Random Walks, Monte Carlo and Errors

- What is a simulation?
- Monte Carlo, random walks and Markov Chains
- Metropolis rejection method
- Error estimates

Quantum Monte Carlo

- We need to use simulation techniques to "solve" many-body quantum problems just as you need them classically.
- Both the wavefunction and expectation values are determined by the simulations. Correlation built in from the start.
- Based on Feynman's imaginary time path integrals.
- QMC gives most accurate method for general quantum many-body systems.
- QMC determined electronic energy is the standard for approximate LDA calculations. (but fermion sign problem!)
- Path Integral Methods provide a exact way to include effects of ionic zero point motion (include all anharmonic effects)
- A variety of stochastic QMC methods:
  - **Variational Monte Carlo VMC (T=0)**
  - **Projector Monte Carlo (T=0)**
    - **Diffusion MC (DMC)**
    - **Reptation MC (RQMC)**
  - **Path Integral Monte Carlo (PIMC) (T>0)**
  - **Coupled Electron-Ion Monte Carlo (CEIMC)**

Equation of State Calculations by Fast Computing Machines

NICHOLAS METROPOLIS, ARIANNA W. ROSENBLUTH, MARSHALL N. ROSENBLUTH, AND AUGUSTA H. TELLER,
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

AND

EDWARD TELLER,* *Department of Physics, University of Chicago, Chicago, Illinois*

(Received March 6, 1953)

A general method, suitable for fast computing machines, for investigating such properties as equations of state for substances consisting of interacting individual molecules is described. The method consists of a modified Monte Carlo integration over configuration space. Results for the two-dimensional rigid-sphere system have been obtained on the Los Alamos MANIAC and are presented here. These results are compared to the free volume equation of state and to a four-term virial coefficient expansion.

I. INTRODUCTION

THE purpose of this paper is to describe a general method, suitable for fast electronic computing machines, of calculating the properties of any substance which may be considered as composed of interacting individual molecules. Classical statistics is assumed, only two-body forces are considered, and the potential field of a molecule is assumed spherically symmetric. These are the usual assumptions made in theories of liquids. Subject to the above assumptions, the method is not restricted to any range of temperature or density. This paper will also present results of a preliminary two-dimensional calculation for the rigid-sphere system. Work on the two-dimensional case with a Lennard-Jones potential is in progress and will be reported in a later paper. Also, the problem in three dimensions is being investigated.

II. THE GENERAL METHOD FOR AN ARBITRARY POTENTIAL BETWEEN THE PARTICLES

In order to reduce the problem to a feasible size for numerical work, we can, of course, consider only a finite number of particles. This number N may be as high as several hundred. Our system consists of a square† containing N particles. In order to minimize the surface effects we suppose the complete substance to be periodic, consisting of many such squares, each square containing N particles in the same configuration. Thus we define d_{AB}, the minimum distance between particles A and B, as the shortest distance between A and any of the particles B, of which there is one in each of the squares which comprise the complete substance. If we have a potential which falls off rapidly with distance, there will be at most one of the distances AB which can make a substantial contribution; hence we need consider only the minimum distance d_{AB}.

* Now at the Radiation Laboratory of the University of California, Livermore, California.

† We will use the two-dimensional nomenclature here since it is easier to visualize. The extension to three dimensions is obvious.

Markov chain MC or Random Walk

- Markov chain is a random walk through phase space:

$$s_1 \rightarrow s_2 \rightarrow s_3 \rightarrow s_4 \rightarrow \ldots$$

  Here "s" is the state of the system.

- ALL QMC is some type of Markov process. VMC is the simplest.
- The transition probability is $P(s_n \rightarrow s_{n+1})$ a *stochastic matrix*

$$P(s \rightarrow s') \geq 0 \qquad \sum_{s'} P(s \rightarrow s') = 1$$

- In a Markov chain, the distribution of s_{n+1} depends only on s_n (by definition). *A drunkard has no memory!*
- Let $f_n(s)$ be the probability after "n" steps. It evolves according to a "master equation."

$$f_{n+1}(s') = \sum_s f_n(s)\, P(s \rightarrow s')$$

$$f_{n+1} = P\, f_n$$

- The stationary states are eigenfunctions of P: $P\, f = e f$

Ergodicity

- Typically simulations are assumed to be ergodic:
  - after a certain time the system loses memory of its initial state, S_0, except possibly for certain conserved quantities such as the energy, momentum.
  - The *correlation time* κ(which we will define soon) is the number of iterations it takes to forget.
  - If you look at (non-conserved) properties for times much longer κ, they are unpredictable as if randomly sampled from some distribution.
  - Ergodicity is often easy to prove for the random transition but usually difficult for the deterministic simulation.

The assumption of egodicity is used for:

- Warm up period at the beginning (or equilibration)
- To get independent samples for computing errors.

Metropolis algorithm

Three key concepts:

1. Sample by using an ergodic random walk.
2. Determine equilibrium state by using detailed balance.
3. Achieve detailed balance by using rejections.

Detailed balance $\pi(s)\, P(s \rightarrow s') = \pi(s')\, P(s' \rightarrow s)$.

Rate balance from s to s'.

Put $\pi(s)$ into the master equation. *(Or sum above Eq. on s.)*

$$\Sigma_s\, \pi(s)\, P(s \rightarrow s') = \pi(s') \Sigma_s\, P(s' \rightarrow s) = \pi(s')$$

- Hence, $\pi(s)$ is an eigenfunction.
- If $P(s \rightarrow s')$ is ergodic, $\pi(s)$ is unique steady state solution.

Rejection Method

Metropolis achieves detailed balance by *rejecting* moves.

General Approach:

1. Choose distribution to sample, e.g., π(s) = exp[−βH(s)]/Z
2. Impose detailed balance on transition: K(s➔s') = K(s'➔s)
   where K(s➔s') = π(s) P(s➔s')
   (*probability of being at s)* * (*probability of going to s')*.
3. Break up transition probability into sampling and acceptance:
   P(s➔s') = T(s➔s') A(s➔s')

(*probability of generating s'* from s) * (*probability of accepting move)*

The optimal acceptance probability that gives detailed balance is:

$$A(s \to s') = \min[1, \frac{T(s' \to s)\pi(s')}{T(s \to s')\pi(s)}] = \min[1, \frac{\pi(s')}{\pi(s)}]$$

Normalization of π(s) is not needed or used!

If T is *constant*!

The "Classic" Metropolis method

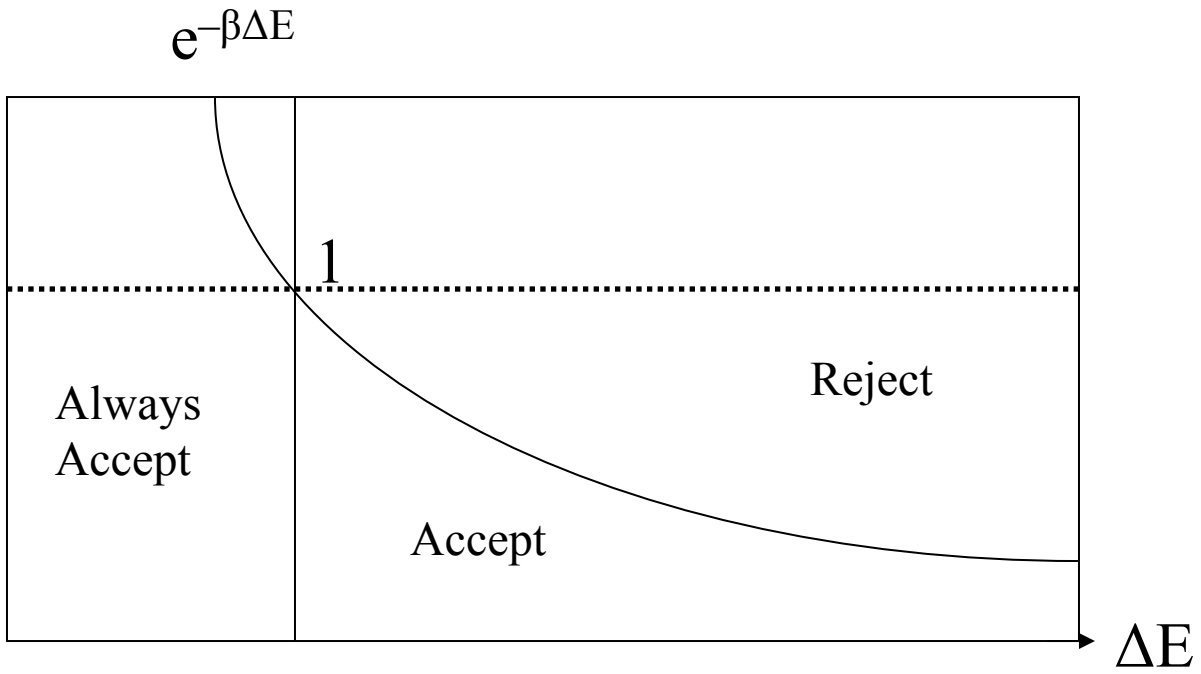
Metropolis-Rosenbluth[2] -Teller[2] (1953) method is:

- Move from s to s' with probability T(s→s')= constant
- Accept with move with probability:

$$\mathbf{A(s \rightarrow s') = \min [\, 1 \,, \exp (- (E(s') - E(s))/k_B T) \,]}$$

- Repeat many times
- Given ergodicity, the distribution of s will be the canonical distribution: $\pi(s) = \exp(-E(s)/k_B T)/Z$
- **Convergence is guaranteed but the rate is not!**

Picture of Metropolis Rejection



- If $\Delta E < 0$, it lowers the system energy → accept.

Otherwise

- Generate UDRN u_n on (0,1)
- Compare u_n to $e^{-\beta\Delta E}$:

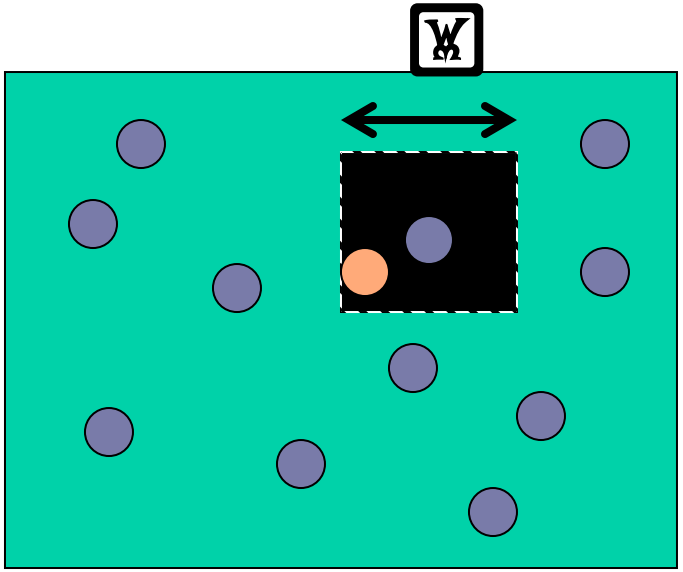
If $u_n < e^{-\beta\Delta E}$, accept.

If $u_n > e^{-\beta\Delta E}$, reject.

How to sample

$$S\_new = S\_old + \Delta \cdot (sprng - 0.5)$$

Uniform distribution in a cube of side "Δ".



Note: It is more efficient to *move one particle at a time* because only the energy of that particle comes in and the *acceptance ratio will be larger*.

$$A(s \to s') = \exp[-\beta(V(s') - V(s))]$$

$$= \exp[-\beta \sum_{j \neq i} (v(r_i' - r_j) - v(r_i - r_j))]$$

For V with cut-off range, difference is local.

MONTE CARLO CODE

```
call initstate(s_old)
E_old = action(s_old)
LOOP{
    call  sample(s_old,s_new,T_new,1)
    E_new = action(s_new)
    call sample(s_new,s_old,T_old,0)
    A=exp(-E_new+E_old) T_old/T_new
    if(A.gt.sprng()) {
            s_old=s_new
          E_old=E_new
          naccept=naccept+1}
     call averages(s_old)          }
```

Initialize the state

Sample snew

Trial action

Find prob. of going backward

Acceptance prob.

Accept the move

Collect statistics

• *Always measure acceptance ratio.* Adjust ratio to *roughly* 0.5 by varying the "step size". RULE: 0.1<a.r.<0.9

• A 20% acceptance ratio actually achieves better diffusion than a 50% acceptance ratio *in this example*.

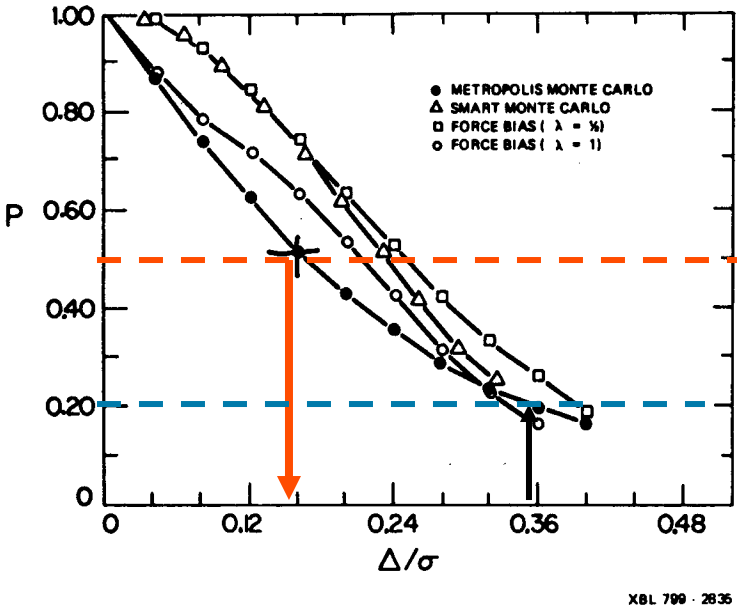


Fig. 1. Average acceptance probability.

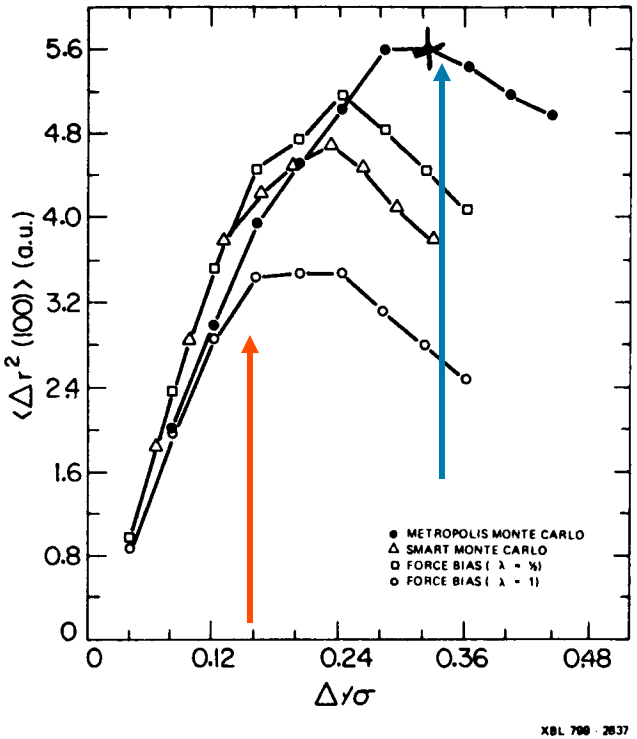
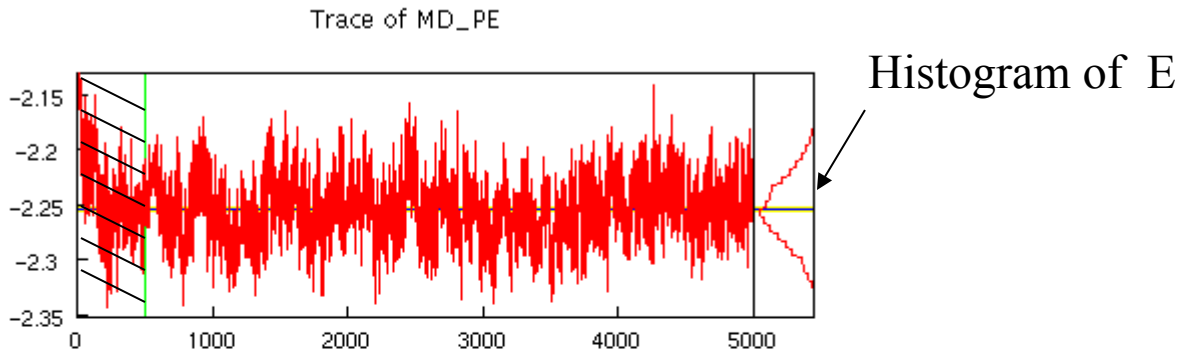


Fig. 3. $\langle(\vec{r}(i) - \vec{r}(i + 100))^2\rangle$

$\vec{r}(i)$ = 3n vector of argon positions at step i.

Estimated Errors

- In what sense do we calculate exact properties? Answer: if we average long enough the error goes to zero, the errors of the simulation are controlled.
- Next, how <u>accurate</u> is the estimate of the exact value?
  - Simulation results without error bars are only suggestive.
    - Without error bars one has no idea of its significance.
    - You should **understand formulas and be able to make an "*eye-ball*" *estimate***.
- **Error bar**: the ***estimated error*** in the ***estimated mean***.
  - Error estimates based on Gauss' ***Central Limit Theorem***.
  - **Average** of statistical processes has *normal* (Gaussian) distribution.
  - **Error bars**: square root of the variance of the distribution divided by the number of ***uncorrelated*** steps.



Central Limit Theorem (Gauss)

Sample N independent values from $F^*(x)dx$, i.e. $(x_1, x_2, x_3, \ldots, x_N)$.

Calculate mean as $y = (1/N)\sum x_i$.

What is the pdf of mean? *Solve by fourier transforms*

Characteristic function: $c_x(k) =< e^{ikx} >= \int_{-\infty}^{\infty} dx\, F^*(x) e^{ikx}$ $c_y(k) = c_x(k/N)^N$

$$\lim_{N\to\infty} \quad c_y(k) = e^{ik\kappa_1 - k^2\kappa_2/2N - ik^3\kappa_3/6N^2 \ldots}$$

Cumulants: Mean = κ_1 Variance= κ_2 Skewness = κ_3 Kurtosis= κ_4

The n=1 moment remains invariant but the rest get reduced by higher powers of N.

Given enough averaging almost anything becomes a Gaussian distribution.

$$P(y) = (N/2\pi\kappa_2)^{1/2} \exp\left[-\frac{N(y-\kappa_1)^2}{2\kappa_2}\right] \quad \text{standard error(y)}=\sigma=\sqrt{\frac{\kappa_2}{N}}$$

Approach to normality

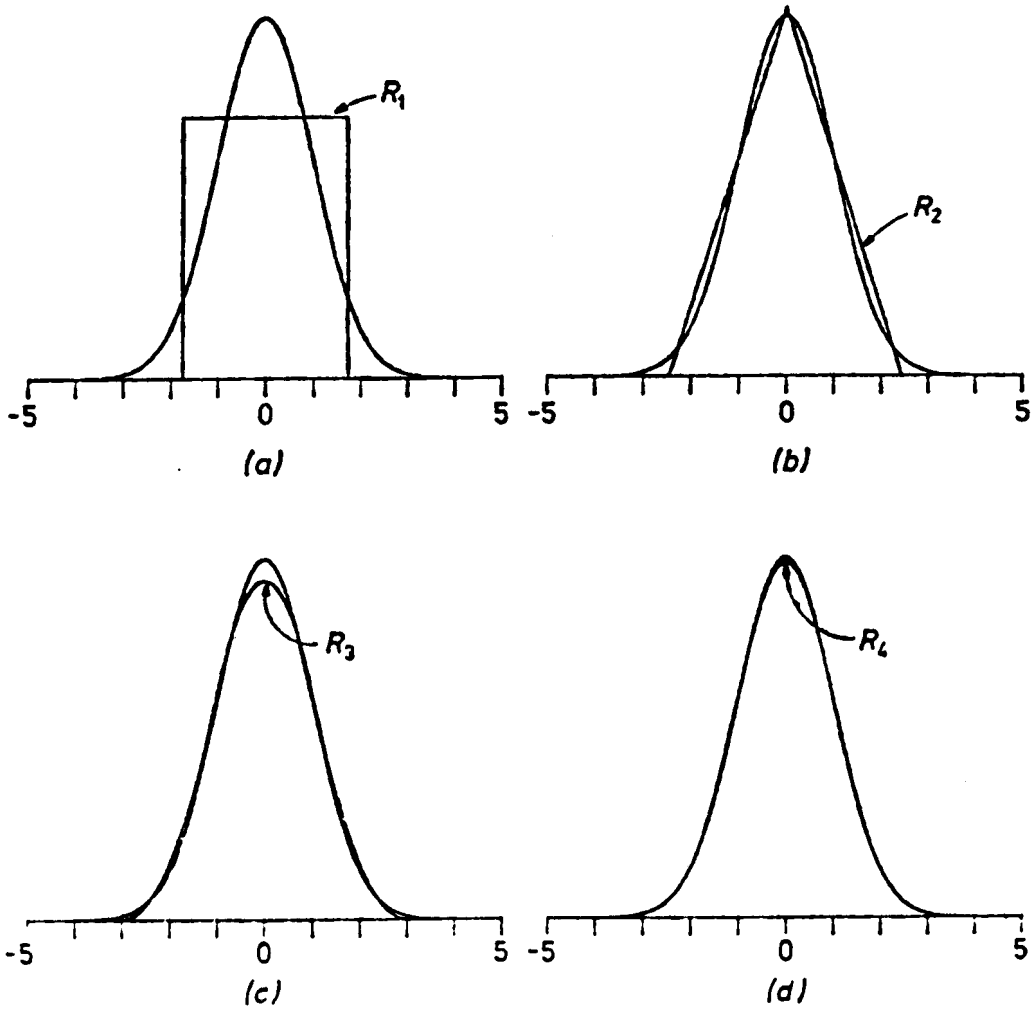


Figure 1. Distributions of sums of uniform random numbers, each compared with the normal distribution. (*a*) R_1, the uniform distribution. (*b*) R_2, the sum of two uniformly distributed numbers. (*c*) R_3, the sum of three uniformly distributed numbers. (*d*) R_{12}, the sum of twelve uniformly distributed numbers.

Conditions on Central Limit Theorem

$$I_n =< x^n >= \int_{-\infty}^{\infty} dx\, F^*(x) x^n$$

- We need the first three moments to exist.
  - If I_0 is not defined ➔ not a pdf
  - If I_1 does not exist ➔ not mathematically well-posed.
  - If I_2 does not exist ➔ infinite variance.
  - Important to know if variance is finite for simulations.
- Divergence could happen because of tails of distribution

$$I_2 =< x^2 >= \int_{-\infty}^{\infty} dx\, F^*(x) x^2$$

We need: $\lim_{x \to \pm\infty} \quad x^3 F^*(x) \to 0$

- OR Divergence because of singular behavior of F^* at finite x:

We need: $\lim_{x \to 0} \quad x F^*(x) \to 0$

Estimating Errors

- Uncorrelated data

$$\{a_t\} \qquad 0 < t \le N$$

$$\langle a_t \rangle \approx \bar{a} = \frac{1}{N}\sum_t a_t$$

$$error(\bar{a}) = \left\langle \left(\bar{a} - \langle a \rangle\right)^2 \right\rangle^{1/2} \approx \left[\frac{\sum_t \delta a_t{}^2}{N(N-1)} \right]^{1/2}$$

$$\delta a_t \equiv a_t - \bar{a}$$

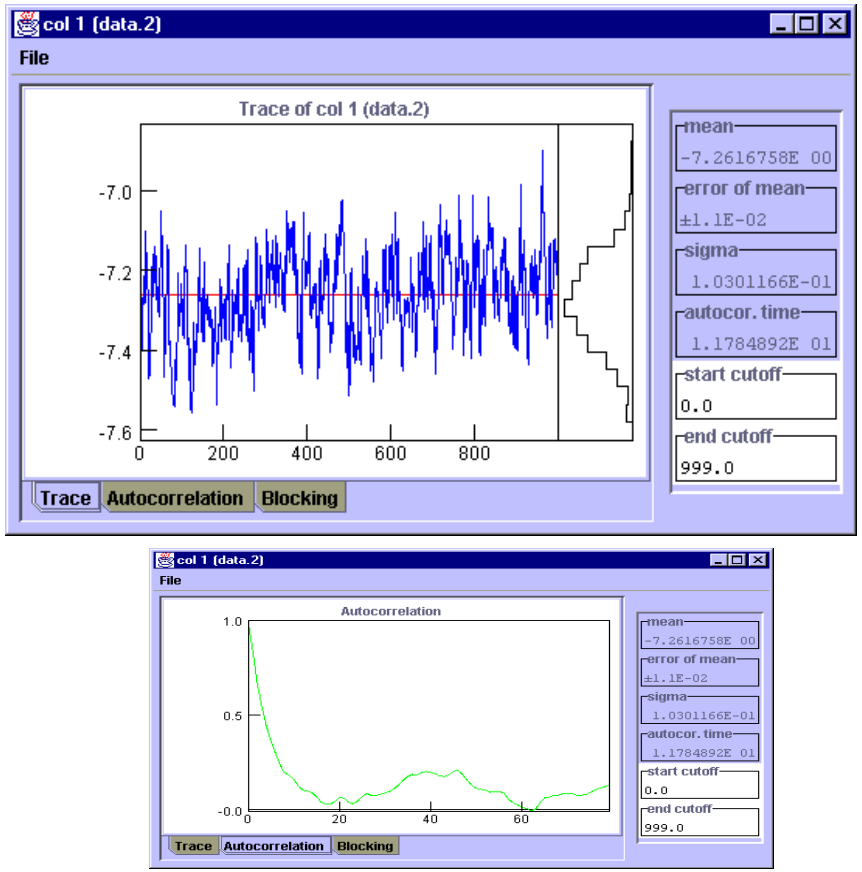
- Correlated data

$$error(\bar{a}) = \left\langle \left(\bar{a} - \langle a \rangle\right)^2 \right\rangle^{1/2} \approx \left\langle \frac{\kappa \sum_t \left(a_t - \bar{a}\right)^2}{N(N-1)} \right\rangle^{1/2}$$

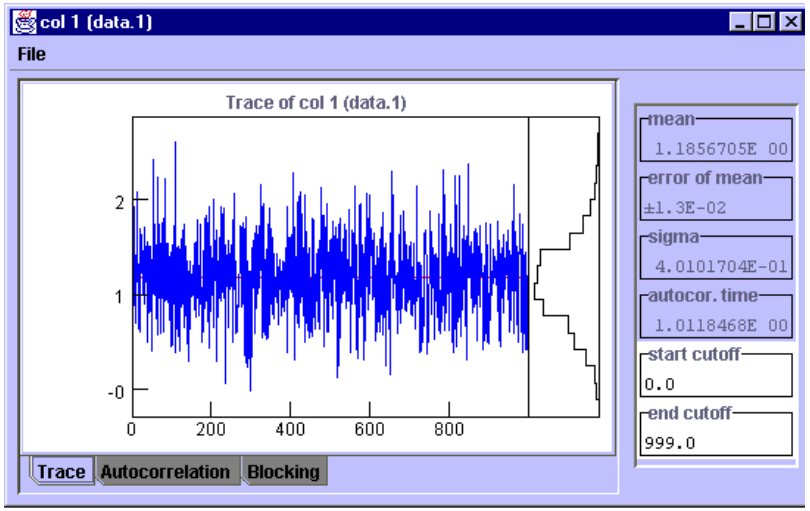
$$\kappa = 1 + 2\sum_{t=1}^{\infty} \frac{\langle \delta a_t \delta a_0 \rangle}{\langle \delta a^2 \rangle} = \text{correlation time}$$

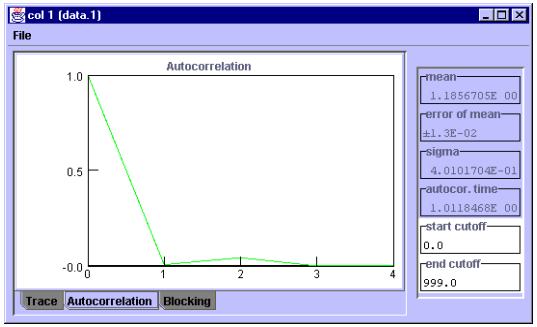
- Problem: how to cut off the summation for κ.
- **Blocking method: average together data in blocks longer than the correlation time until it is uncorrelated.**

Correlated data



Uncorrelated data





Estimate of errors

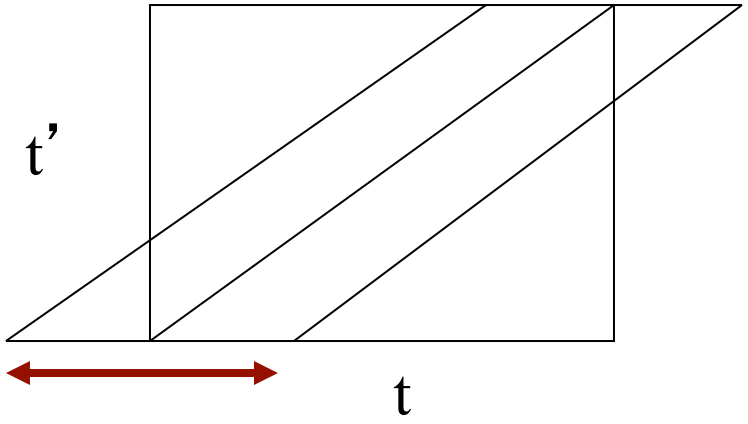
$$error\left(\bar{a}\right)=\left\langle\left(\bar{a}-\langle a\rangle\right)^2\right\rangle^{1/2}\approx\left\langle\frac{\kappa\sum_t\left(a_t-\bar{a}\right)^2}{N(N-1)}\right\rangle^{1/2}$$

$$\boxed{\bar{a}=\frac{1}{N}\sum_t a_t}$$

$$\kappa=1+2\sum_{t=1}^{\infty}C\left(t\right)=\text{correlation time}\approx 2\int_0^{\infty}\frac{dt}{\delta t}\text{C(t)}$$

$$C(t,t')\equiv\frac{\left\langle\delta a_t\delta a_{t'}\right\rangle}{\left\langle\delta a^2\right\rangle}=C\left(\left|t-t'\right|\right)=\text{autocorrelation function}$$

$$\left\langle\left(\bar{a}-\langle a\rangle\right)^2\right\rangle=\left\langle\frac{1}{N^2}\sum_{t,t'}^{N}\delta a_t\delta a_{t'}\right\rangle=\frac{\left\langle\delta a^2\right\rangle}{N^2}\sum_{t,t'}^{N}C_{|t-t'|}\;\le\;\frac{\left\langle\delta a^2\right\rangle}{N^2}\sum_{t'=1}^{N}\sum_{t=-\infty}^{\infty}C_t=\left\langle\delta a^2\right\rangle\frac{\kappa}{N}$$



Statistical vs. Systematic Errors

- What are statistical errors?
  - Statistical error measures the distribution of the averages about their avg.
  - ***Statistical error can be reduced by extending or repeating runs***, increase N.

$$\text{standard error(y)}=\sigma=\sqrt{\frac{\kappa_2}{N}}$$

- The efficiency is how we measure the rate of convergence of the statistical errors.

$$\boxed{\zeta = \frac{1}{T\sigma^2}}$$

  - It depends on the computer, the algorithm, the property etc. But not on the length of the run.
- What are systematic errors ?
  - Systematic error measures the other errors. Even if you sample forever the systematic errors remain constant.
  - Systematic error is caused by round-off error, non-linearities, bugs, non-equilibrium, etc.

Statistical Vocabulary

- **Trace of A(t)**:
- **Equilibration time**.
- **Histogram** of values of A (P(A)).
- **Mean** of A (a).
- **Variance** of A (v).
- **estimate of the mean:** $\Sigma A(t)/N$
- **estimate of the variance**
- **Autocorrelation** of A (C(t)).
- **Correlation time** k .
- The (estimated) **error** of the (estimated) **mean** (s).
- **Efficiency** [= 1/(CPU time * error ^{2})]

Statistical thinking is slippery: be careful

- "Shouldn't the energy settle down to a constant"
  - NO. It fluctuates forever. It is the overall mean which converges.
- Because data is correlated, the central limit theorem is invalid
- "The cumulative energy has converged".
  - BEWARE. Even pathological cases have smooth cumulative energy curves.
- "Data set A differs from B by 2 error bars. Therefore it must be different".
  - This is normal in 1 out of 10 cases. If things agree too well, something is wrong!
- "My procedure is too complicated to compute errors"
  - NO! Run your whole code 10 times and compute the mean and variance from the different runs. If a quantity is important, you MUST estimate its errors.

Recap: problems with estimating errors

- Any good simulation quotes *systematic and statistical* errors for anything important.
- The *error and mean* are simultaneously determined from the same data. HOW?
- Central limit theorem: the distribution of an average approaches a normal distribution (*if the variance is finite*).
  - One *standard deviation* means ~2/3 of the time the correct answer is within σ of the sample average.
- Problem in simulations is that *data is correlated in time*.
  - It takes a "correlation" time κ to be "ergodic"
  - Correction errors for autocorrelation.
  - throw away the initial transient.
- We need about 25 *independent* data points to estimate errors. (so that the error of the error is only 1/sqrt(N)= 20%)