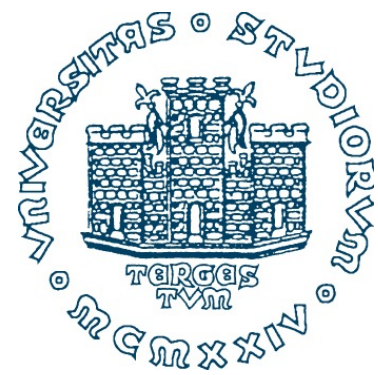


993SM - Laboratory of Computational Physics unit XI December 4, 2023

Maria Peressi
Università degli Studi di Trieste - Dipartimento di Fisica
Sede di Miramare (Strada Costiera 11, Trieste)
e-mail: peressi@units.it
tel.: +39 040 2240242

Lattice gas models

idea: recover the treatment of RWs
but the walkers now move together and interact

other topics:

- Macroscopic systems towards equilibrium
- Stochastic fluctuations
- Simulated annealing *(A. Marrazzo, tomorrow; Python)*

Random Walks

Dependence of $\langle R^2(t) \rangle$ on t :

- **normal** behavior: $\langle R^2(t) \rangle \sim t$
  for the brownian motion
- **superdiffusive** behavior: $\langle R^2(t) \rangle \sim t^{2\nu}$ with $\nu > 1/2$
  in models where self-intersections are unfavored
- **subdiffusive** behavior $\langle R^2(t) \rangle \sim t^{2\nu}$ with $\nu < 1/2$
  in models where self-intersections are favored

t (time) $\longleftrightarrow$ N (number of steps); $t = N\,\Delta t$

$\langle\,\rangle$ = avg. over walkers

RW and diffusion

- consider the normal behaviour: $\langle R^2(t) \rangle \sim t$

The **quantity**: $D(t) = \frac{1}{2dt} \langle \Delta R(t)^2 \rangle$

(where d is the dimensionality of the system)

should go asymptotically to a constant value for large t,

the **autodiffusion coefficient:** $D = \lim_{t \to \infty} D(t)$

Using the time discretization: $t = N\Delta t$ and $\langle \Delta R_N^2 \rangle = N\ell^2$

we have: $$D = \lim_{t \to \infty} \frac{1}{2dt} \langle \Delta R^2(t) \rangle = \frac{N\ell^2}{2dt} = \frac{\ell^2}{2d\Delta t}$$

$\langle \; \rangle$ = avg. over walkers

RW and diffusion in 1D

The probability that a RW of N steps (N large) ends at position x is given by:

$$P_N(x) = \sqrt{\frac{2}{\pi N}}\ \exp\left(-\frac{x^2}{2N}\right)$$

Considering that $t = N\Delta t$, defining $D = \frac{\ell^2}{2\Delta t}$, and measuring x in units of ℓ, we get:
$Dt = N\ell^2/2$ and therefore

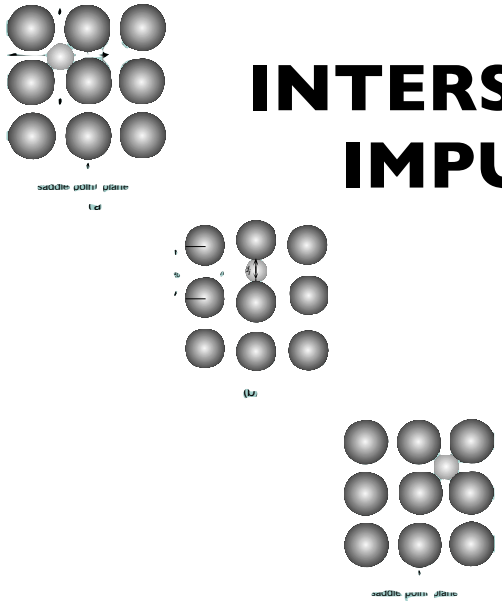
$$P(x,t) = \sqrt{\frac{1}{\pi Dt}}\ \exp\left(-\frac{x^2}{4Dt}\right)$$

which is the fundamental solution of the diffusion equation, a part from a factor of 2 in the normalization due to the spatial discretization. The continuum solution is:

$$P(x,t) = \sqrt{\frac{1}{4\pi Dt}}\ \exp\left(-\frac{x^2}{4Dt}\right)$$

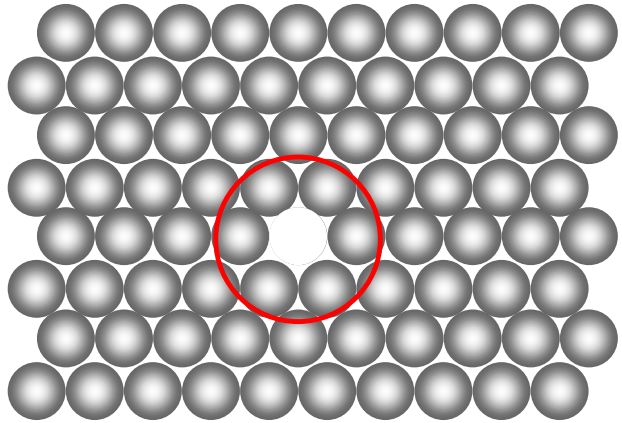
i.e., a Gaussian distribution with $\sigma^2 = 2Dt$ which describes a pulse gradually decreasing in height and broadening in width in such a manner that its area is conserved.

Example of diffusion in solids



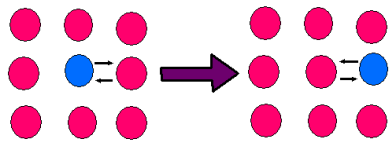
INTERSTITIAL IMPURITIES

VACANCIES DIFFUSION

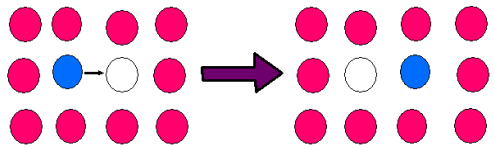


SUBSTITUTIONAL IMPURITIES

Direct exchange



Vacancy assisted diffusion



... but typically:
more than one single interstitial,
more than one single impurity,
or more than one single vacancy....

A SIMPLE RW MODEL IS NOT ENOUGH!

Lattice Gas model

interaction !

Consider a finite lattice with some density ρ of N_p particles. The particles can move on the lattice by jumps to the nearest sites, but two particles can not occupy the same site. This is a simple example of a **restricted** random walk (see above). The physical interpretation is e.g. vacancies moving in a lattice.

To simulate this kind of system, we need a bit more of an advanced approach than before. First of all, we need to simulate the motion of all the particles at the same time, not taking the average over many independent single-particle motions as was done before.

In terms of a Metropolis Monte Carlo approach:

$$\Delta E = \begin{cases} 0 & if\ no\ overlap \\ +\infty & if\ overlap \end{cases} \quad \Longrightarrow e^{-\beta \Delta E} = \begin{cases} 1 & new\ configuration\ accepted \\ 0 & new\ configuration\ NOT\ accepted \end{cases}$$

2D Lattice Gas model

1° Choose number of particles N_p, number of steps N_{steps}, side length L. Set Δt and lattice size a. $(\text{our old } \ell)$

2° Set all positions in the $L \times L$ grid to be empty

3 a° Generate N_p particle coordinates randomly on the grid, checking that no two particles end up on the same points.

3 b° Mark the points with the particles in the $L \times L$ grid as filled.

4° Loop over MC steps of time Δt

5° Loop from 1 to N_p

6° Pick one particle i at random

7° Find which positions it can jump to. If none, return to step 6° (*)

8° Let the particle jump to one of the allowed directions j by a displacement $x_i = x_i + \delta x_j, y_i = y_i + \delta y_j$, enforce periodic boundaries on x and y

9° Set $dx_i = dx_i + \delta x, dy_i = dy_i + \delta x$ (where periodic boundaries **do not** play a role!)

10° End loop from 1 to N_p

11° Update time $t = t + \Delta t$

12° End loop over MC steps

13° Output $\langle \Delta R^2 \rangle = \langle dx_i^2 + dy_i^2 \rangle$ and calculate diffusion coefficient $D(t) = \frac{1}{2dt} \langle \Delta R(t)^2 \rangle$

average over the particles

Lattice Gas model

(*) Different dynamics can be implemented, for instance:

- find which nearest neighbour sites are free and jump in one of them randomly chosen (if any) (this is actually mentioned in the previous slide and implemented in the code we are going to discuss) OR
- choose randomly one nearest neighbour site and jump only if it is free

NOTE - Here:

Different dynamics => different behaviour with concentration

(and somehow a different definition of the time unit)

Lattice Gas model

The crucial difference here to the previous random walk algorithms is that the outer loop goes over MC steps, the inner one over particles. When the walkers are independent of each other ("non-interacting") we can deal with one walker at a time, saving memory since storage of all particles is not needed.

But here the walkers (the particles) are "interacting"

Programs:

on moodle2

latticegas.f90
entropy.f90
box.f90
simulated_annealing.f90

Implementation of the model on 2D SQ lattice (latticegas.f90)

```
...
logical,allocatable::lattice(:,:) ! (occ./non occ.=.true./.false.)
integer,allocatable::x(:),y(:) ! instantaneous positions of Np labelled particles
double precision, allocatable :: dx(:),dy(:) ! displ. from the starting point
integer :: free(4),nfree           ! occupation of nearest neighbors
integer :: dxtrial(4),dytrial(4)   ! trial move (instantaneous displacements)
integer :: xnew(4),ynew(4)         ! 4 new possible positions
 .....
allocate(lattice(0:L-1,0:L-1))
allocate(x(Np),y(Np))
allocate(dx(Np),dy(Np))

 ...
lattice = .false.          ! Mark all positions as empty

 ...
! Enumerate directions: 1=right; 2=left; 3=up; 4=down
dxtrial(1)=+1; dytrial(1)= 0;
dxtrial(2)=-1; dytrial(2)= 0;
dxtrial(3)= 0; dytrial(3)=+1;
dxtrial(4)= 0; dytrial(4)=-1;
```

```
! INIZIALIZE THE LATTICE : Generate Np particles on LxL lattice
  do i=1,Np
    do ! Loop until empty position found,  UNBOUNDED LOOP!
        call random_number(rnd)    !which has dimension(2)
        x(i)=int(rnd(1)*L)
        y(i)=int(rnd(2)*L)
        if (lattice(x(i),y(i))) then
           ! Position already filled, loop to find new trial
           cycle   !REMEMBER: JUMP AT THE END OF THIS LOOP (NOT EXIT)
        else
           lattice(x(i),y(i))=.true.
           !  Successful, place next particle
           exit
        endif
     enddo
     dx(i)=0.0d0; dy(i)=0.0d0;     (NOTE: you could rewrite some instructions in a more compact way…)

  enddo
```

```
! MONTE CARLO LOOP

do istep=0,Nsteps-1 ! Loop over MC steps
    do isubstep=1,Np ! Move each particle once every MC step (on av.)
       ! Pick one particle at random
       call random_number(rnd1)
       i=int(rnd1*Np)+1  ! 1 =< i =<  Np;
    ! Find possible directions (j=1,...,4) for moving, store them
    in free() ... (NOTE: different possible recipes !!!)
    ! If no free positions, get a new particle ; otherwise choose
    ! one possible direction (j) and update (x,y) with (xnew,ynew):
        ......
       !Empty the old  position  and  fill the new one:
       lattice(x(i),y(i))=.false.
       lattice(xnew(j),ynew(j))=.true.

    enddo
     t=t+deltat
enddo
```

Another fundamental part: calculation of distance from initial pos. for each particle (do not use PBC for that!), accumulation of data...

```
! Get total displacement using dx,dy
! dx,dy are individual displacements from the
! starting point  => these d*sum are summed
! over time and particles
dxsum=0.0d0; dysum=0.0d0;
dxsqsum=0.0d0; dysqsum=0.0d0;
do i=1,Np
dxsum=dxsum+dx(i);   dysum=dysum+dy(i);
dxsqsum=dxsqsum+dx(i)*dx(i);
dysqsum=dysqsum+dy(i)*dy(i);
enddo
print *,'dxsum',dxsum,' dysum',dysum
print *,'dxsqsum',dxsqsum,' dysqsum',dysqsum
```

Concentration dependent diffusion coefficient

And here is a series of results:

Np	L	concentration Np/L^2	D (cm^2/s)	
10	100	0.001	9.76	E-008
10	100	0.001	1.12	E-007
100	100	0.01	1.02	E-007
100	100	0.01	9.46	E-008
10000	1000	0.01	9.89	E-008
1000	100	0.1	9.11	E-008
1000	100	0.1	9.42	E-008
100000	1000	0.1	9.40	E-008
3000	100	0.3	8.28	E-008
3000	100	0.3	7.91	E-008
6000	100	0.6	5.89	E-008
6000	100	0.6	5.91	E-008
9000	100	0.9	1.77	E-008
9000	100	0.9	1.78	E-008
900000	1000	0.9	1.82	E-008
9900	100	0.99	1.83	E-009
9900	100	0.99	1.86	E-009

Here: 2d example

$1 \text{ MC step} = 1 \text{ ns}$

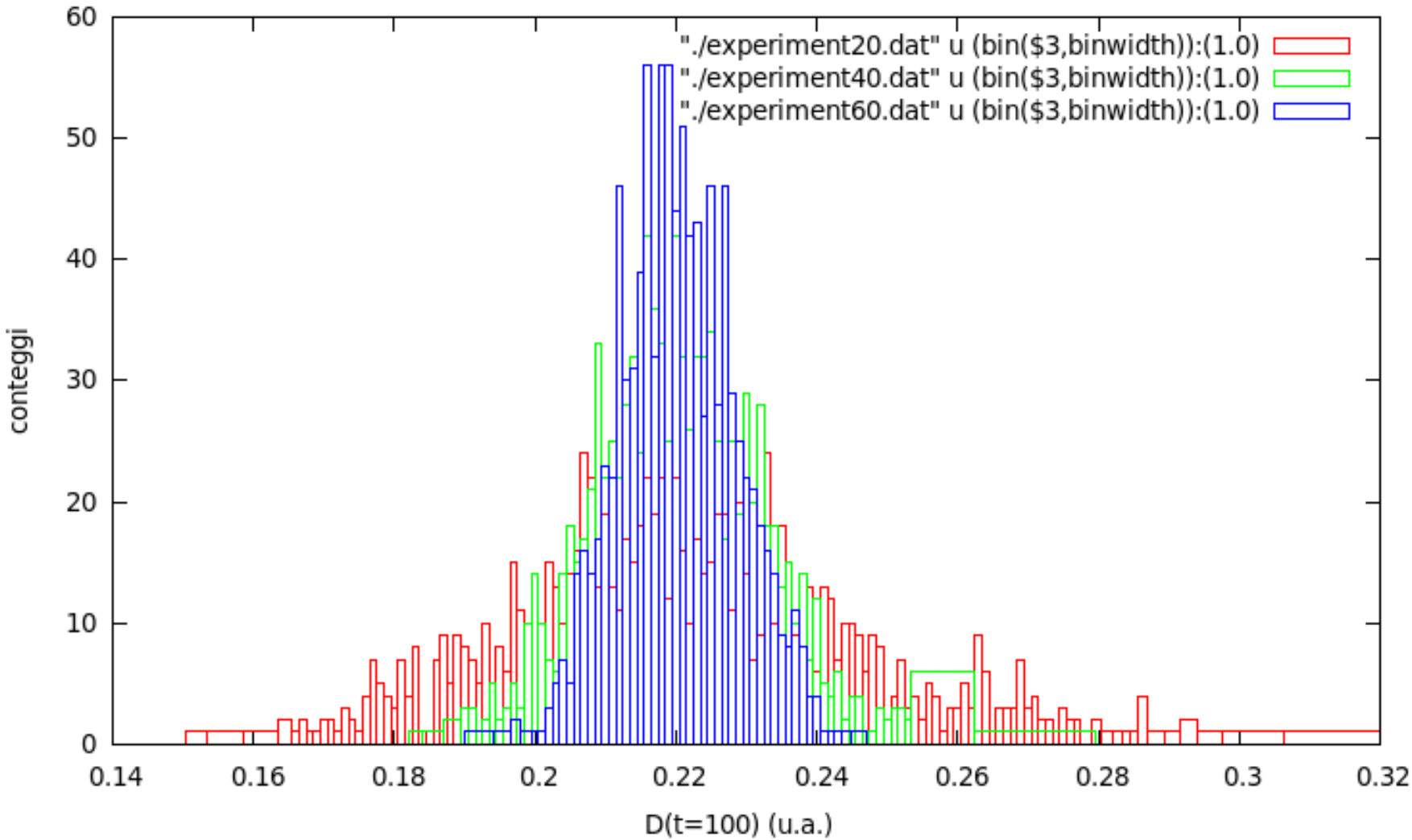
$\text{unit step length} = 2 \text{ Å}$

What does this mean? At small concentrations, the system behaves essentially as an unconstrained random walk. For that one, we know that $\langle \Delta R^2 \rangle$ should be equal to $a^2 N$, where N is the number of steps, and a is the jump distance, and the result for the diffusion coefficient should be

$$D = \frac{\langle \Delta R^2 \rangle}{4t} = \frac{(2 \text{ Å})^2 N}{4 N \Delta t} = \frac{(2 \text{ Å})^2}{4 \times 1 \text{ ns}} = 10^{-7} \frac{\text{cm}^2}{\text{s}}$$

Sample averages (size effect)

A usually, we can estimate the statistical error associated to the estimate of D (here: histogram done collecting data in the time evolution of D(t))

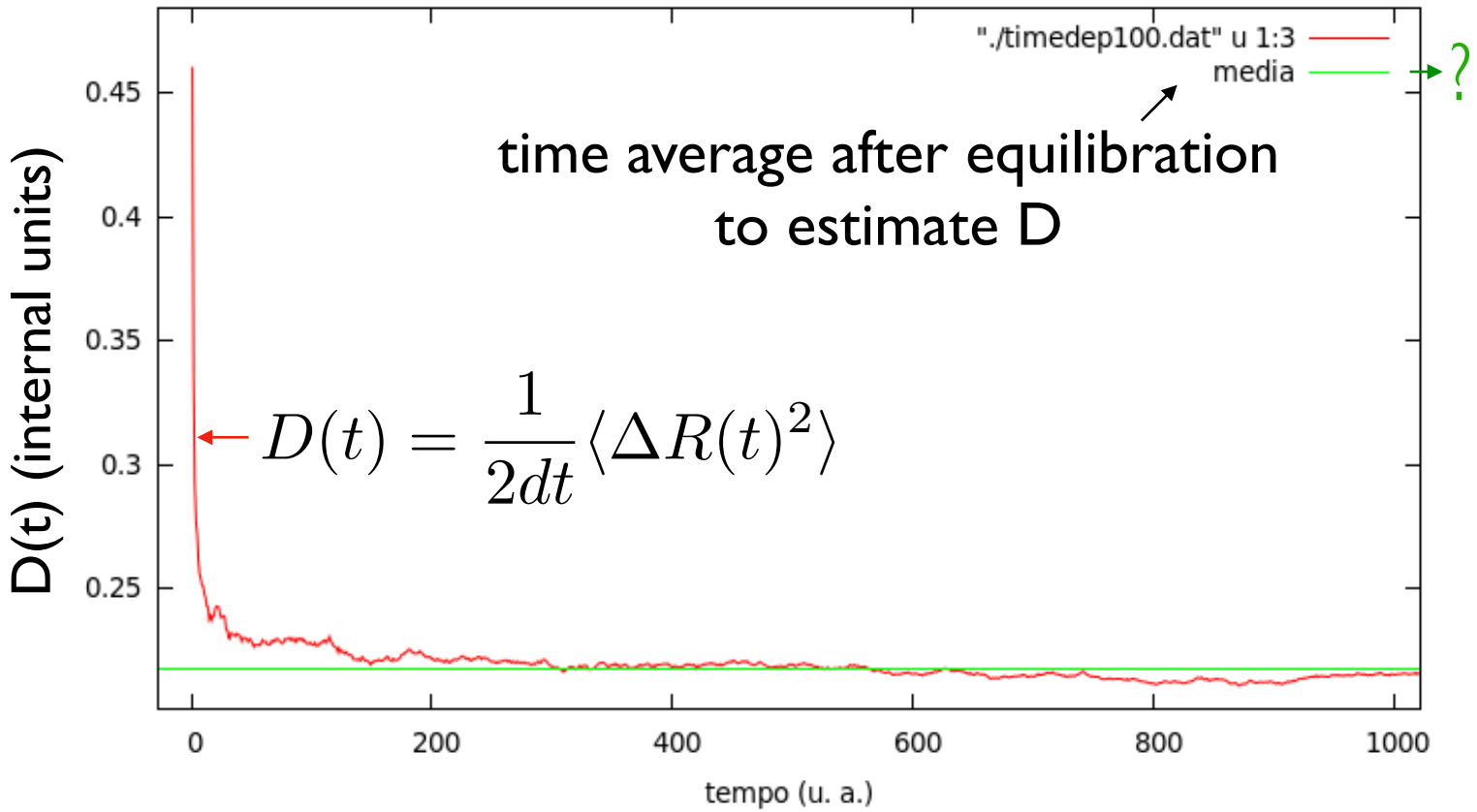


size effect: concentration ρ fixed, changing the lattice dimension (20,40,60))

(more later)

Discussing Ex. 1

(1.a) Study D(t) for a fixed value of ρ, for instance 0.2. Although D is defined as the limit $t \to \infty$, it is instructive to follow D(t) as a function of time: for this model, it fluctuates after a short equilibration time and no appreciable improvements in the statistics are achieved by increasing t.



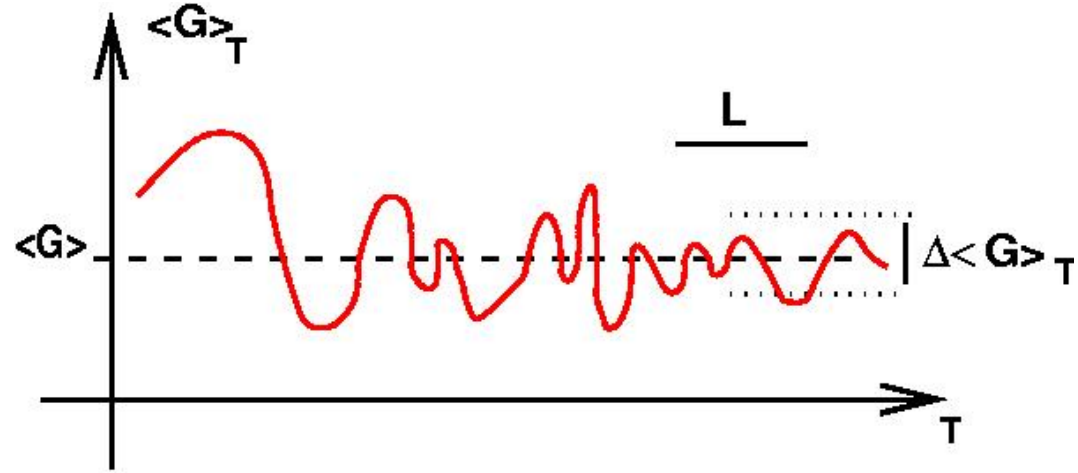
this is D(t) or D_t (instantaneous, averaged over particles); calculate it for $t \to \infty$

Temporal averages

$$< G >_T = \frac{1}{T} \sum_{t=1}^{T} G_t$$

Thermally equilibrated averages:

$$< G > = \lim_{T \to \infty} < G >_T$$



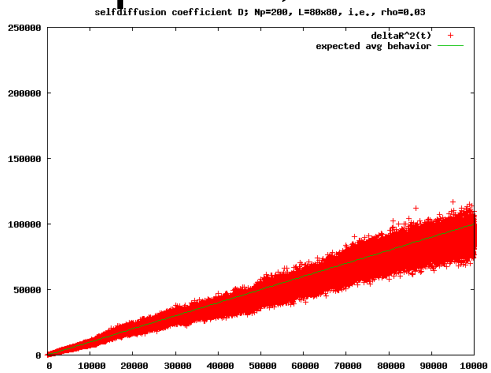
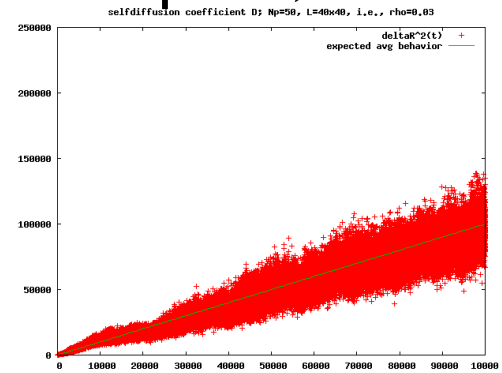
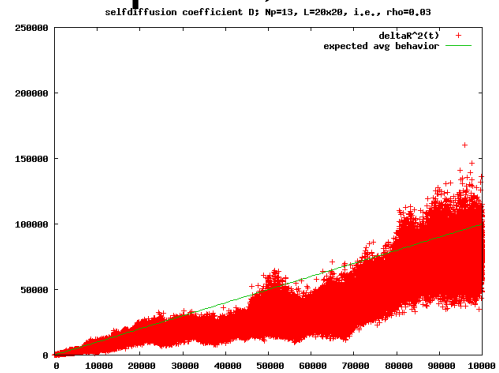
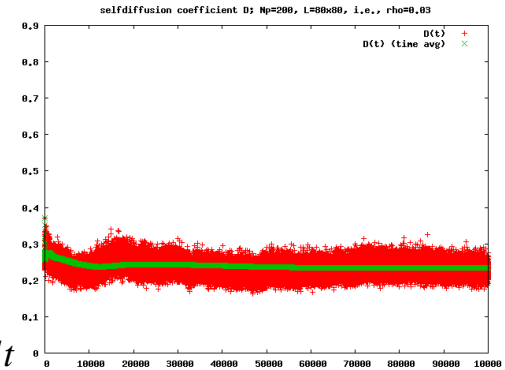
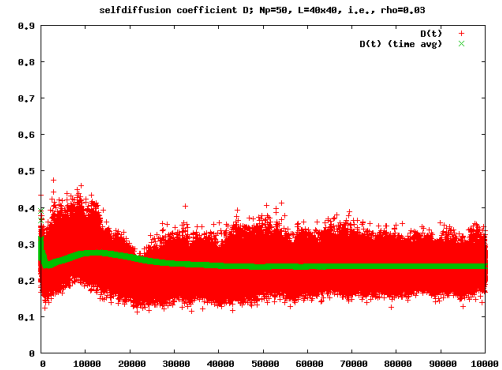
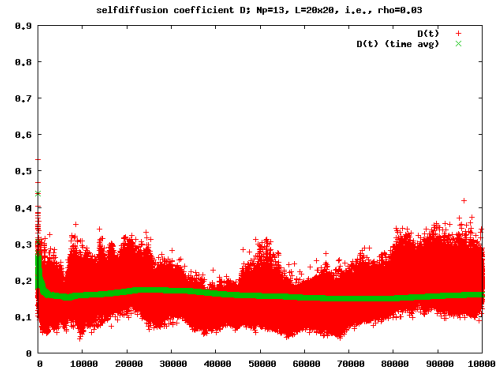
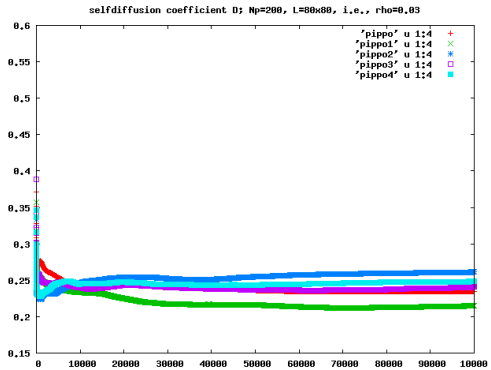
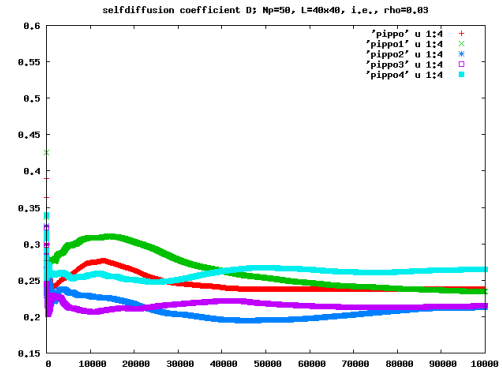
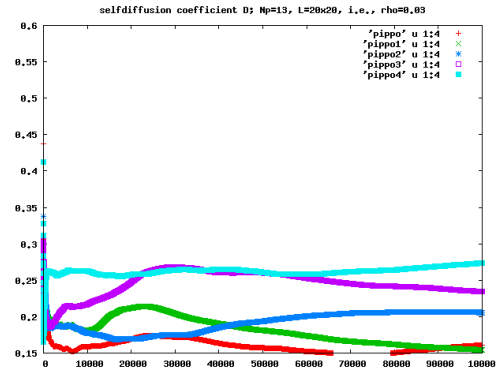
But in practice T is finite, and $< G >_T$ oscillates(varying T):
divide T into intervals $A, B, C \ldots$ of length L and sum (block averages):

$$< G >_T = \frac{L}{T} \sum_{I=A,B,C,\ldots} < G >^{(I)}$$

$$\Delta < G >_T = \left[\frac{L}{T} \sum_I \left(< (G^{(I)})^2 > - (< G^{(I)} >^2 \right) \right]^{1/2} \quad \begin{matrix} \longrightarrow \\ T \to \infty \end{matrix} \quad \begin{matrix} (\sigma_s/\sqrt{s}) \\ \sim \\ (\sigma_n/\sqrt{n}) \end{matrix} \frac{1}{\sqrt{T}}$$

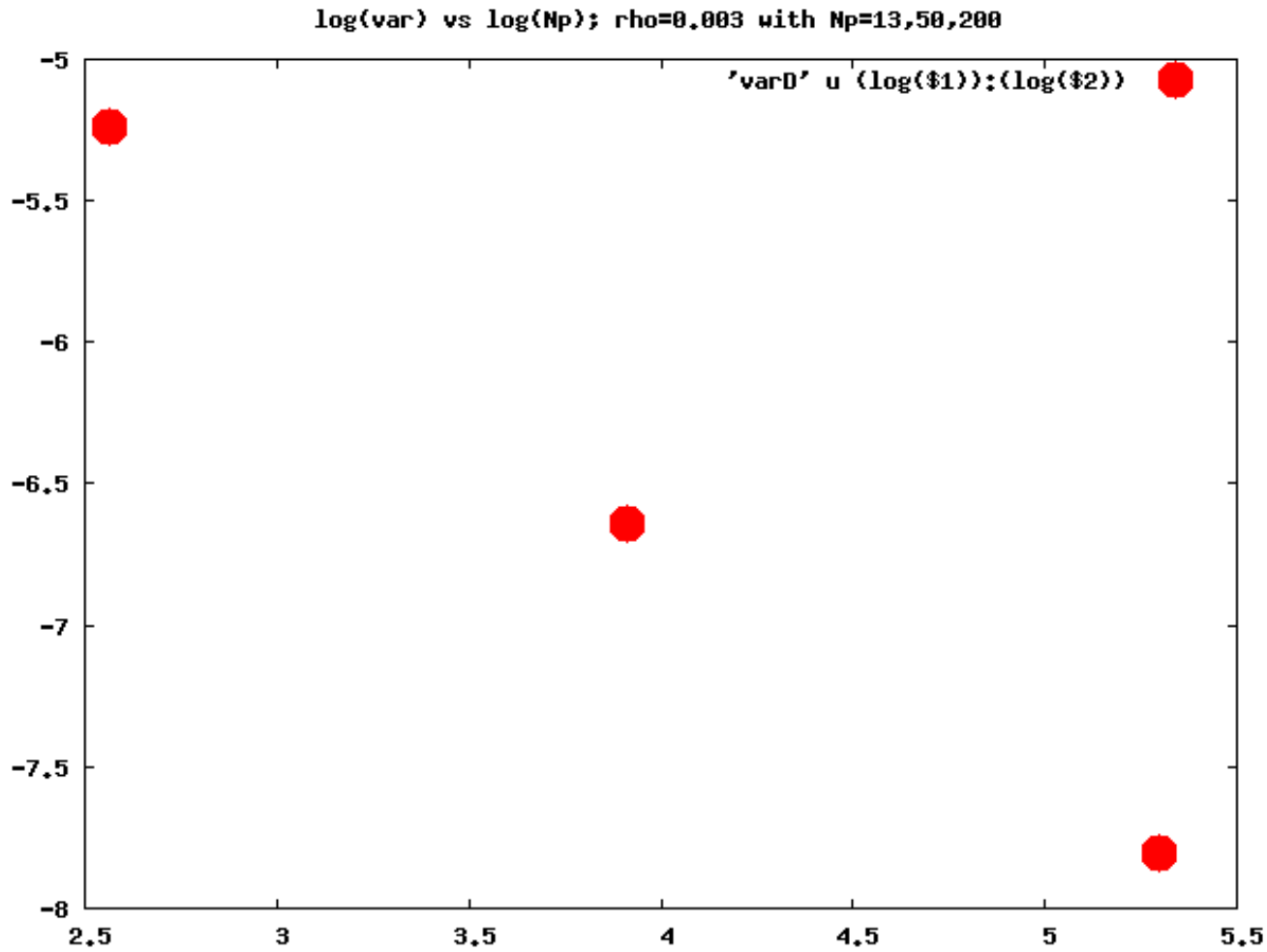
Note: not always $\Delta < G >_T$ is a good indicator of the actual error!
(remind "ergodicity")

(I.1) ... Better statistics for D can be obtained by averaging D over as many particles as possible (i.e., for a given ρ)... Here **ρ=0.03**

	Np=200, 80x80	Np=50, 40x40	Np=13, 20x20
$\langle \Delta R^2(t) \rangle$ and expected behavior			
D(t) and $\langle D \rangle_T$ time averaged: $\langle D \rangle_T = \int_0^T D(t)dt$			
$\langle D \rangle_T$ in 5 different runs			

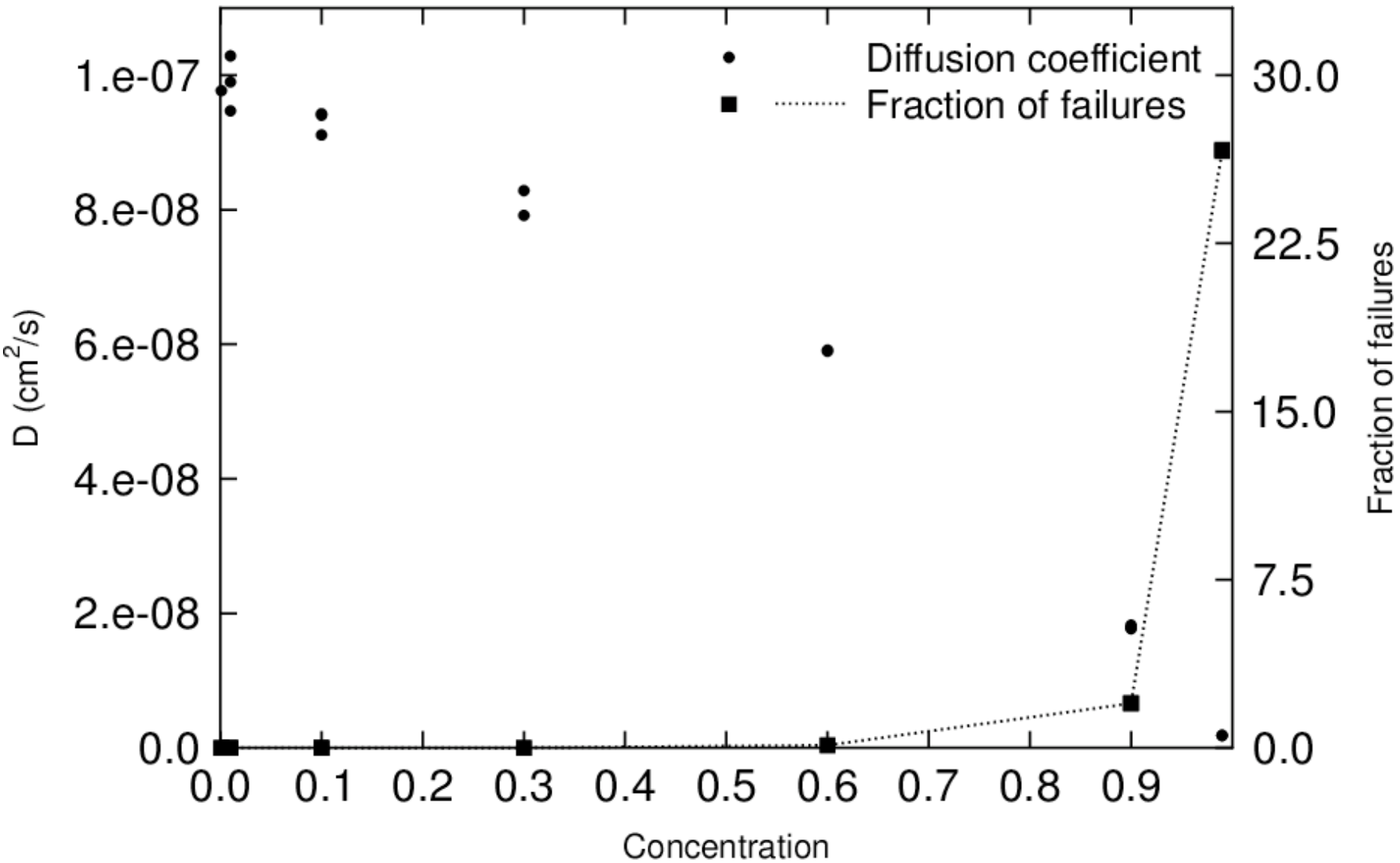
(we expect the limit of the simple 2D RW on a square lattice, with D=0.25)

Ex. 1 (...) Verify that deviations of $\langle D(t) \rangle_t$ from its mean value are proportional to the inverse square root of the total number of particles.



σ^2_D proportional to 1/Np

Concentration dependent diffusion coefficient



the lattice gas problem is suitable to be afforded
by embedding the "number crunching" part in Fortran90
in a Python structure:
do it yourself!

Another example of restricted random walks: self-avoiding walks (SAW)

polyethylene $\cdots$–CH_2–CH_2–CH_2–CH_2–$\cdots$

Experiments on polymers have shown that when the length of the "noodle" is measured, the average mean square end-to-end length has been found to have the following dependence:

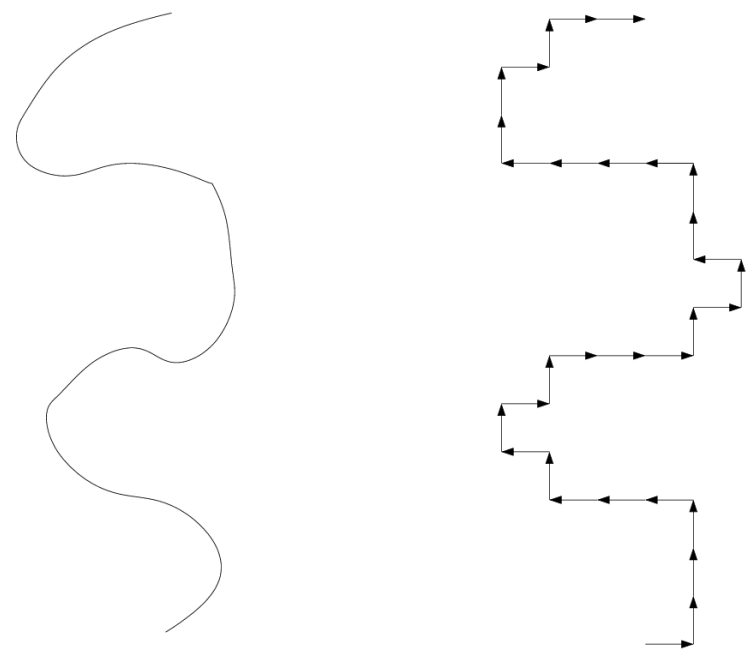
$$\langle \Delta R^2(N) \rangle \propto N^{2\nu} \quad \text{with} \quad \nu \approx 0.592$$

for a wide range of polymers, regardless of their other properties. Here N is the number of monomers. The fact that such very general behaviour is observed indicates that there is some very simple general reason for the behaviour.

in a polymer the monomers
certainly can not occupy the same space

add the simple requirement that

the walker should never return
to a position it has already
occupied.



SAW

Coding the SAW efficiently is not quite trivial. It could seem easy. Just do random walks one at a time as usual for non-interacting walkers, store all the positions visited to an 2D or 3D array, and if a new step enters a previously visited site, disregard it.

But herein lies the problem. We can not just disregard the last step, and look for a new direction. This would skew the statistics; we have to disregard the whole walk. If we want to make a walk of any sensible length (say, $N > 30$), the probability of the walker entering a previously visited site becomes enormously large. Hence we end up disregarding almost all walks.

SAW

The idea is that once a walk attempts to do a step N that is impossible, we do not disregard the whole walk, but only this step. We then pick some other, possible step. A weight factor $W(N)$ is used to ensure that the statistics remains correct.

The way the weighting is done can be written as follows. Consider a situation where we have just done step $N-1$, and look at step N. Three outcomes are possible:

1° No step is possible. Set $W(N) = 0$ and restart

2° All steps other than the step right backward are possible, set W(N)=W(N-1)

3° Only m steps are possible with $1 \leq m < 3$ (2D) or $1 \leq m < 5$ (3D). In this case we choose randomly one of the possible steps, and set $W(N) = \frac{m}{3} W(N-1)$ (2D) or $W(N) = \frac{m}{5} W(N-1)$(3D).

SAW

The correct value of the final average $\langle \Delta R^2(N) \rangle$ is obtained by weighting $R_i^2(N)$ for each step N in a given walk i with the weight $W_i(N)$ obtained in the same walk. To get the average, we have to divide by the sum of $W_i(N)$ instead of N, i.e.

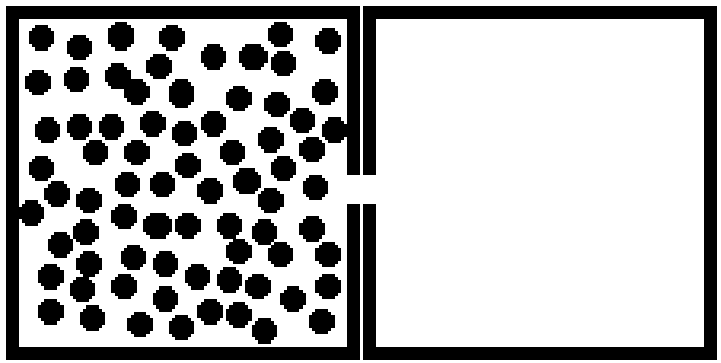
$$\langle \Delta R^2(N) \rangle = \frac{\sum_{i=1}^{N_{\text{walks}}} W_i(N) R_i^2(N)}{\sum_{i=1}^{N_{\text{walks}}} W_i(N)}$$

$W(0)$ is initialized to 1.0.

Statistical averages and stochastic fluctuations

Macroscopic systems towards equilibrium

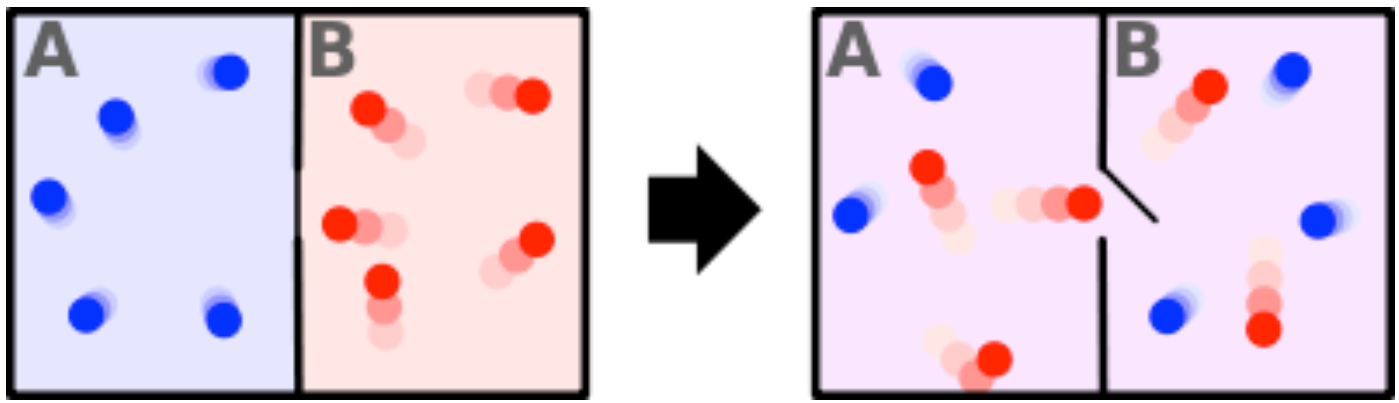
simple example of non-interacting classical particles in a box (gas diffusion)



A box is divided into two parts communicating through a small hole. One particle randomly can pass through the hole per unit time, from the left to the right or viceversa.

$N_{left}(t)$: number of particles present at time t in the left side
Given $N_{left}(0)$, what is $N_{left}(t)$?

Macroscopic systems towards equilibrium



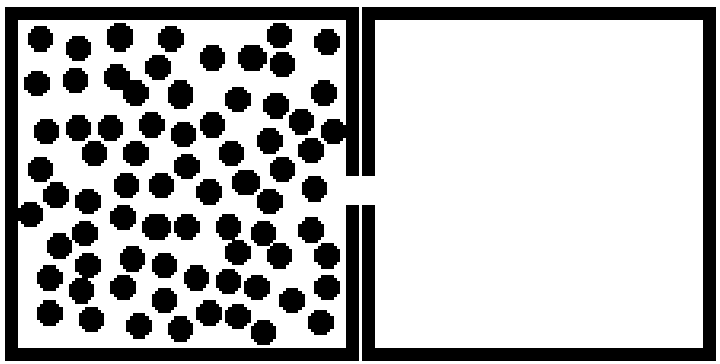
Another version: particles blue/red in both sides
(interdiffusion of two gases):
per unit time, one from each side is picked at random and put in the other side: $N_{left}^{blue}(t)+N_{left}^{red}(t)=constant$; $N_{left}^{red}(t)=?$

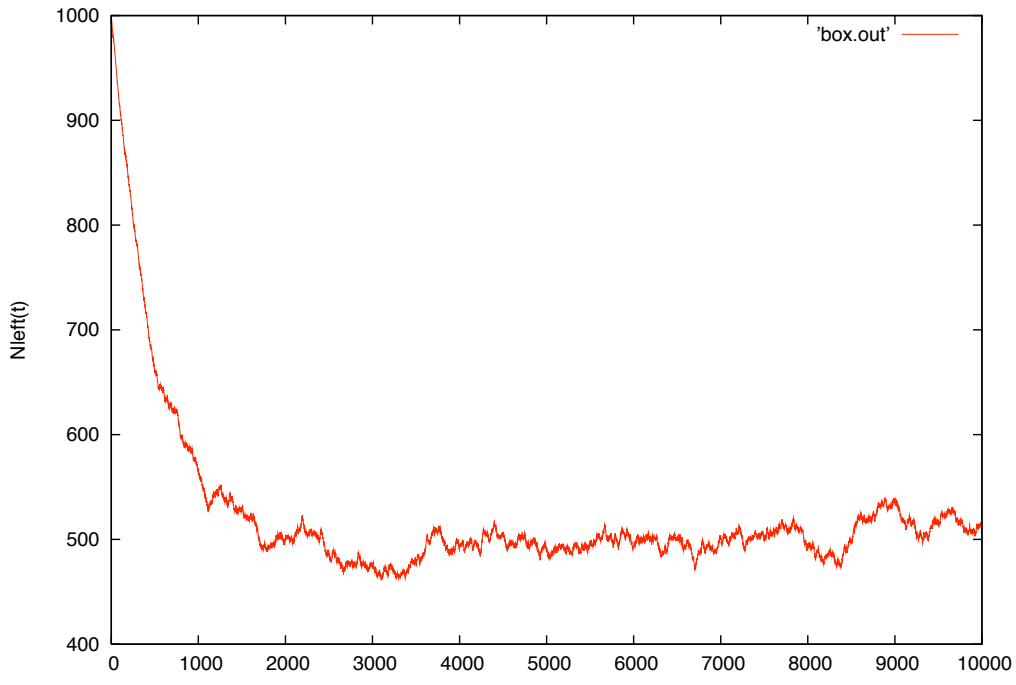
Paul Ehrenfest (1880-1933)

Stochastic fluctuations

Fluctuations are always present, due to the nature of the system, also when evolving towards equilibrium.

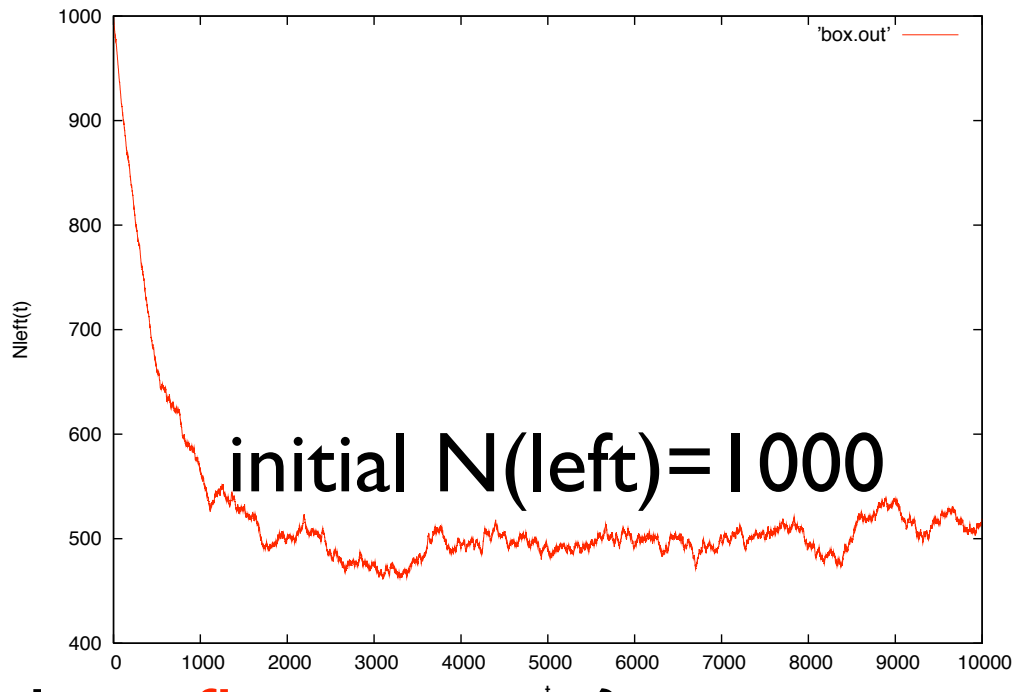
A simple example: non-interacting classical particles in a box (gas diffusion)





Approach to equilibrium with fluctuations

Stochastic fluctuations

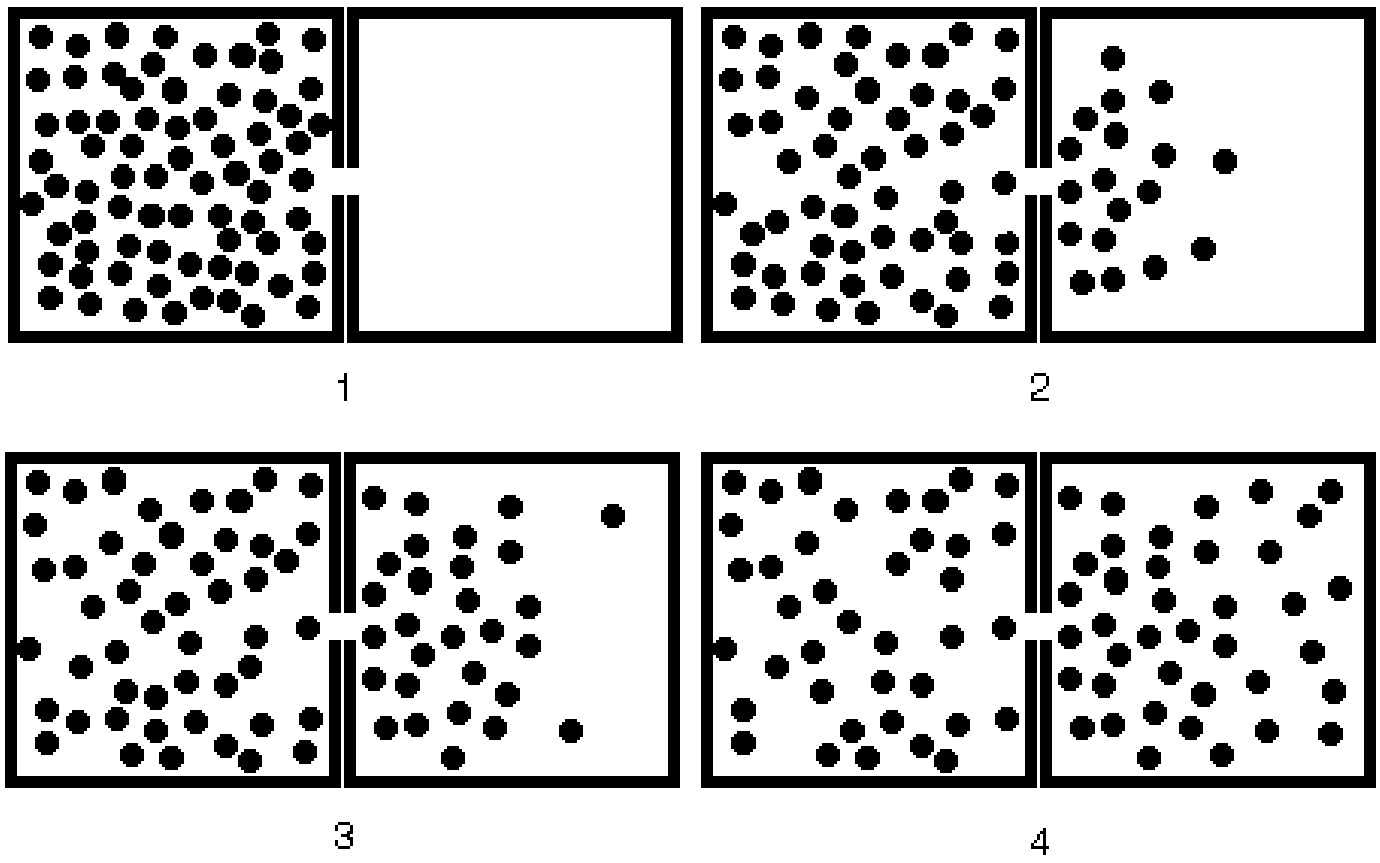


How to reduce fluctuations?

- more particles
- average over many simulation runs
- ...

What can we do with fluctuations?

Approach to equilibrium



macrostate: specified by the **number** of particles n on the left side;

microstate: specified by the **specific list** of the n particles on the left side

Macroscopic dynamics can also be studied exactly.
n_*left(t)* is a Markov chain with transition probability:

$$\begin{cases} P(n \to n-1) = \dfrac{n}{N} \\ P(n \to n+1) = 1 - \dfrac{n}{N} \end{cases}$$

(notes on Stat Mech by Nino Zanghi' - web source)

Equilibrium and entropy

$$\text{number of microstates} = \frac{N!}{n!(N-n)!} = \binom{N}{n} = \binom{N}{N-n}$$

The number of microstates for the "particle in a box" model with N=10.
The macrostate is specified by the number of particles on the left side, *n*.
The total number of microstates for N=10 is 2^{10}=1024

n	# of microstates	log(# of micr.)
0	1	0
1	10	2,3
2	45	3,81
3	120	4,79
4	210	5,35
5	252	5,53
6	210	5,35
7	120	4,79
8	45	3,81
9	10	2,3
10	1	0

⇦ the most "random"!

Equilibrium =
Maximum number of possible microstates =
Maximum entropy

(optional)

Entropy: Coincidence method

(S.K. Ma, J. Stat. Phys. 26, 221 (1981))

Equilibrium = Maximum entropy = Maximum number of possible microstates

Too much effort to enumerate all of them!

Alternative procedure (good for computing):
A system evolving in time will duplicate a microstate, before or later...
The longer it takes for duplication, the fewer are the microstates in the corresponding macrostate. Hence, the lower is the entropy.
Idea: measure the ratio of the number of pairs of duplicated microstates to the total number of possible pairs; entropy is the log of the inverse ratio.

E.g.: suppose as in the previous slide N=10, and the **macrostate n=1**; consider 20 different **microstates** labelled with the "name" of the particle:

8 7 5 10 7 2 4 6 2 10 3 4 3 9 6 5 2 9 2 4

Possible pairs: 20*(20-1)/2=190. Here: 6 pairs for particle "2"; 1 pair with particle "10" etc etc... Sum all of them: get 15.
Ratio = 15/190 , Entropy: $S \propto \log(190/15) \sim 2.5$

Remind the definition of entropy:

$$S = -k_B \sum_s P_s \ln P_s$$ in the canonical ensemble

$$S = k_B \log \Omega$$ in the microcanonical ensemble, where all the microstates corresponding to a macrostate have the same energy
(Ω is the number of microstates)

Metropolis method in the canonical ensemble and the simulated annealing

a general purpose global optimization algorithm
(Kirkpatrick S, Gelatt CD Jr, Vecchi MP
Science 220(4598), 671-80, 1983)

(more tomorrow - A. Marrazzo)

Metropolis and simulated annealing - I

- Stochastic search for global minimum. Monte Carlo optimization.

- The concept is based on the manner in which liquids freeze or metals recrystallize. Sufficiently high starting temperature and slow cooling are important to avoid freezing out in metastable states. A "cost function" is treated as the energy.

Metropolis and simulated annealing - II

- **Thermodynamic system at temperature T, energy E.**
- *Perturb configuration (generate a new one).*
- *Compute change in energy dE. If dE is negative the new configuration is accepted. If dE is positive it is accepted with a probability given by the Boltzmann factor : exp(-dE/kT).*

usual Metropolis procedure in the canonical ensemble

- *The process is repeated many times for good sampling of configuration space.*
- **then the temperature is slightly lowered and the entire procedure repeated, and so on, until a frozen state is achieved.**

Metropolis and simulated annealing - II

necessary:

- **Thermodynamic system at temperature T, energy E.**
- *Perturb configuration (generate a new one).* ← a move generation strategy
- *Compute change in energy dE. If dE is negative the new configuration is accepted. If dE is positive it is accepted with a probability given by the Boltzmann factor : exp(-dE/kT).*

usual Metropolis procedure in the canonical ensemble

- *The process is repeated many times for good sampling of configuration space.* ← a freezing schedule
- **then the temperature is slightly lowered and the entire procedure repeated, and so on, until a frozen state is achieved.** ← a stopping criterion

Example

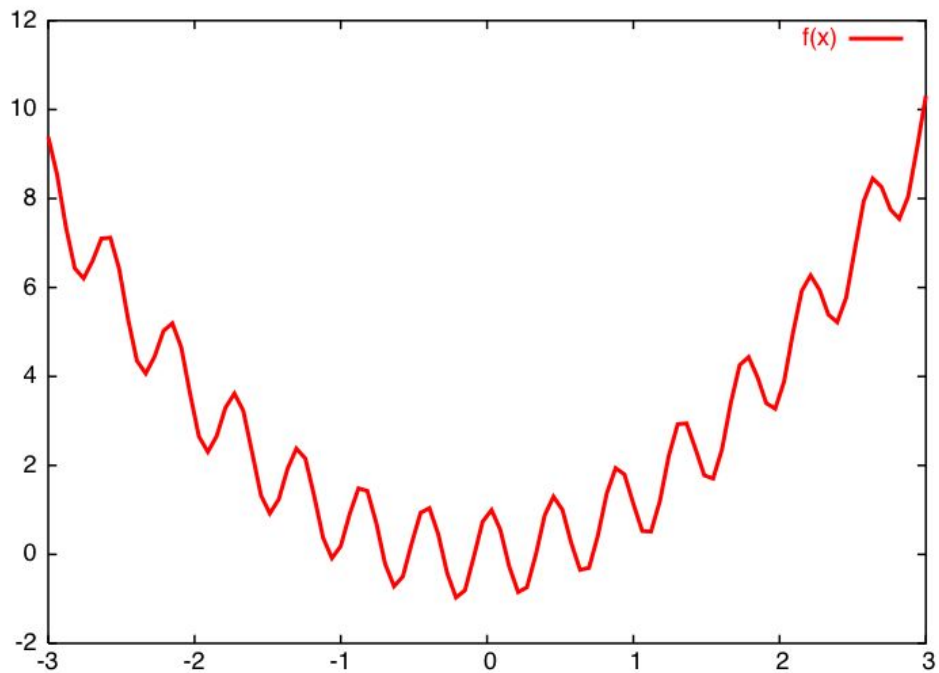
in **`simulated_annealing.f90:`**

minimization of

`f(x)=(x+0.2)*x+cos(14.5*x-0.3)`

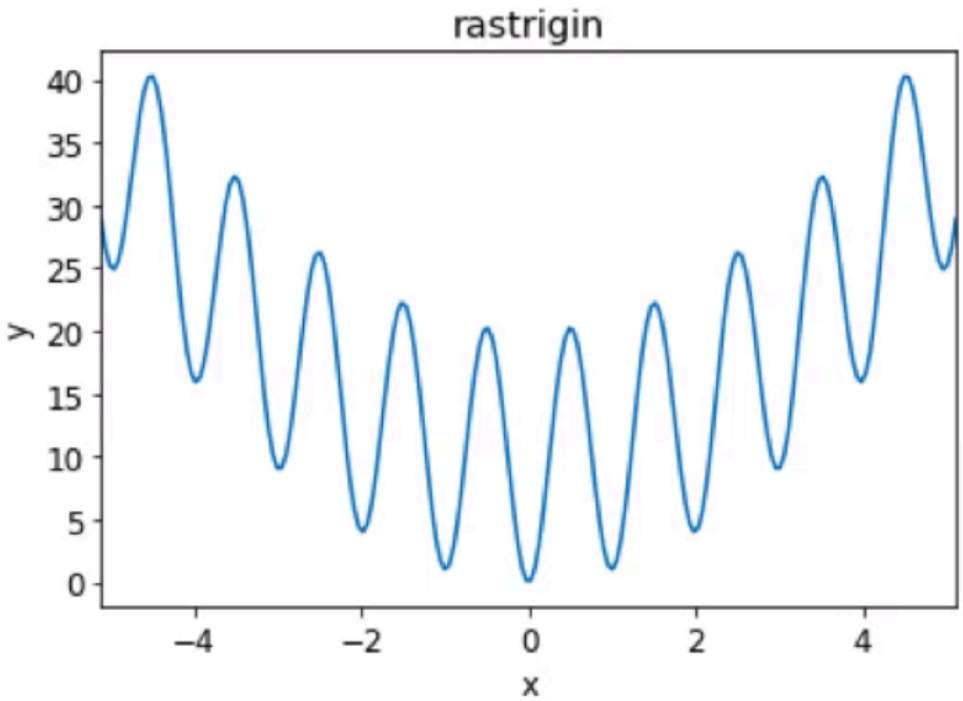
considered as an energy function and

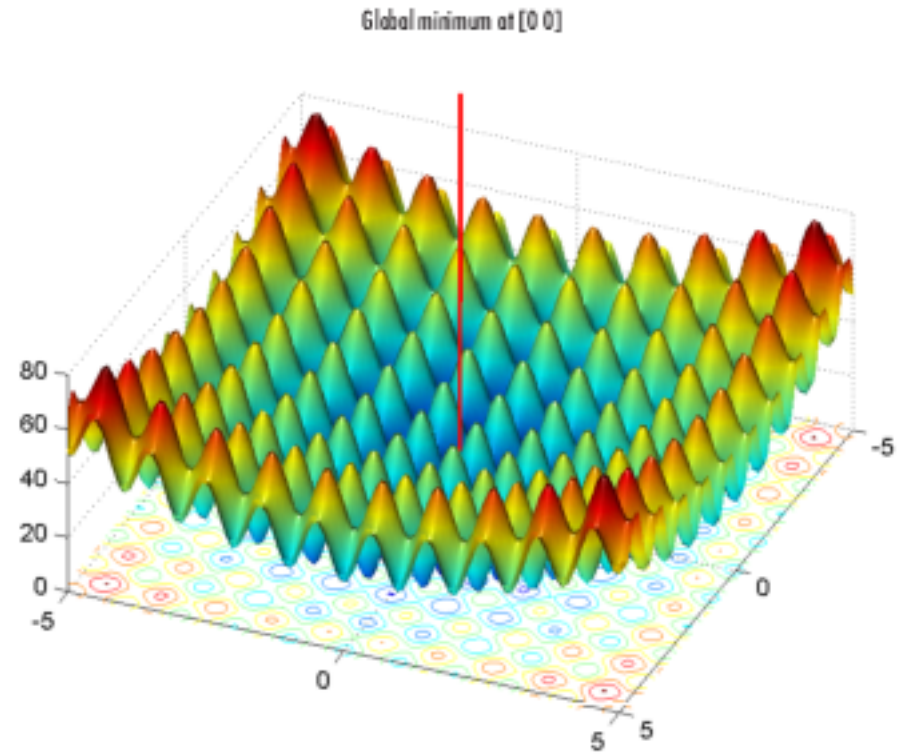
using a fictitious temperature



***Rastrigin function*:**

- non-convex *function* used as a performance test problem for optimization algorithm
- typical example of non-linear multimodal *function;*
- first proposed by *Rastrigin* as a 2-dimensional *function;* later generalized by Rudolph.





$$f(\boldsymbol{x}) = nA + \sum_{i=1}^{n}[x_i^2 - Acos(2\pi x_i)]$$

$i=1,\ldots n:$ independent variables

Function to be minimized: **f(x)** ; Starting point: **x, fx=f(x)**

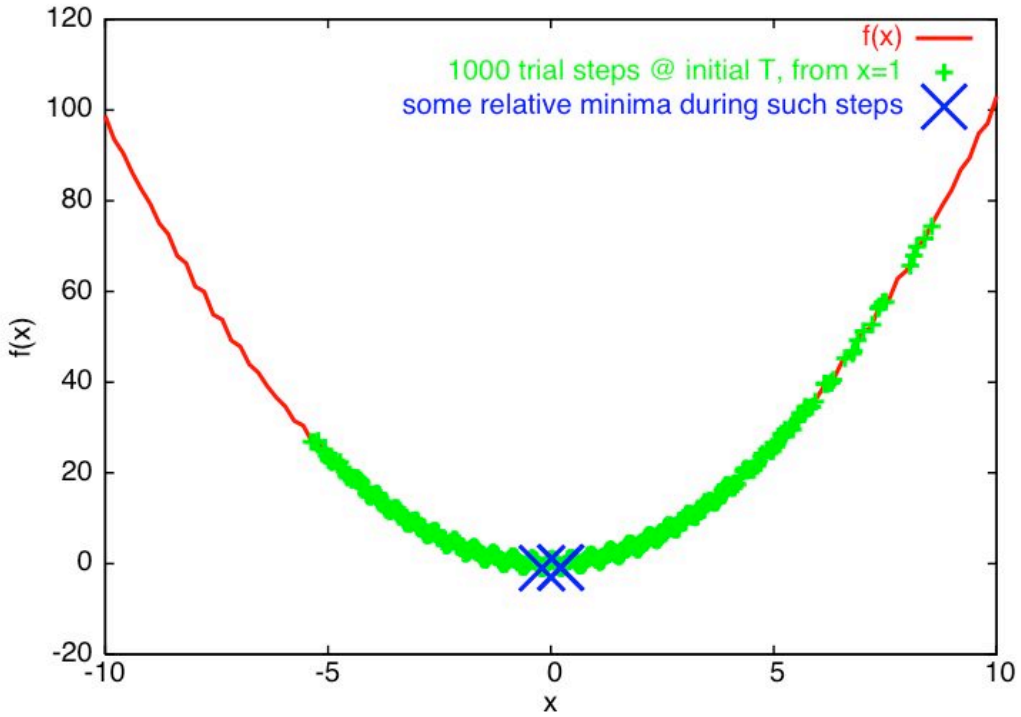
	initial (high) temperature:	**temp**
Annealing schedule:	annealing temperature reduction factor:	**tfactor (<1)**
	number of steps per block:	**nsteps**

'ad hoc' parameter for trial move: **scale**

```
DO WHILE (temp > 1E-5) ! anneal cycle

  DO istep = 1, nsteps
    CALL RANDOM_NUMBER(rand) ! generate 2 random numbers; dimension(2) :: rand
    x_new = x + scale*SQRT(temp)*(rand(1) - 0.5) ! stochastic move
    fx_new = func(x_new) ! new object function value
    IF (EXP(-(fx_new - fx)/temp) > rand(2)) THEN ! success, save
      fx = fx_new
      x = x_new
    END IF
    IF (fx < fx_min) THEN
      fx_min = fx
      x_min = x
      PRINT '(3ES13.5)', temp, x_min, fx_min
    END IF
  END DO

  temp = temp * tfactor ! decrease temperature
END DO
```



initial T: 10 (K_B units)
initial x: 1.000000
initial f(x): 1.137208

final T: 2.50315E-01
final x: -1.95067E-01
final f(x):-1.00088E+00