Mont Carlo Simulation

Monte Carlo Simulation in MCE

- Isolated system for which N, V and E is fixed.
- The macrostate is defined by these values.
- What is microstate?.
- The properties of these microstates are consistent with the known physical quantities of the system.
- Guided by *equal a priori probabilities*.

Monte Carlo Simulation in MCE

The probability, P_s

$$\begin{aligned} P_s &= \frac{1}{\Omega}, && \text{if } s \text{ accessible} \\ &= 0 && \text{otherwise} \end{aligned}$$

The sum of P_s over all Ω states is unity.

The Demon Algorithm

- How can we do an ensemble average at fixed N, V, E?
- Enumerate all the microstates and calculate the ensemble average.
- Too many states!!
- Another approach was developed by Cruetz and co-workers.
- Add an extra degree of freedom, *DEMON*.

The Demon Algorithm

- Choose a particle randomly and change its position, *trial*.
- Compute the change in the energy of the system due to this change.
- If $\Delta E \leq 0$, the system gives the amount of energy $\mid \Delta E \mid$ to the demon, *i.e.* $E_d = E_d - \Delta E$.
- The move is accepted.

The Demon Algorithm

- In case $\Delta E > 0$, if the demon has sufficient energy, $E_d \geq \Delta E$, the demon gives sufficient energy to the system and accept the move.
- Othewise, reject the move.

Important

Demon cannot have negative energy

Iterations

Till the sufficient states have been obtained.

The Demon Algorithm

How do we know about the desired results?

The *ergodic* hypothesis!!

Ergodic hypothesis

At equilibrum, generally they give the equivalent results.

One dimensional ideal gas

- Not a good idea....but ideal point to start.
- The energy of a configuration is independent of the positions of the particles.
- The total energy is the sum of kinetic energies of individual particles.
- The coordinate of interest is velocity.
- Choose a particle at random and change its velocity by a random amount.

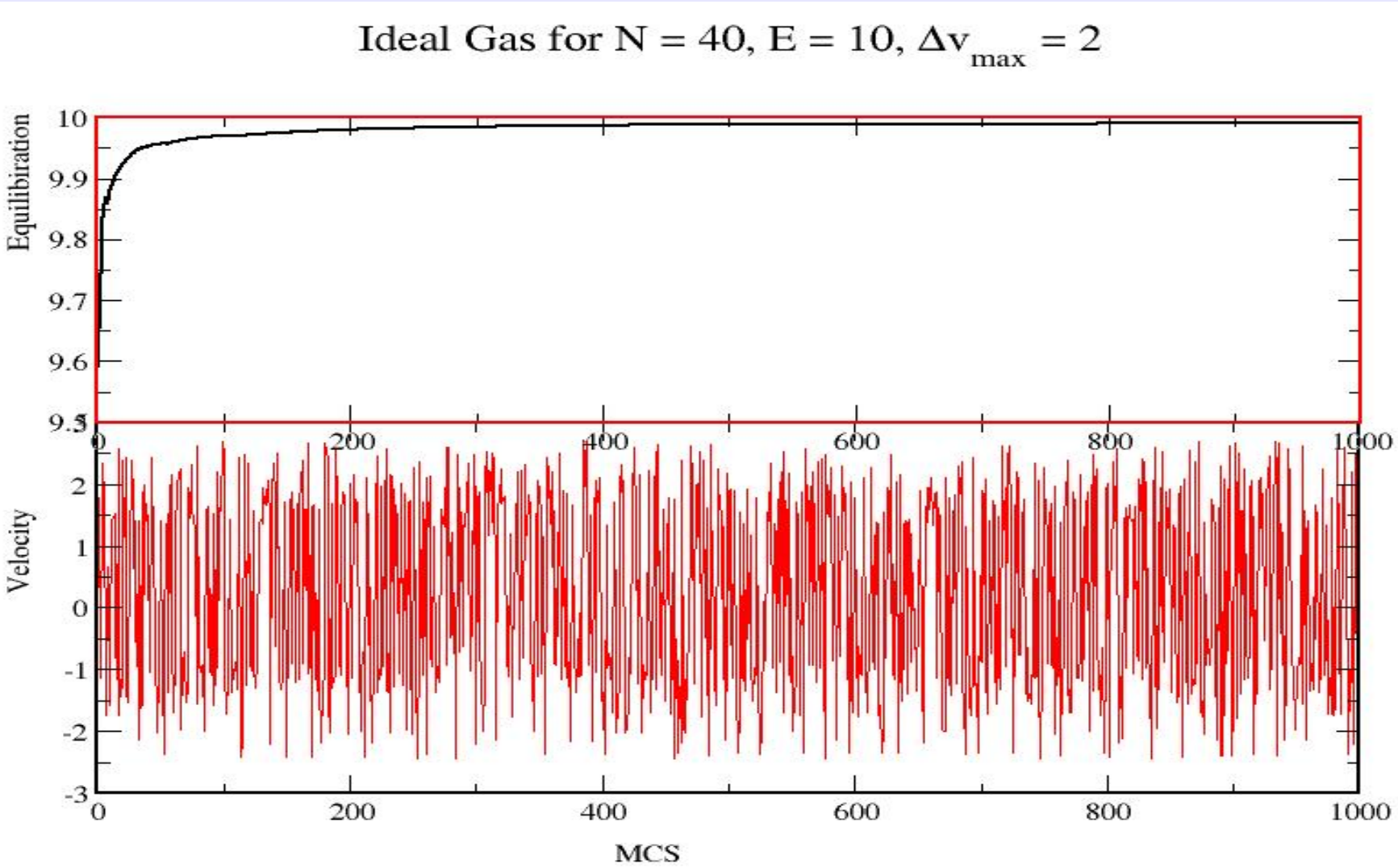
One dimensional ideal gas

A problem

Assign the same velocity to all the particles. Choose number of particles, $N = 40$, the initial total energy $E = 10$, the initial demon energy, $E_d = 0$ and maximum change in the velocity as 2.

What is the mean value of the particle velocities after equilibrum has been reached?

One dimensional ideal gas



One dimensional ideal gas

The configuration corresponding to all particles having the same velocity is not very likely, and it would be better to choose an initial configuration that is more likely to occur when the system is in equilibrium. Because this choice is not always possible, we should let the system evolve for a number of Monte Carlo steps per particle before we accumulate data for the averages. We call this number the *equilibration time*. Modify `Program ideal` so that the changes are made for `nequil` Monte Carlo steps per particle before averages are taken. We can estimate this time from a plot of the time average of the demon energy or other quantity of interest versus the time. Determine the mean demon energy and mean system energy per particle for the parameters in part (a).

Compute the mean energy of the demon and the mean system energy per particle for $E = 20$ and $E = 40$. Choose `mcs` $= 50000$ if possible. Use your result from part (b) and obtain an approximate relation between the mean demon energy and the mean system energy per particle.

In the microcanonical ensemble the total energy is fixed with no reference to temperature. Define the temperature by the relation $\frac{1}{2}m\langle v^2\rangle = \frac{1}{2}kT_{\rm kin}$, where $\frac{1}{2}m\langle v^2\rangle$ is the mean kinetic energy per particle. Use this relation to obtain $T_{\rm kin}$. How is $T_{\rm kin}$ related to the mean demon energy? Choose energy units such that Boltzmann's constant k is equal to unity.

The Ising model

- Porposed by Lenz and invesigated by Ising.
- For ferromagnetic systems in 1D and found that no phase transition in 1D.
- A lattice of N sites and assuming that each site can be in ± 1 state.
- The macroscopic properties of the system can be determined by number of accessible states.

The Ising model

Total energy

$$E = -J \sum_{i,j(nn)}^{N} s_i s_j - H \sum_{i=1}^{N} s_i$$

where, H is proportional to a uniform magnetic field.

The exchange constant J is the measure of the strength of the interaction between two spins.

The Ising model

- If $J > 0$, then ferromagnetic state is preferred over paramagnetic state.
- If $J < 0$ the state of lowest energy is *anti-ferromagnetic*.
- K.E. of the atoms associated with lattice sites are ignored and only nearest neighbour interaction are considered.
- Dynamics?....other methods.

The Ising model: Demon Algorithm

Use again the periodic boundary condition and assume the chain as a ring.

The magnetization, M

$$M = \sum_{i=1}^{N} s_i$$

How the temperature can be determined?

The Ising model: Demon Algorithm

- As probability is proportional to $e^{-\beta E_d}$, we can determine T from

$$\ln[P] = -\beta E_d - \ln Z$$

- Here E_d is not continuous.
- In absence of H this can be written as,

$$kT = \frac{4J}{\ln(1 + \frac{4J}{<E_d>})}$$

The Ising model: Demon Algorithm

- Choose a spin randomly.
- Flip spin up or down.
- Calculate the change in energy.
- Choose PBC and compute average magnetization as,

$$M = \sum_{i=1}^{N} s_i$$

In Canonical Ensemble

The probability that a particle can found in state s with energy E_s is,

$$P_s = \frac{1}{Z} \exp(-\beta E_s)$$

The average energy, E is

$$< E >= \sum_{s=1}^{M} E_s P_s = \frac{1}{Z} \sum_{s=1}^{M} E_S \exp(-\beta E_s)$$

The Metropolis Algorithm

The average can be estimated as,

$$\langle f \rangle \approx f_m = \frac{\sum_{s=1}^{m} f_s e^{-\beta E_s}}{\sum_{s=1}^{m} e^{-\beta E_s}}$$

f_s is the value of quantity f in microstate s.

Most of the values may be rejected

The Metropolis Algorithm

Importance sampling

$$f_m \approx \frac{\sum_{s=1}^{m} \frac{f_s}{\pi_s} \pi_s e^{-\beta E_s}}{\sum_{s=1}^{m} \frac{1}{\pi_s} \pi_s e^{-\beta E_s}}$$

If we generate microstates with probability π_s then it is

$$f_m \approx \frac{\sum_{s=1}^{m} \frac{f_s}{\pi_s} e^{-\beta E_s}}{\sum_{s=1}^{m} \frac{1}{\pi_s} e^{-\beta E_s}}$$

The Metropolis Algorithm

If we average over a biased sample, we need to weight each microstate by $\frac{1}{\pi_s}$ to eliminate the bias.

A reasonable choice

$$\pi_s = \frac{\exp(-\beta E_s)}{\sum_{s=1}^{m} \exp(-\beta E_s)}$$

The mean is now,

$$f_m = \frac{1}{m} \sum^{m} f_s$$

The Metropolis Algorithm

- Establish an initial microstate.
- Make a trial change.
- Calculate the change in energy.
- If $\Delta E \leq 0$, accept the change.
- If $\Delta E > 0$, compute, $w = e^{-\beta \Delta E}$.
- Generate a random number r and compare it with w.
- In case $w \geq r$, accept the change.

The Metropolis Algorithm

- Repeat all previous steps to obtain a sufficient number of microstates.
- Periodically compute averages over microstates.
- These conditions tells that the system is in microstate $\{s_j\}$ given that system was in microstate $\{s_i\}$.

The Metropolis Algorithm

Mathematically

$$W(i \to j) = \min(1, e^{-\beta \Delta E})$$

where $\Delta E = E_j - E_i$

- No need to normalize the probability as we have to calculate the ratio, $P_j/P_i = exp(-\beta \Delta E)$.
- Partition function can not be evaluated.