrogen molecule); (b) Diffusion Monte Carlo (Helium atom). For the variational approach a Monte Carlo method is used to evaluate an integral arising in the problem. In this calculation you will find the total electronic energy of

the system, the probability density. For the probability density you can compare with the non-interacting electron model to see the effects of Coulomb interactions. More details are given below.

### Option 1: Pivot and Rosenbluth-PERM MC simulation of Polymers [1]

MC simulation of polymers is difficult due to the fact that most local MC moves do not change the polymer configuration much as many local moves are rejected due to overlap with other parts of the polymer chain [1]. Rosenbluth and Rosenbluth invented a method to overcome this difficulty and PERM [1] is a further advance in the method. A second approach, the pivot algorithm was invented later and is best for extended systems. MD methods are also often used and are also but enable simulation of polymer collapse at low temperature.

To begin we need a model for the polymer chain [1]. Note that similar ideas apply to proteins and DNA, but the potentials used are more complex. The model we use for a polymer chain is the so-called bead-spring model that is a standard in polymer physics. The model consists of beads connected to each other by springs. The location of each bead is  $\vec{r}_i$ , where  $i = 1 \dots N$  labels the  $N$  beads in the polymer chain. The springs have the Hooke law restoring force  $k(|\vec{r}_i - \vec{r}_{i+1}| - l_0)^2$  where  $l_0$  is the bond length characteristic of the polymer of interest e.g. for alkanes  $l = 1.54 \text{ Angstrom}$ . In many cases this restoring force is much stronger than all other forces in the problem, so the bond lengths along the chain are set to  $l_0$ . In addition in polymers there is a bond angle force that favors certain bond angles, for example for alkanes it is about 108 degrees, we take this to be  $\theta_0$ . The restoring force for these angles is taken to be  $\alpha(\theta - \theta_0)^2$ . Finally the beads along the chain also interact through so-called "non-bonded" interactions such as the van der Waals or Lennard-Jones interaction and the Coulomb interaction. Here we just consider the Lennard-Jones interaction,

$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \quad (3)$$

We take the value of  $\sigma \geq l_0$  as is physically reasonable and it also prevents crossing of the polymer chain through the strong repulsion of LJ at distances below  $\sigma$ .

The Rosenbluth method grows polymer chains and during this growth calculates the overall probability of the chain in the ensemble average. This can then be used to calculate averages of physical quantities. The growth procedure starts with one atom and adds a second at a distance

$l_0$  from the first atom and at a randomly chosen angle. Note that in three dimensions the angle must be chosen with the correct weight. In two dimensions it is chosen randomly on  $[0, 2\pi]$ . The probability associated with the chosen angle is  $P_i = w_i(\theta_i) = \exp[-\beta E(\theta_i)]/Z_i$ , where  $Z_i$  is the local partition function  $Z_i = \sum_i w_i$  and is the sum of the weights due to all possible angles for the  $i^{\text{th}}$  bead. Typically six or so possible angles are allowed as we don't want to calculate the energy at every angle. Once the chain growth is complete, the probability of the chain is  $\prod_i P_i$ .

Quantities of interest in polymer physics include the end-to-end distance,  $R$ , of the chain, or its radius of gyration  $R_g$ . For a random walk model where the chain does not interact with itself these quantities have a diffusive behavior  $R \sim R_g \sim N^{1/2}$ . However the hard core repulsion of the chain with itself makes real polymer chains expand, and the Flory prediction for the real chain is  $R \sim R_g \sim N^{3/(d+2)}$ , where  $d$  is the spatial dimension. For two dimensions  $R \sim R_g \sim N^{3/4}$ . A log-log plot of the radius of gyration of your chains as a function of the number beads used  $N$  should see the difference between the Gaussian chain model and the Flory prediction. Note that the Flory prediction is observed in experiments on single chains in solution, however in dense melts the Gaussian chain form is observed. Beautiful neutron scattering experiments using dilute deuterated chains revealed this in the 1970's.

The pivot algorithm in its naive form is simply a method where a monomer is chosen at random and then MC moves at that site are chosen randomly for one edge while keeping all other bonds fixed. The energy of the move is calculated and a Metropolis test is used. To make the procedure efficient, it is important to quickly decide if a pivot leads to unphysical "collisions" or crossing configurations (see[1]) below.

[1] J Baschnagel, J. Wittmer and H. Meyer, in Proceedings of Von Neuman conference, vol 23, 83-110 (2004)

[2] P. Grassberger, Pruned-enriched Rosenbluth method: Simulations of polymers of chain length up to 1 000 000. Phys. Rev. E 56, 3682 - 3693 (1997).

## Option 2: Wolff cluster algorithm for spin half Ising model [1]

The Ising model was invented to provide an understanding of phase transitions in ferromagnets, where it is known that magnetism is lost for  $T > T_c$  where  $T_c$ , is the Curie temperature. The behavior near  $T_c$  is complicated and co-operative so that there is actually a singular behavior in

many physical properties at  $T_c$ . In addition the geometry of the magnetic domains at  $T_c$  is fractal. All of these properties can be deduced by using the Monte Carlo method to find the average properties of Ising magnets. The Hamiltonian of a spin 1/2 Ising magnet in a magnetic field is given by,

$$H = -J \sum_{\langle ij \rangle} S_i S_j - h \sum_i S_i \quad (4)$$

where  $J > 0$  is a ferromagnetic exchange constant,  $S_i = \pm 1$  is a spin variable, and the sum is over nearest neighbor sites on a lattice. We take the square lattice as our example (you can choose another lattice if you want). Our detailed analysis will focus upon the magnetization,  $m = (\sum_i \langle S_i \rangle) / N$ . Other interesting things to calculate include the internal energy, the susceptibility and the specific heat. The project is to use the cluster (Wolff) Monte Carlo method to find the average value of these quantities as a function of temperature and by fitting to the expression magnetization expression  $m \sim (T_c - T)^\beta$  to obtain an estimate of  $\beta$ . You should also compare the convergence of the cluster algorithm to the standard Metropolis MC method for this problem. Another interesting thing to calculate is  $m$  versus  $h$  for fixed  $T < T_c$  to demonstrate the magnetization jump at  $h = 0$ .

The Wolff algorithm [1] was developed after the Swendsen-Wang algorithm and is more convenient. The way it works is as follows: (i) Start with a random spin configuration; (ii) Choose a spin at random in this configuration; (iii) Starting from this "seed" spin, grow a cluster by using the Wolff cluster growth procedure that works as follows. a) Find a neighboring spin with the same orientation as the seed (if one exists). b) draw a bond to that spin with probability  $p = 1 - \exp(-\beta \delta E)$ . If a bond is drawn, add this spin to the cluster. c) Continue growing the cluster until no further growth is possible. d) Flip the spin of the cluster. This process leads to a sequence of spin configurations that are used for averaging in the usual way. In your writeup you should demonstrate that this procedure satisfies detailed balance.

The Swendsen-Wang algorithm is quite similar - Google it and compare with the Wolff algorithm.

[1] Collective Monte Carlo Updating for Spin Systems. Ulli Wolff, Phys. Rev. Lett. 62, 361 (1989)

### Option 3: Variational QMC for the Hydrogen molecule

Quantum problems provide an added complexity for Monte Carlo methods and many approaches have been developed. Here we use the variational method where we use a wavefunction form that is inspired by the physics and minimize the energy with respect to the parameters in the wavefunction. This approach requires good physical insight to find a good variational form for the wavefunction. This is possible for the Hydrogen molecule (and many other molecules) where we know the basic structure of the electronic orbitals.

The mathematical form seems simple: we write a variational wavefunction  $\Psi$  and we find the energy

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad \text{where } E \geq E_G \quad (5)$$

where  $E_G$  is the ground state energy of the molecule. Of course we get equality if we find the exact ground state. All other wavefunctions give higher energy - this is the variational principle.

The Hamiltonian of the Hydrogen molecule, in the Born-Oppenheimer approximation where we assume that the nuclear motion is negligible, includes the kinetic and potential energies of the two electrons as well as their interaction. The positions of the two atomic nuclei are assumed to be symmetrically located and on the x-axis at positions  $-s/2, s/2$ . The nuclei are thus a distance  $s$  apart. The positions of the two electrons are  $\vec{r}_1$  and  $\vec{r}_2$ . The Hamiltonian is then

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \left[ \frac{e^2}{|\vec{r}_1 + \frac{s}{2}\hat{i}|} + \frac{e^2}{|\vec{r}_1 - \frac{s}{2}\hat{i}|} + \frac{e^2}{|\vec{r}_2 + \frac{s}{2}\hat{i}|} + \frac{e^2}{|\vec{r}_2 - \frac{s}{2}\hat{i}|} \right] + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \quad (6)$$

where the first part is the kinetic energy of the two electrons, the second part (square brackets) is the four attraction terms between the two electrons and the two nuclei and the last term is the Coulomb repulsion between the two electrons.

The variational wavefunction is given by,

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1)\phi(\vec{r}_2)\psi(\vec{r}_1, \vec{r}_2) \quad (7)$$

where

$$\phi(\vec{r}) = e^{-(\vec{r} - \frac{s}{2}\hat{i})/a} + e^{-(\vec{r} + \frac{s}{2}\hat{i})/a} \quad (8)$$

where  $a$  is a variational parameter. Note that we could take  $a = a_0$  the Bohr radius, but allowing  $a$  to vary gives my variational freedom. The key new thing here is the assumption of an form for the interaction term  $\psi$ . A form that is very useful is (see Jos Thijssen's book, Equation 12.9 of the first edition),

$$\psi(\vec{r}_1, \vec{r}_2) = \exp\left[\frac{|\vec{r}_1 - \vec{r}_2|}{\alpha(1 + \beta|\vec{r}_1 - \vec{r}_2|)}\right] \quad (9)$$

The first step is to find convenient expressions for the energy  $E$  given above using the variational wavefunction and Hamiltonian above. This is quite laborious but interesting exercise. The resulting expressions are six dimensional integrals in the electron co-ordinates  $\vec{r}_1$  and  $\vec{r}_2$ . The MC part of the project is to use a diffusion method to approximate these integrals.

The method should be carried out to find the energy  $E$  as a function of the interatomic separation  $s$  to find the ground state size of the hydrogen molecule. The electron density minus the electron density of the non-interacting H atoms at the same separation should also be plotted to illustrate the effect of the e-e Coulomb repulsion on the electronic configuration. Compare with the reference below [1].

Diffusion MC uses the fact that the Schrodinger equation looks like a diffusion equation so we can sample the wavefunction using random walks. Of course we have to keep track of the complex weights which makes it more difficult, but not excessively so.

[1] L. Wolniewicz. Nonadiabatic energies of the ground state of the hydrogen molecule J. Chem. Phys. 103, 1792 (1995).