993SM - Laboratory of Computational Physics week VIII November 15, 2024

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1. **Sampling physical quantities with gaussian distribution: direct sampling and Metropolis sampling**

Consider the quantum harmonic oscillator and its ground state. The exact solution and the expectation values of kinetic, potential and total energy are know analytically, and can be used to compare the numerical results.

$$\langle E_{pot} \rangle = \frac{\langle \psi | \frac{1}{2} x^2 | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int \frac{1}{2} x^2 |\psi(x)|^2 dx}{\int |\psi(x)|^2 dx}$$

$$\langle E_{kin} \rangle = \frac{\langle \psi | -\frac{1}{2} \nabla^2 | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int \left(\frac{1}{4\sigma^2} - \frac{x^2}{8\sigma^4} \right) |\psi(x)|^2 dx}{\int |\psi(x)|^2 dx}$$

TO DO:

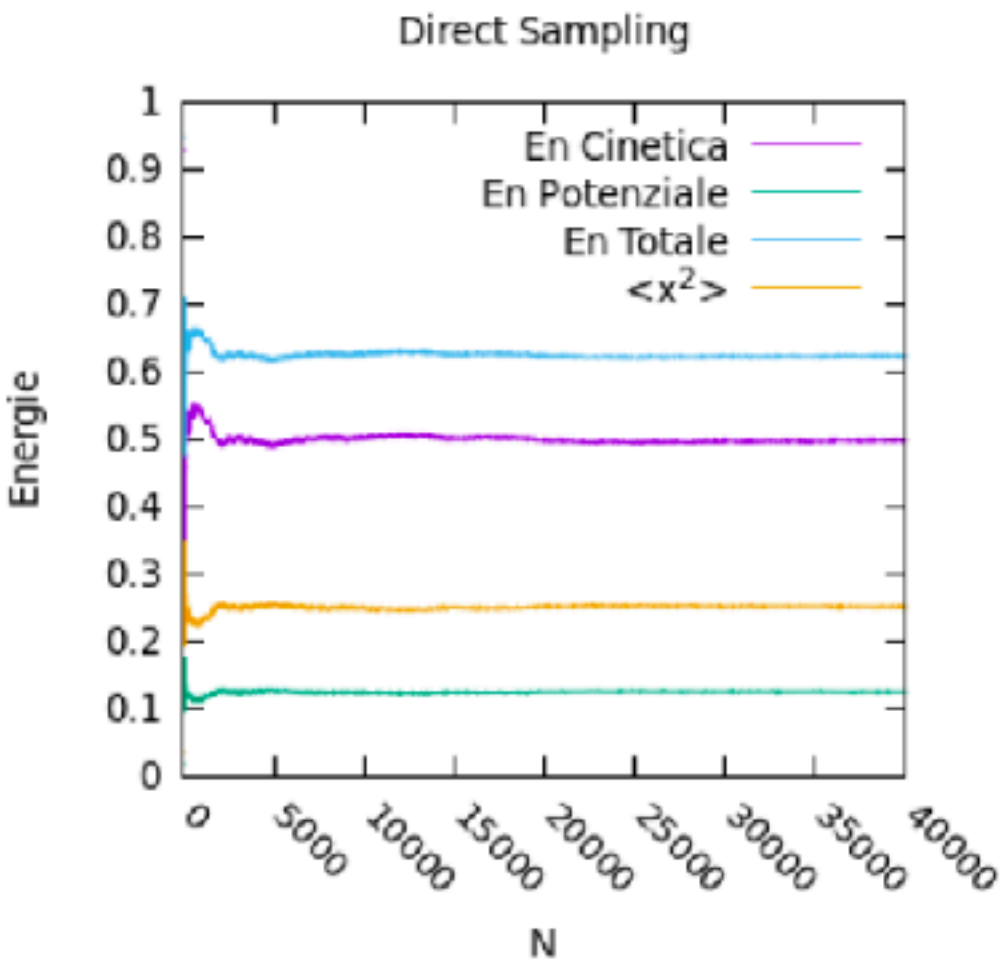
Consider a wavefunction (not necessarily the ground state) : $\psi(x) = \exp(-x^2/4\sigma^2)$

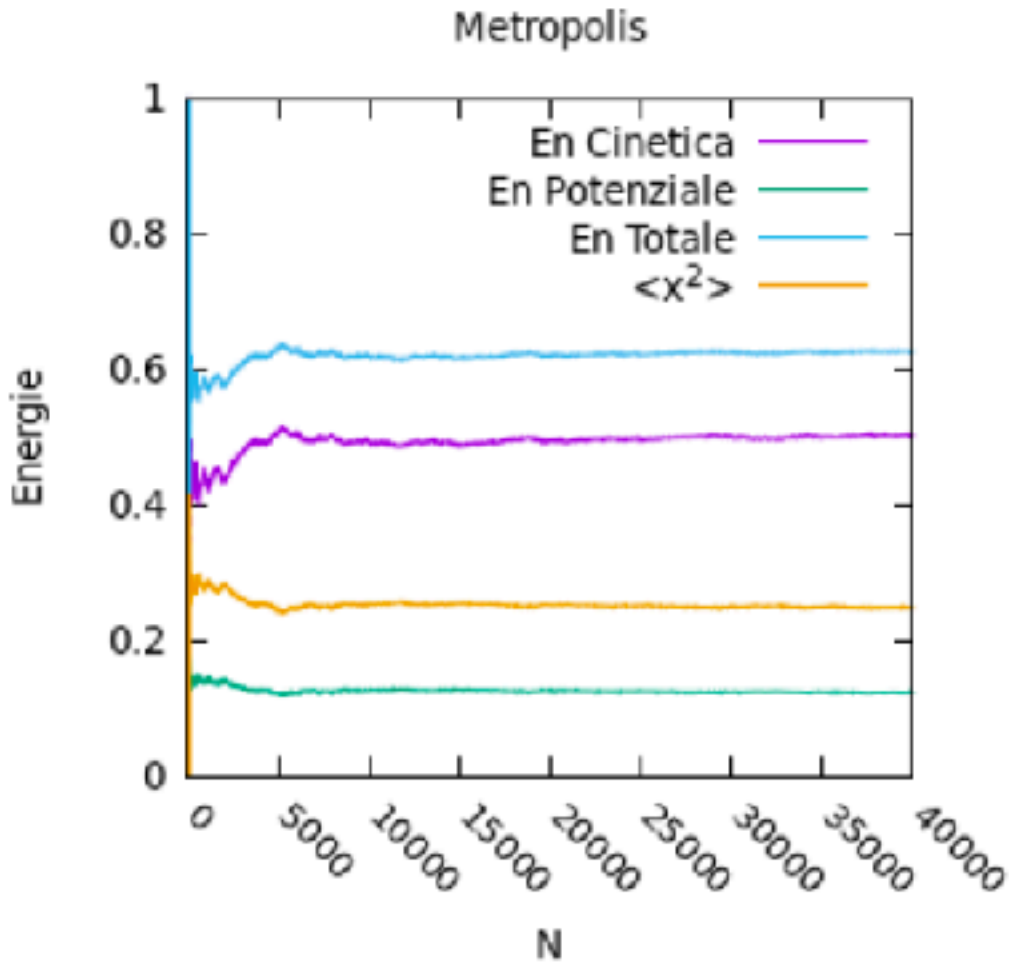
Generate random numbers *x* with a distribution proportional to $|\psi(x)|^2$ calculated on such points *x* and accumulate the quantities to be integrated,

$$\left(\frac{1}{2} x^2 \text{ and } \left(\frac{1}{4\sigma^2} - \frac{x^2}{8\sigma^4} \right) \right)$$

For $\sigma = 1$, we expect : $\langle E_{pot} \rangle = \frac{1}{2}\sigma^2 = 0.5, \quad \langle E_{kin} \rangle = \frac{1}{8\sigma^2} = 0.125$

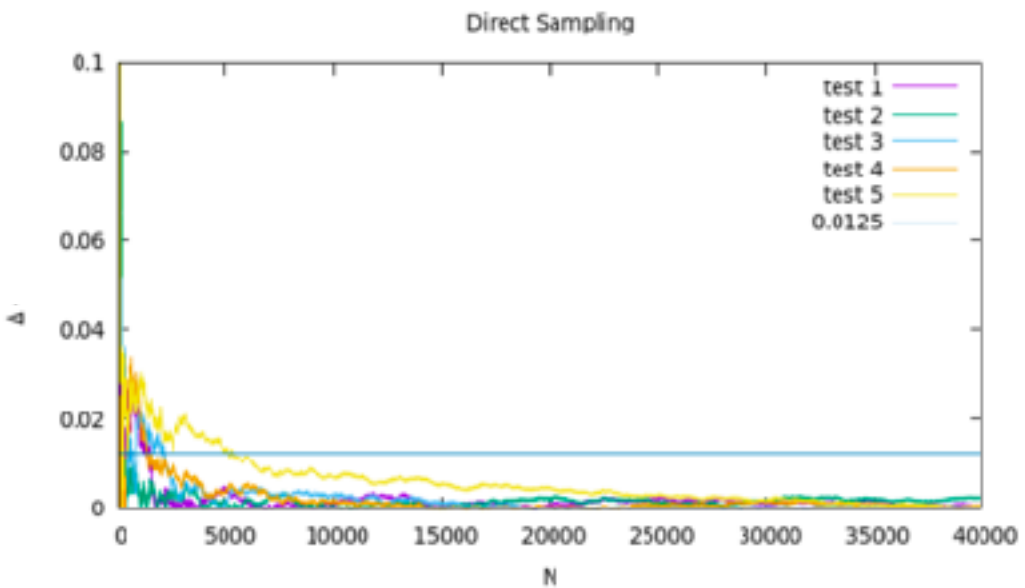
convergence w.r.t the number of steps (one seed)

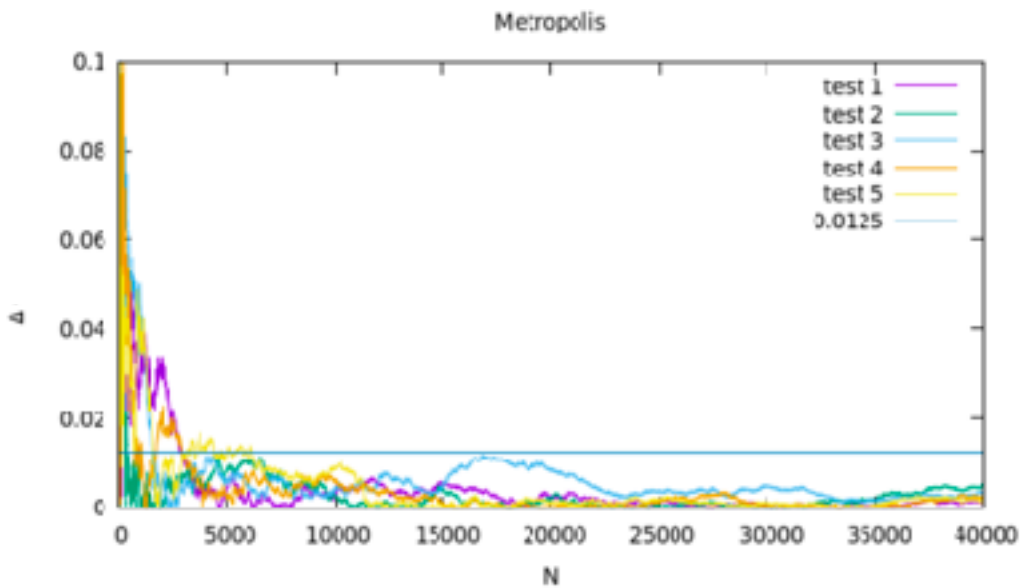




$$\Delta = \left| \frac{\langle x^2 \rangle_{calc} - \langle x \rangle_{calc}^2}{\sigma^2} - 1 \right|$$

convergence w.r.t the number of steps (different seeds)





Correlations - Metropolis algorithm

2. Correlations

Calculate the autocorrelation function $C(j) = \dfrac{\langle x_i x_{i+j}\rangle - \langle x_i\rangle^2}{\langle x_i^2\rangle - \langle x_i\rangle^2}$ for a sequence or random numbers with a gaussian distribution using the Metropolis method, with different values of δ/σ: 1, 5, 10, 25, 50.

In gauss_metropolis.f90 , δ is defined as the full amplitude of the possible displacement:

```
xp = x + delta * (rnd-0.5_dp)
```

Correlations - Metropolis algorithm

Random number sequence generated with the Metropolis algorithm and different values of δ/σ

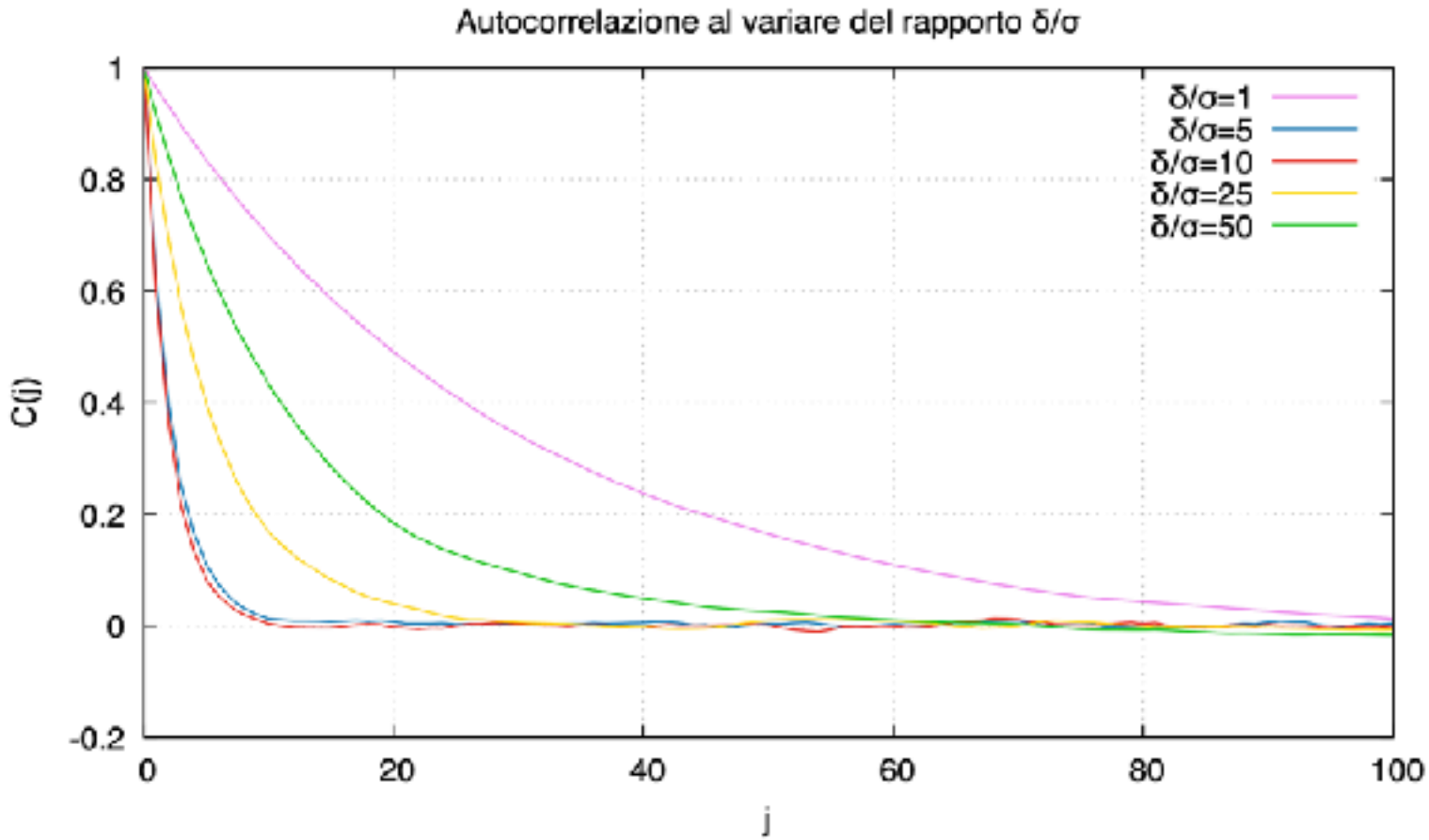
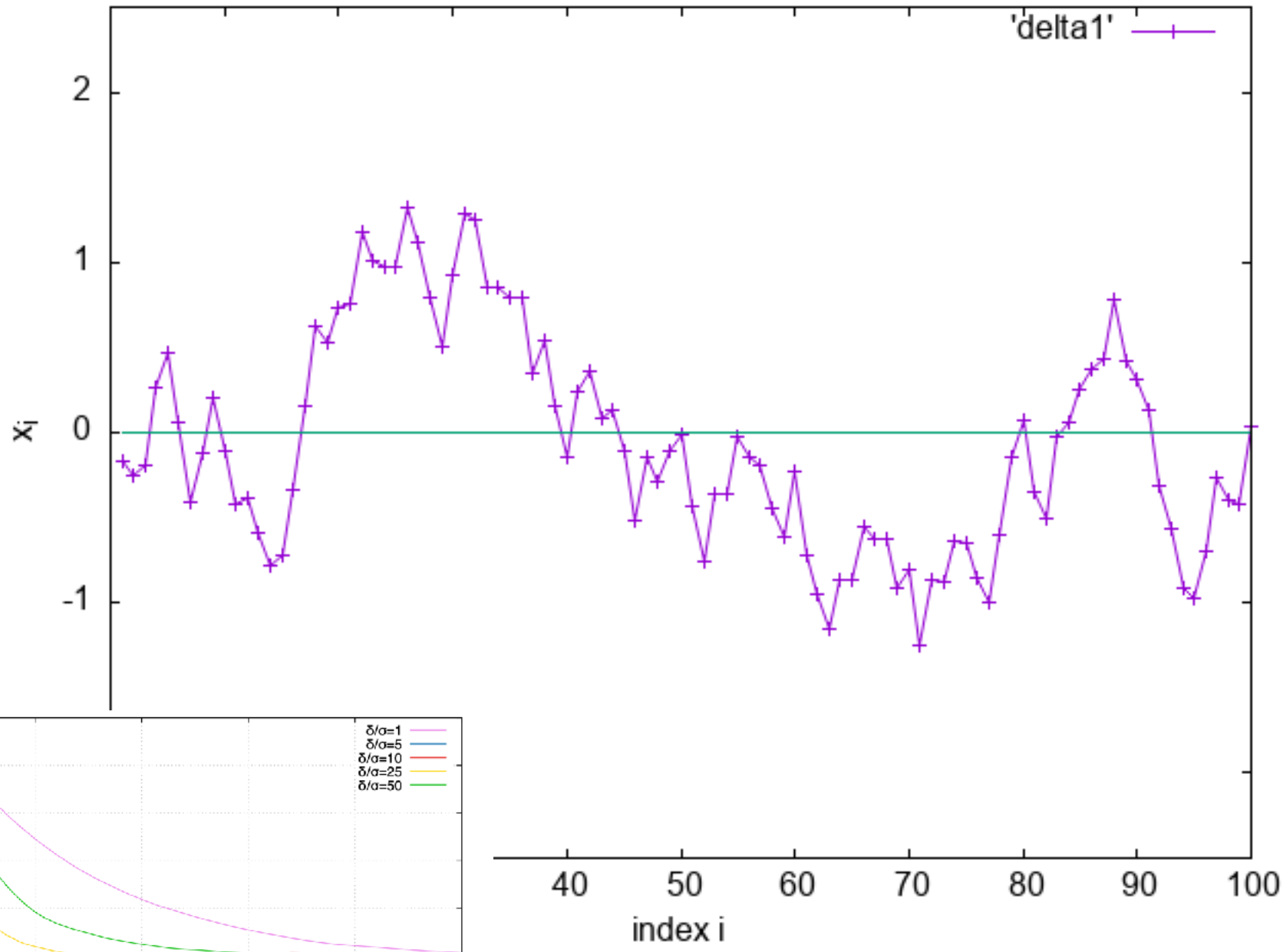
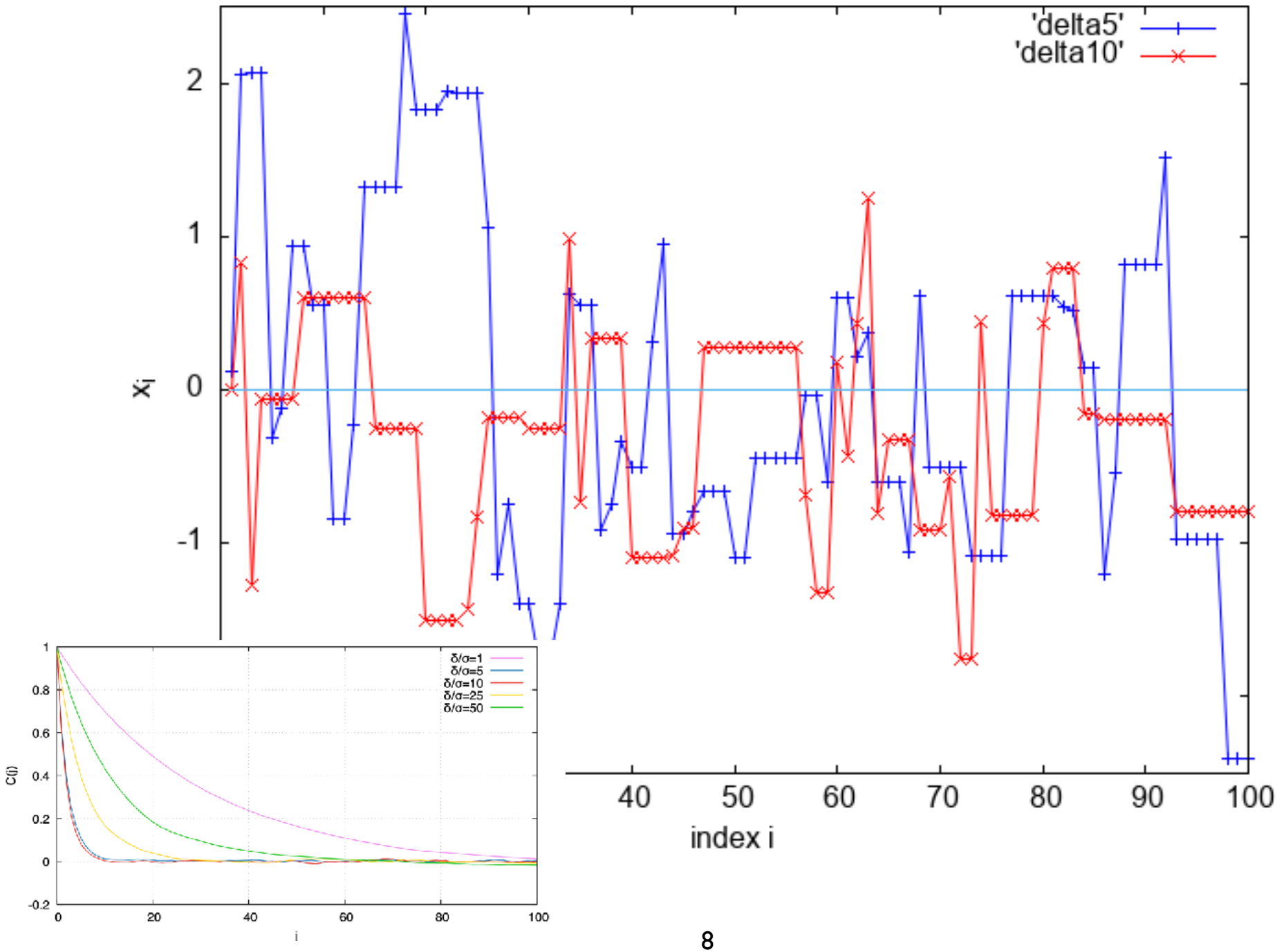


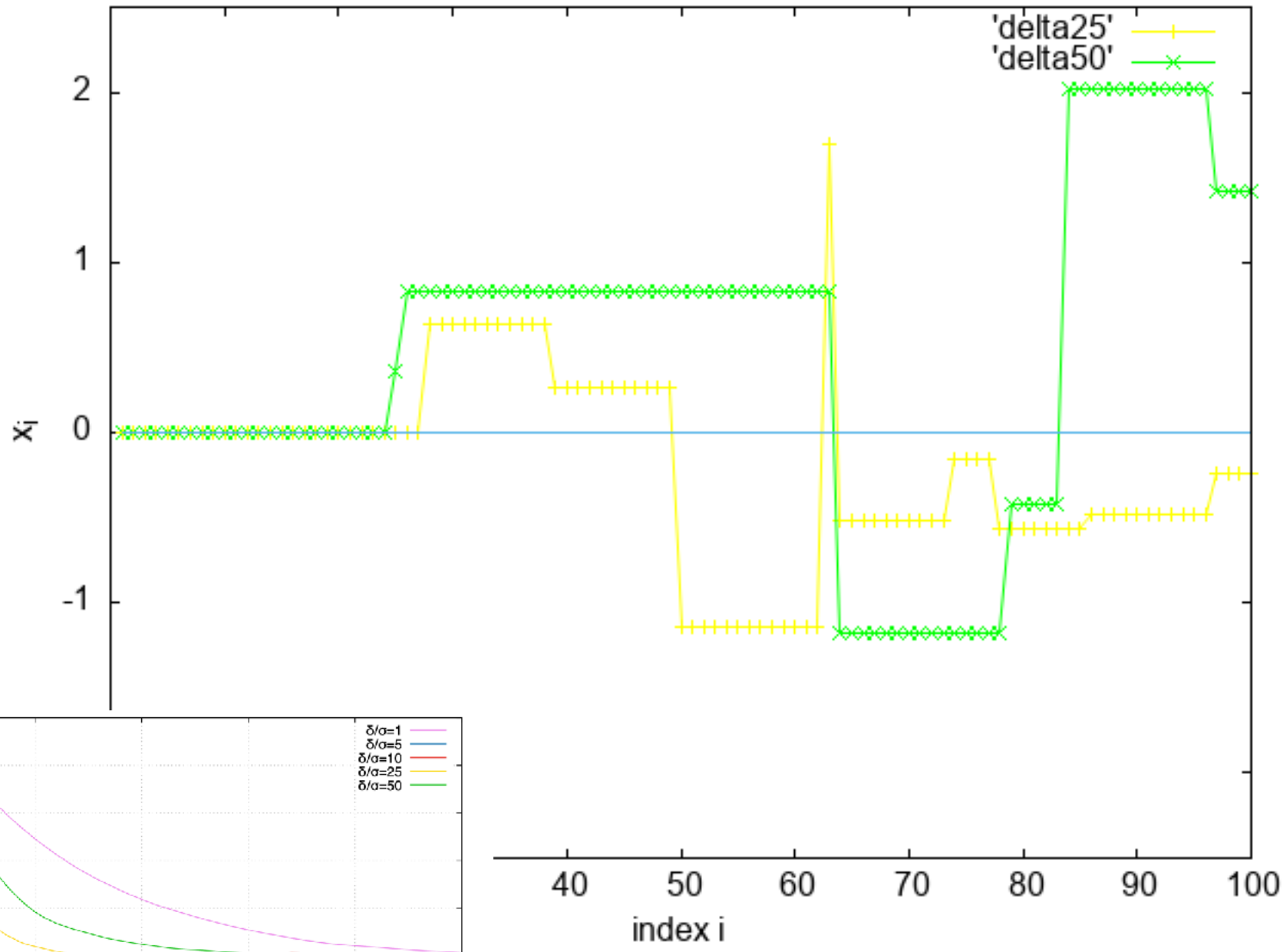
Figura 11: Andamento della funzione di autocorrelazione tra i punti generati con l'algoritmo Metropolis al variare di alcuni valori del parametro δ/σ

for values of the parameter δ/σ that are too low (< 5) or too high (> 10) the autocorrelation function decays very slowly: to effectively generate random numbers that are not correlated with each other it is therefore necessary to choose a ratio δ/σ such that $5 \leq \delta/\sigma \leq 10$, which corresponds to the acceptance ratio range between ≈ 1/3 and ≈ 1/3


'delta1'
2
1
0
-1
x_i
40
50
60
70
80
90
100
index i

δ/σ=1
δ/σ=5
δ/σ=10
δ/σ=25
δ/σ=50
C(i)
1
0.8
0.6
0.4
0.2
0
-0.2
0
20
40
60
80
100
i


'delta5'
'delta10'
x_i
index i
δ/σ=1
δ/σ=5
δ/σ=10
δ/σ=25
δ/σ=50
C(i)
i


'delta25'
'delta50'
2
1
0
-1
x_i
40
50
60
70
80
90
100
index i

δ/σ=1
δ/σ=5
δ/σ=10
δ/σ=25
δ/σ=50
C(i)
1
0.8
0.6
0.4
0.2
0
-0.2
0
20
40
60
80
100
i

Metropolis algorithm in the canonical ensemble

3. **Verification of the Boltzmann distribution**

We can verify directly that the Metropolis algorithm yields the Boltzmann distribution. We consider **a single classical particle** in one dimension in equilibrium with a heath bath (*canonical ensemble*). We fix therefore the temperature T, which labels a *macrostate*. The energy E can vary according to the particular *microstate* (in this particular case, it is enough to label a microstate, a part from the sign of the velocity).

Metropolis algorithm in the canonical ensemble

Reminder: the detailed balance in the canonical ensemble is verified by:

$$T(i \to j) = \min(1, e^{-\beta \Delta E}) \quad \text{(Metropolis algorithm)},$$

where $\Delta E = E_j - E_i$.

We can prove empirically that with this T(i⟶j)
Metropolis algorithm generates states with Boltzmann distribution

1 free particle in 1D: Energy: $E = \frac{1}{2} m v^2$
in this case, velocity or energy labels a microstate

(the energy with a factor of 2 , due to +/- sign of v);

Different microstates are generated by **random variations of the velocity** and we accept/reject with Metropolis => obtain:

1) the average <E>
2) P(E)

Boltzmann distribution in the canonical ensemble

ideal classical 1D gas

A particle moving randomly has in each direction a distribution of the component of the velocity:

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_B T} \qquad (1)$$

$$\langle v_x^2 \rangle = \int_{-\infty}^{+\infty} v_x^2 f(v_x) dv_x = \frac{k_B T}{m} \qquad (2)$$

In 1D:

$$f(v)2dv = P(E)dE$$

that gives:

$$P(E) = \frac{1}{(\pi k_B T)^{1/2}} \frac{1}{\sqrt{E}} e^{-E/k_B T}$$

In 3D:

$$P(E) = \frac{2}{\sqrt{\pi}} \frac{1}{(k_B T)^{3/2}} \sqrt{E} \exp\left(-\frac{E}{k_B T}\right) \qquad (3D)$$

Boltzmann distribution

$$T = 1 \rightarrow \langle E \rangle (expected) = 0.5 \qquad (m = 1)$$

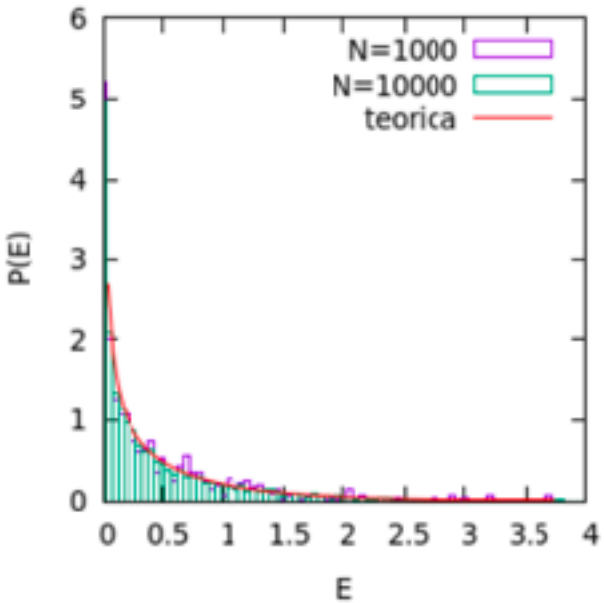


Figura 4.1: Distribuzione dell'energia

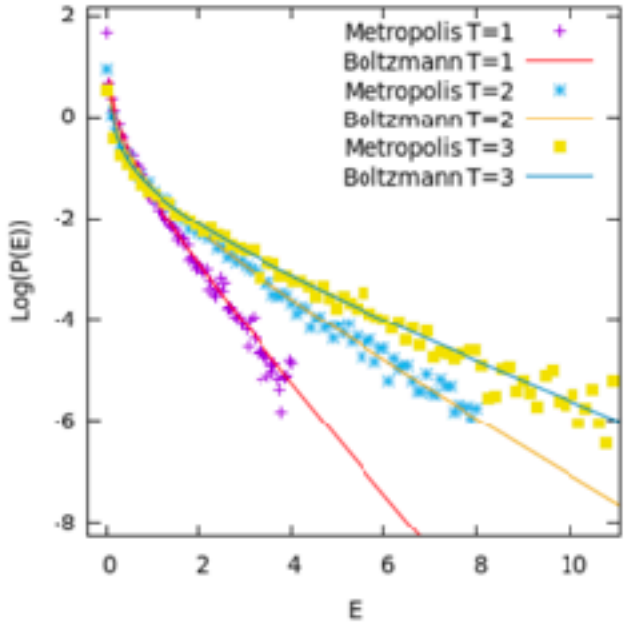


Figura 4.2: Distribuzione a varie temperature, N=10000

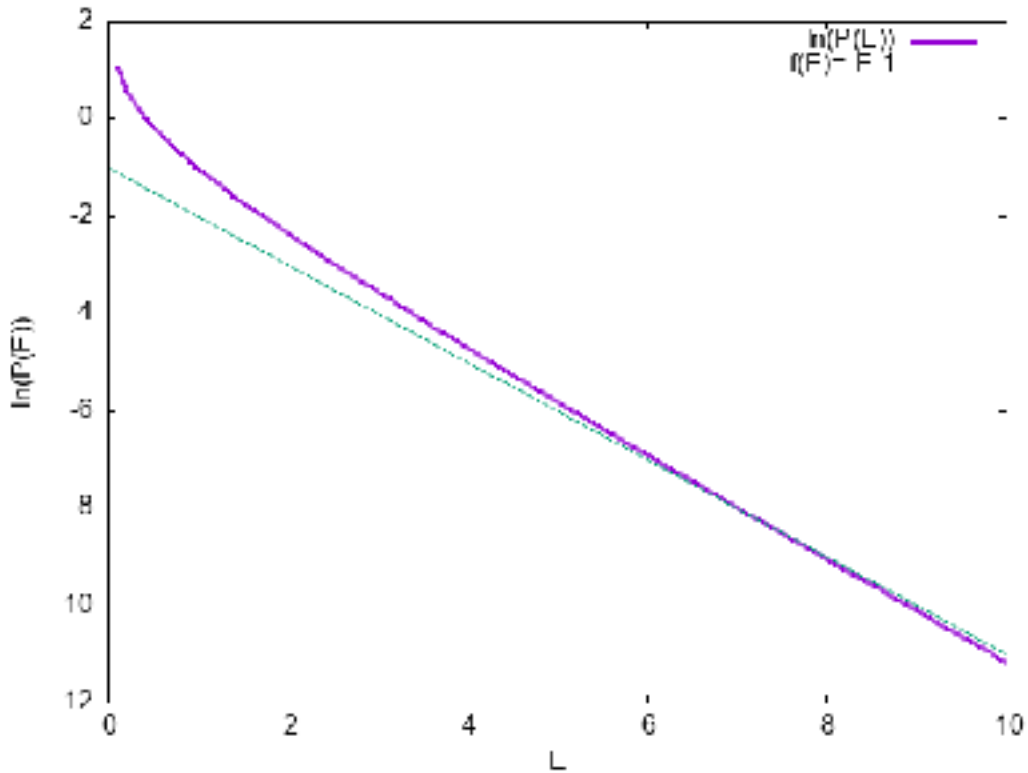
Un numero di 1000 step è sufficiente per un'accuratezza dell'1% su <E> e del 10% su <v>, tuttavia se vogliamo riprodurre la distribuzione servono molti piu' punti

Boltzmann distribution

1D: $$P(E) \propto \frac{1}{\sqrt{E}} e^{-\beta E}$$

T=1 here

$$\Rightarrow ln(P(E)) \propto -\frac{1}{2} ln(E) - \beta E$$



Boltzmann distribution for many particles

many particles: Energy: $E = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2$

in this case, the energy is NOT a label of a microstate

(there are several microstates with the same total energy)

Note: the energy histogram is NOT the distribution of microstates!

$$P(E) = \sum_{\substack{states\ s \\ with\ E_s = E}} P_s \quad \text{with} \quad P_s = \frac{1}{Z} e^{-\beta E_s}$$

$$P(E) \propto= e^{\frac{-(E-\langle E \rangle)^2}{2\sigma^2}} \quad \text{with } \langle E \rangle \text{ average over all the microstates}$$

What is P(E)? (exercise)

Boltzmann distribution for many particles

Possible approach n. 1: 1 MC step corresponds to a loop on all the particles, the configs in the Markov chain can differ just by a single particle value of velocity

```
real, public, dimension(:), allocatable :: P,vel,E
```

```
subroutine Metropolis()
  real :: dv,vtrial,de,rnd
  integer::i

 do i= 1,N
  call random_number(rnd)
  E(i)      = 0.5 * vel(i) * vel(i)
  dv = (2*rnd - 1) * dvmax ! trial variation for v, within dvmax
  vtrial = vel(i) + dv                          ! trial velocity v
  de = 0.5 * (vtrial*vtrial - vel(i)*vel(i))   ! corresponding ΔE
  call random_number(rnd)
  if (de >= 0.0) then
     if ( exp(-beta*de) < rnd ) return ! trial step not accepted
  end if
  vel(i) = vtrial
  accept = accept + 1
  E(i)= E(i) + de
end do
end subroutine Metropolis
```

E is an array labelled by the index of the MC step for the purpose of accumulate it at the end

Boltzmann distribution for many particles

Possible approach: 1 MC step corresponds to a loop on all the particles,
the configs in the Markov chain can differ just by a single particle value of velocity

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     if ( exp(-beta*de) < rnd ) return ! trial step not accepted
  end if
  vel(i) = vtrial
  accept = accept + 1
  E(i)= E(i) + de
end do
end subroutine Metropolis
```

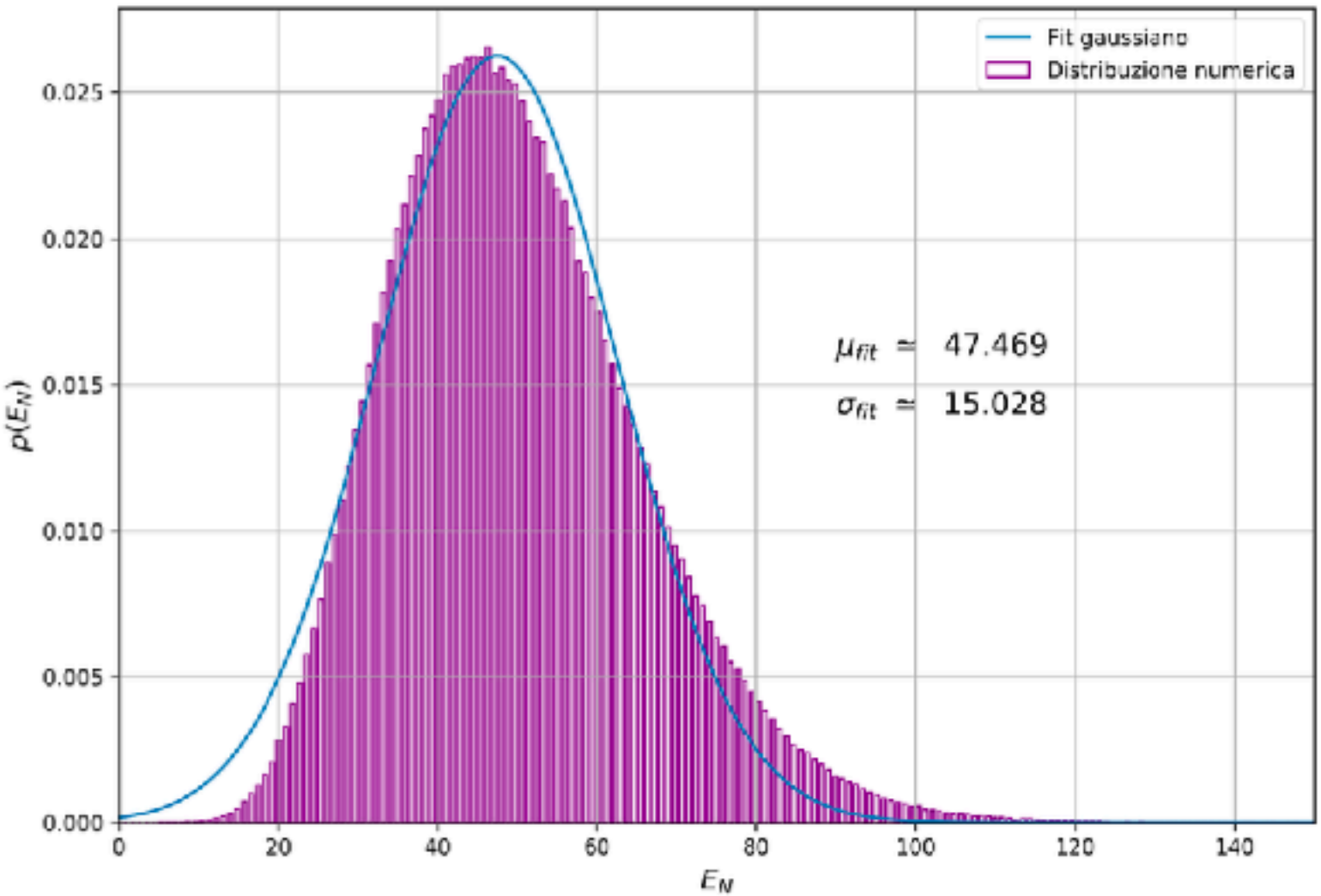
E is an array labelled by the index of the MC step
for the purpose of accumulate it at the end
but we can also avoid

Boltzmann distribution for many particles

Alternative approach:
1 MC step corresponds to a trial move on a single particle
=> drawback: the length of the trajectory is system size dependent

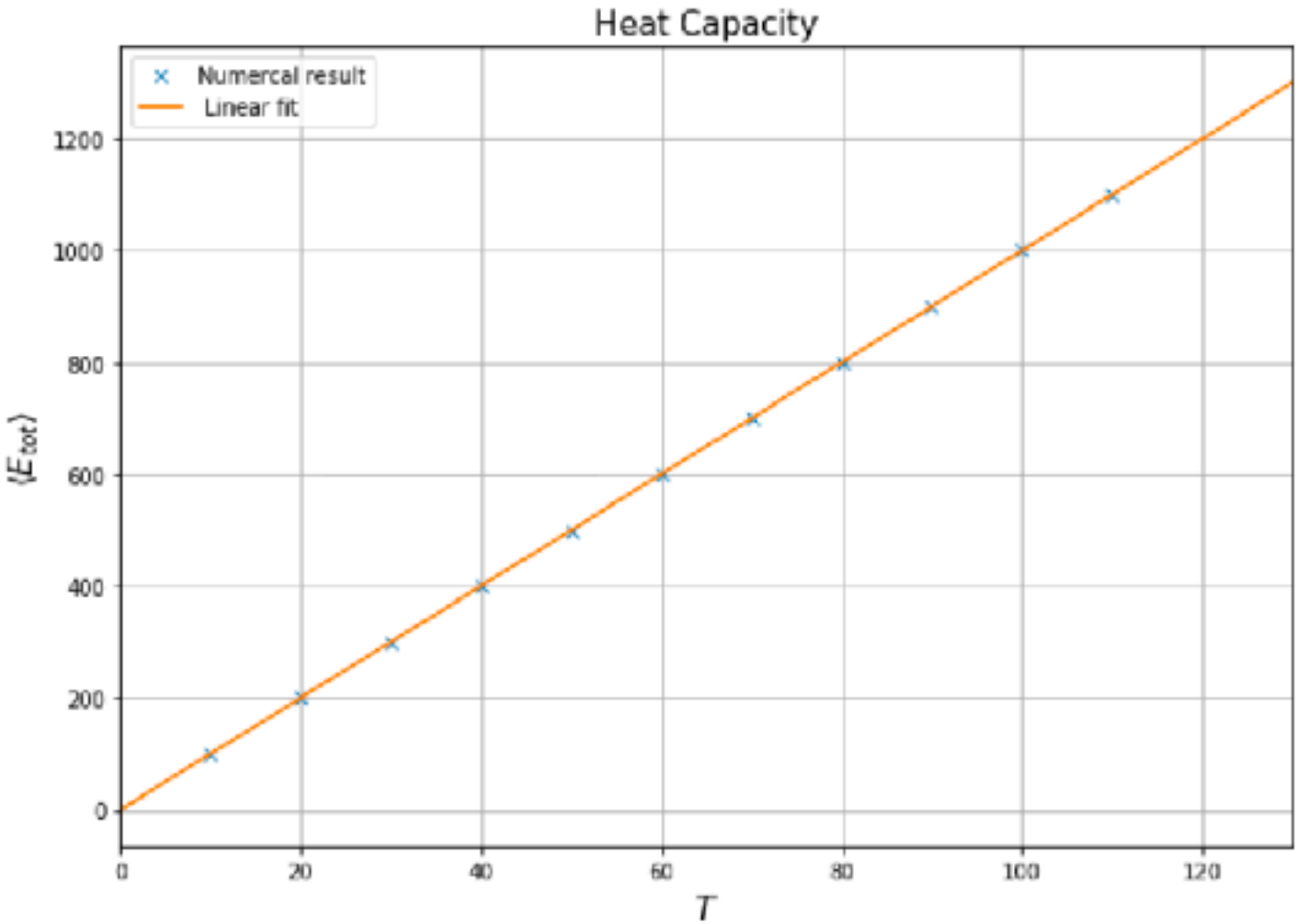
Alternative approach:
1 MC step corresponds to a loop on all the particles,
a new configuration in the Markov chain is considered after the loop on all the particles

Boltzmann distribution for many particles



N=20
T=50

Boltzmann distribution



$$E_{tot} = \frac{1}{2} N k_B T$$

$$C = \frac{\partial \langle E_{tot} \rangle}{\partial T}$$