

## Outline of Lectures 4-5

- Monte Carlo method for integration
  - **Errors in Monte Carlo vs. methodical sampling**
  - **Monte Carlo evaluation of statistical-mechanics integrals**
  - **Importance sampling**
- Metropolis Monte Carlo
  - **Importance sampling and detailed balance condition**
  - **Metropolis Monte Carlo algorithm**
- Examples of application of Metropolis Monte Carlo
- Brief review of kinetic Monte Carlo
- Areas of application of Molecular dynamics, Metropolis and kinetic Monte Carlo

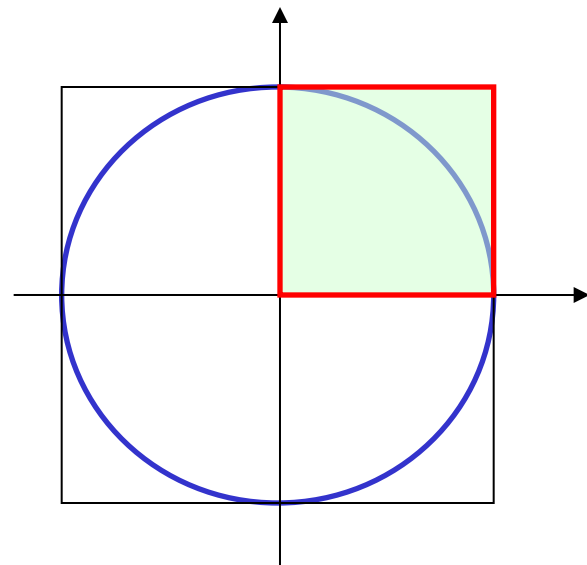


## Monte Carlo Calculation of $\pi$

Let us illustrate the use of the MC technique as a method of integration and let us begin with a simple geometric MC experiment which calculates the value of  $\pi$  based on a "hit and miss" integration.

```
x=(random #)  
y=(random #)  
R= (x2 + y2)1/2  
if R < 1 then hits=hits+1.0
```

$$\pi = \frac{4 N_{\text{hit}}}{N_{\text{shot}}}$$





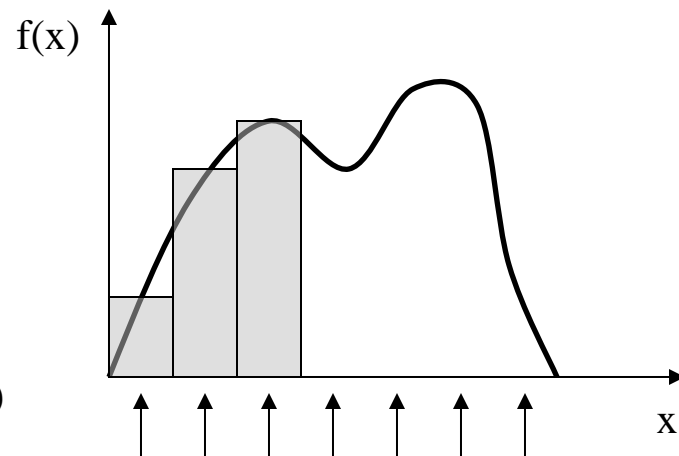
# Monte Carlo integration

**Conventional approaches:** rectangle, trapezoidal, Simpson's methods ...

$$I = \int_a^b f(x) dx$$

Quadrature formula:

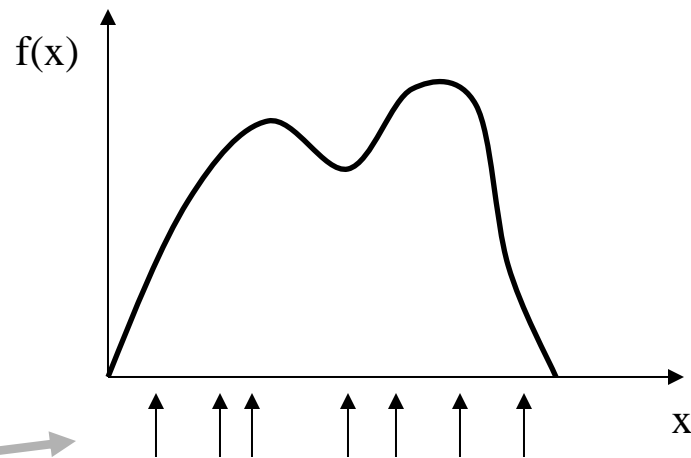
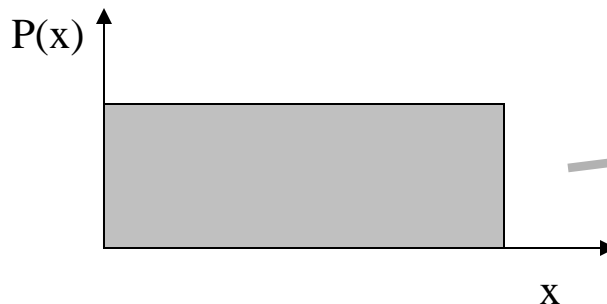
$$I \approx \Delta x \sum_{i=1}^n f(x_i) = \frac{b-a}{n} \sum_{i=1}^n f(x_i)$$



$n$  uniformly separated points

**Monte Carlo Integration:** same quadrature formula, different selection of points

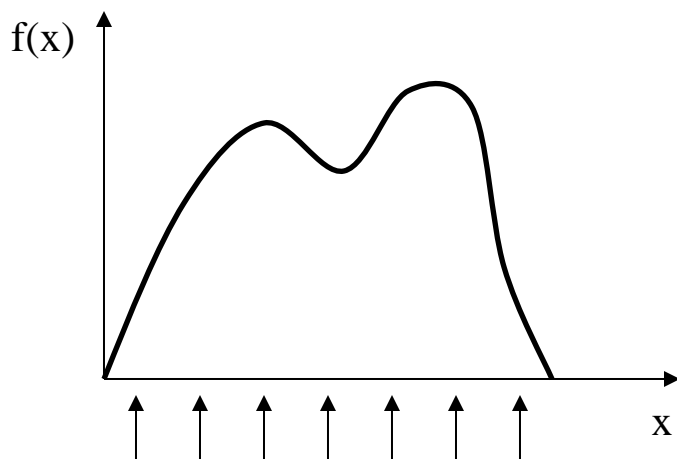
$$I \approx \frac{b-a}{n} \sum_{i=1}^n f(x_i)$$



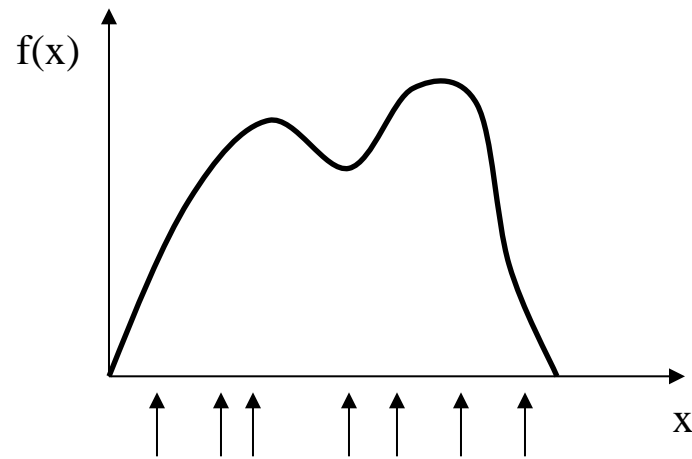
$n$  points selected at random from uniform distribution  $P(x)$



## Errors in Monte Carlo vs. methodical sampling



Methodical approach:  $\delta I \sim \Delta x^2 \sim n^{-2}$  for trapezoidal rule



Monte Carlo approach:  $\delta I \sim n^{-1/2}$  – error is purely statistical

For one-dimensional integrals, Monte Carlo error vanishes slower with increasing number of points,  $\mathbf{n}$ , and methodical approach is more efficient.

As dimension of the integral,  $\mathbf{d}$ , increases, Monte Carlo becomes more efficient.

Methodical approach:  $\delta I \sim \Delta x^2 \sim n^{-2/d}$  e.g., in 3D to have the same  $\Delta x$  as in 1D we need  $n^3$  points.

Monte Carlo approach:  $\delta I \sim n^{-1/2}$

**Monte Carlo “wins” at  $d > 4$**



# Monte Carlo evaluation of statistical-mechanics integrals

Why are we interested in integration?

Ensemble average of quantity  $A(\mathbf{r}, \mathbf{p})$  can be calculated for a given distribution function. For NVT ensemble we have distribution function  $\rho(\mathbf{r}, \mathbf{p})$ ,

$$\rho(\vec{r}^N, \vec{p}^N) = \frac{1}{Z} \exp \left( - \frac{E(\vec{r}^N, \vec{p}^N)}{kT} \right) d\vec{r}^N d\vec{p}^N$$

$$\langle A(\vec{r}^N, \vec{p}^N) \rangle = \frac{1}{Z} \int A(\vec{r}^N, \vec{p}^N) \exp \left( - \frac{E(\vec{r}^N, \vec{p}^N)}{kT} \right) d\vec{r}^N d\vec{p}^N$$

Energy can always be expressed as a sum of kinetic and potential contributions. The contribution of the kinetic part is trivial and we can consider integral in only configurational  $3N$  dimensional space, where  $Z$  is configurational integral.

$$\langle A(\vec{r}^N) \rangle = \frac{1}{Z} \int A(\vec{r}^N) \exp \left( - \frac{U(\vec{r}^N)}{kT} \right) d\vec{r}^N \quad Z = \int \exp \left( - \frac{U(\vec{r}^N)}{kT} \right) d\vec{r}^N$$



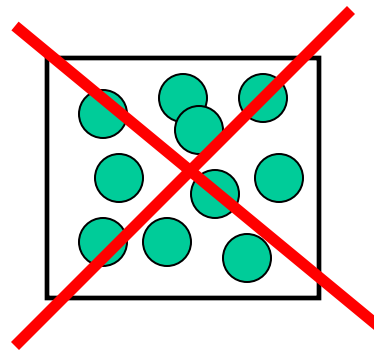
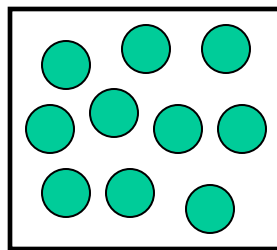
## Monte Carlo evaluation of statistical-mechanics integrals

$$\left\langle A(\vec{r}^N) \right\rangle = \frac{1}{Z} \int A(\vec{r}^N) \exp \left( - \frac{U(\vec{r}^N)}{kT} \right) d\vec{r}^N$$

$$Z = \int \exp \left( - \frac{U(\vec{r}^N)}{kT} \right) d\vec{r}^N$$

Statistical-mechanics integrals typically have significant contributions only from very small fractions of the  $3N$  space. For example for hard spheres contributions are coming from the areas of the configurational space where there are no spheres that overlap:

$$\exp \left( - \frac{U(\vec{r}^N)}{kT} \right) \neq 0$$



***Random sampling of the configurational space is highly inefficient.***

We have to restrict the sampling to the areas of space contributing to the integral – ***concept of importance sampling.***

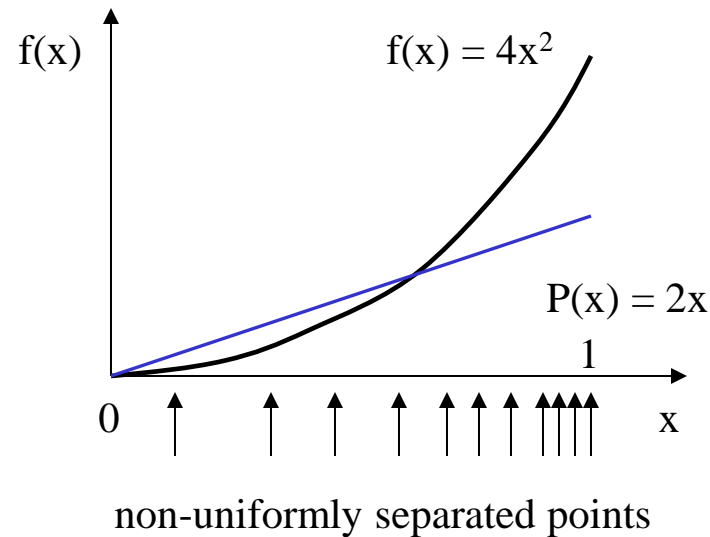


## Importance sampling

We want to have more points in the region from where integral is getting its greatest contributions.

$$I = \int_0^1 4x^2 dx$$

Contribution to the integral is coming from the region near  $x = 1$ . We want to have more points there!



We can go from even distribution of random points to a non-uniform distribution, for example linear dependence from  $x$ :  $P(x) = 2x$ .

To evaluate the importance-sampled integral let us consider rectangle-rule quadrature with unevenly spaced points/measurements.

$$I \approx \sum_{i=1}^n f(x_i) \Delta x_i \quad \Delta x_i = \frac{b-a}{n} \frac{1}{P(x_i)} \quad \text{where } \Delta x_i \text{ is spacing between points.}$$

$$I \approx \frac{b-a}{n} \sum_{i=1}^n \frac{f(x_i)}{P(x_i)} \quad \text{where points } x_i \text{ are chosen according to } P(x_i).$$



## Importance sampling: Metropolis Monte Carlo

$$\langle A(\vec{r}^N) \rangle = \int A(\vec{r}^N) \underbrace{\frac{\exp\left(-\frac{U(\vec{r}^N)}{kT}\right)}{Z}}_{P(\vec{r}^N)} d\vec{r}^N \quad Z = \int \exp\left(-\frac{U(\vec{r}^N)}{kT}\right) d\vec{r}^N$$

We can use importance sampling Monte Carlo to calculate ensemble average of quantity  $A$ : Average over measurements of  $A$  for configurations generated according to distribution  $P(\mathbf{r}^N)$ .

To generate configurations according to the desired distribution  $P(\mathbf{r}^N)$  we can create random walk in the phase space, sampling it with the ensemble distribution. This can be realized in different ways. The approach that is used in famous Metropolis Monte Carlo algorithm uses random walk in the phase space with transition probability to go from state  $\mathbf{m}$  to state  $\mathbf{n}$  equal to  $\mathbf{1}$  if the move is downhill in energy ( $\Delta U_{\mathbf{nm}} < \mathbf{0}$ ). If the move is uphill in energy ( $\Delta U_{\mathbf{nm}} > \mathbf{0}$ ) than the move is accepted with a probability defined by **the ratio of probabilities of initial and final states**:

$$\frac{\rho_n}{\rho_m} = \frac{\frac{1}{Z} \exp\left(-\frac{U_n}{kT}\right)}{\frac{1}{Z} \exp\left(-\frac{U_m}{kT}\right)} = \exp\left(-\frac{U_n - U_m}{kT}\right) = \exp\left(-\frac{U_{nm}}{kT}\right)$$





## Metropolis Monte Carlo: Detailed balance condition

Let us set up a random walk through the configurational space (so-called Markov chain of configurations) by the introduction of a fictitious dynamics. The "time"  $t$  is a computer time (marking the number of iterations of the procedure), not real time - our statistical system is considered to be in equilibrium, and thus time is irrelevant.

$P(m, t)$  is the probability of being in configuration  $m$  at time  $t$ ,  $P(n, t)$  the probability of being in configuration  $n$  at time  $t$ ,  $W(m \rightarrow n, t)$  is the probability of going from state  $m$  to state  $n$  per unit time (transition probability). Then we have

$$P(m, t+1) = P(m, t) + \sum_n [W(n \rightarrow m)P(n, t) - W(m \rightarrow n)P(m, t)]$$

At large  $t$ , once the arbitrary initial configuration is "forgotten," we want  $P(m, t)$  to be  $P(m)$ . Clearly a sufficient (but not necessary) condition for an equilibrium (time independent) probability distribution is the so-called **detailed balance condition**:

$$W(n \rightarrow m)P(n, t) = W(m \rightarrow n)P(m, t)$$

This can be applied to any probability distribution, but if we choose the Boltzmann distribution we have

$$\frac{W(m \rightarrow n)}{W(n \rightarrow m)} = \frac{P(n)}{P(m)} = \frac{\frac{1}{Z} \exp\left(-\frac{U_n}{kT}\right)}{\frac{1}{Z} \exp\left(-\frac{U_m}{kT}\right)} = \exp\left(-\frac{U_{nm}}{kT}\right) \quad \text{where } U_{nm} = U_n - U_m$$

$Z$  does not appear in this expression, and it only involves quantities that we know,  $T$ , or can easily calculate,  $U$ .



## Metropolis Monte Carlo: Detailed balance condition

There are many possible choices of the  $\mathbf{W}$  which will satisfy detailed balance. Each choice would provide a dynamic method of generating an arbitrary probability distribution. Let us make sure that Metropolis algorithm satisfies the detailed balance condition.

$$W(m \rightarrow n) = \exp\left(-\frac{U_{nm}}{kT}\right) \quad (U_{nm} > 0)$$

$$W(m \rightarrow n) = 1 \quad (U_{nm} \leq 0)$$

if  $U(n) > U(m)$

$$\frac{W(m \rightarrow n)}{W(n \rightarrow m)} = \frac{\exp\left(-\frac{U_{nm}}{kT}\right)}{1} = \exp\left(-\frac{U_{nm}}{kT}\right)$$

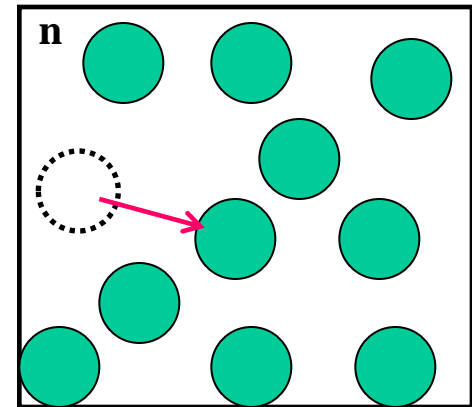
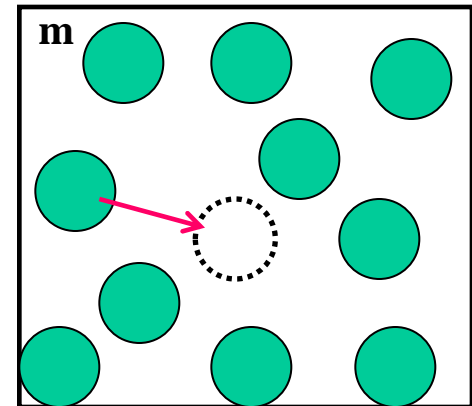
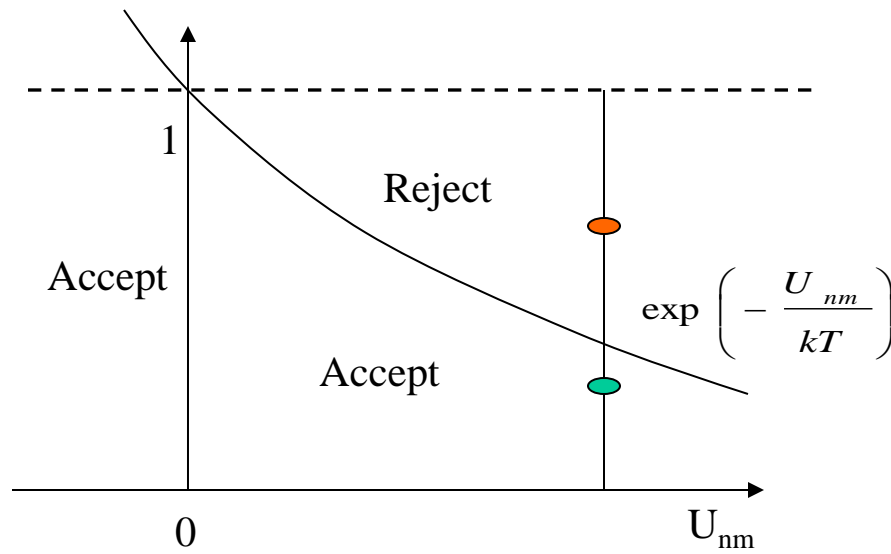
if  $U(n) < U(m)$

$$\frac{W(m \rightarrow n)}{W(n \rightarrow m)} = \frac{1}{\exp\left(-\frac{U_{mn}}{kT}\right)} = \exp\left(-\frac{U_{nm}}{kT}\right)$$

Thus, the Metropolis Monte Carlo algorithm generate a new configuration  $n$  from a previous configuration  $m$  so that the transition probability  $W(m \rightarrow n)$  satisfies the detailed balance condition.

# Metropolis Monte Carlo algorithm

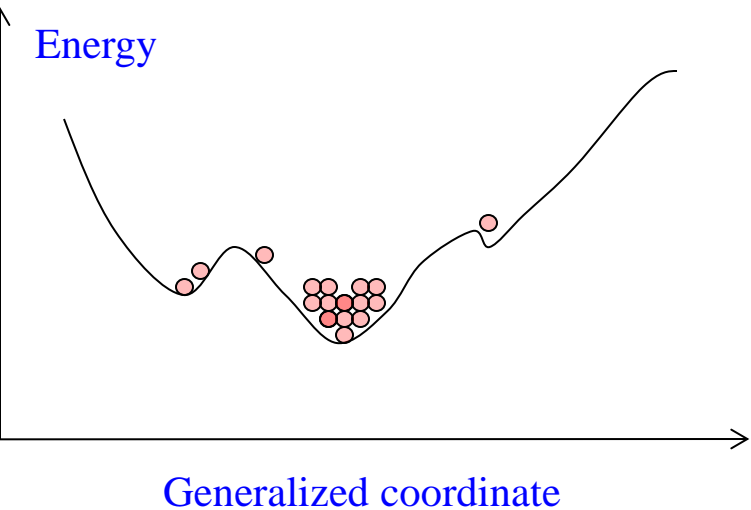
1. Choose the initial configuration, calculate energy
2. Make a “move” (e.g., pick a random displacement). Calculate the energy for new “trail” configuration.
3. Decide whether to accept the move:
  - if  $U_{nm} = U_n - U_m < 0$ , then accept the new configuration,
  - if  $U_{nm} = U_n - U_m > 0$ , then calculate  $W(m \rightarrow n) = \exp\left(-\frac{U_{nm}}{kT}\right)$ 
    - draw a random number  $R$  from 0 to 1.
    - if  $W(m \rightarrow n) > R$  then accept the new configuration,
    - otherwise, stay at the same place.
5. Repeat from step 2, accumulating sums for averages



# Metropolis Monte Carlo: Summary

**MC simulation gives properties via ensemble averaging.** Random numbers are used to generate large number of states of the system (members of an ensemble) with a distribution characteristic for a given statistical mechanics ensemble.

**Metropolis Monte Carlo** – a method to generate a **sequence of random states** of the system with probability distribution characteristic for the system in equilibrium.



What if we start our simulation away from the equilibrium (in a region of the configurational space that is unlikely to be sampled at equilibrium)?

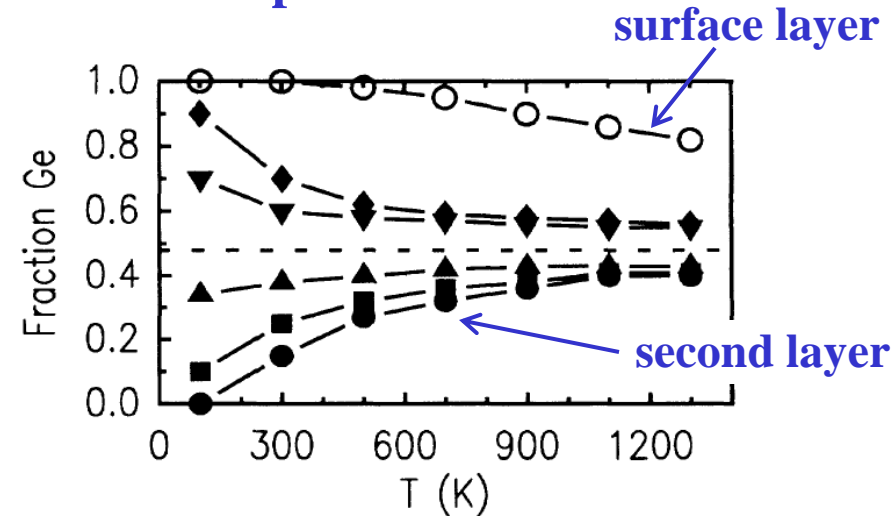
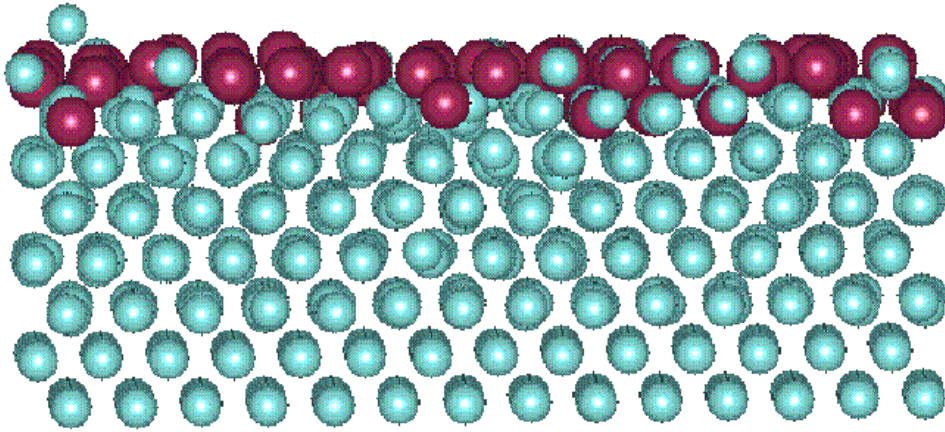
The random walk in MC should bring us to the equilibrium.

**We can use this method to find equilibrium structure and composition!**

**MC can be easily adapted to the calculation of averages in any statistical mechanics ensemble.** For example, simulation of isothermal – isobaric ensemble involves random volume change (volume is added to the set of independent variables that characterize the state of the system); simulation of grand-canonical ensemble have “moves” that insert/delete atoms/molecules.

**MC cannot address kinetics or dynamical properties** (diffusion, mean square displacements, velocity autocorrelation functions, vibrational spectra etc.)

## Metropolis Monte Carlo: Example

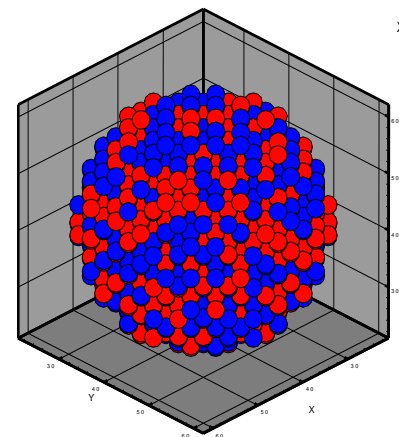


Oscillatory surface segregation of Si-Ge alloys Kelires & Tersoff, *Phys. Rev. Lett.* **63**, 1164, 1989.

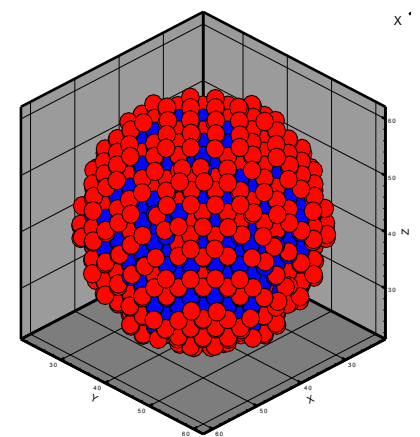
Two types of Monte Carlo moves – small atomic displacements and interchange of atom type are used to investigate surface segregation vs temperature in Si-Ge alloys.

Adam DiNardo, undergraduate REU student from Penn State University, Metropolis Monte Carlo simulations of the compositional ordering in Si-Ge clusters.

Si - blue, Ge - red



initial

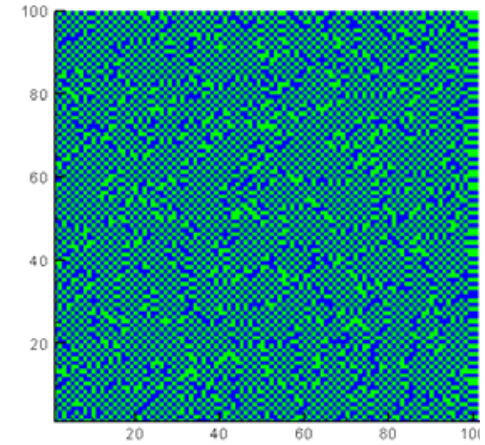
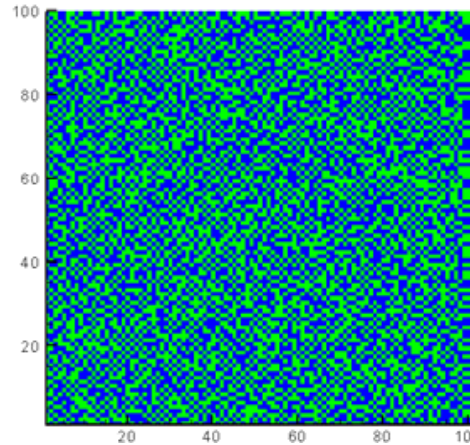
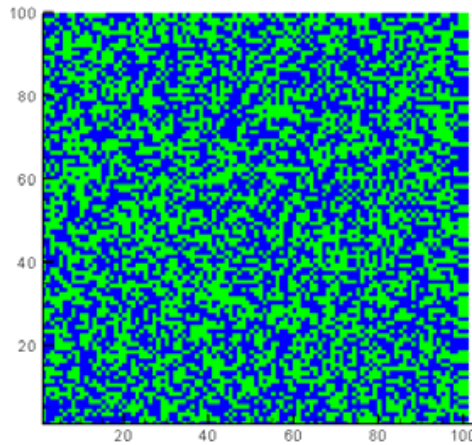


final

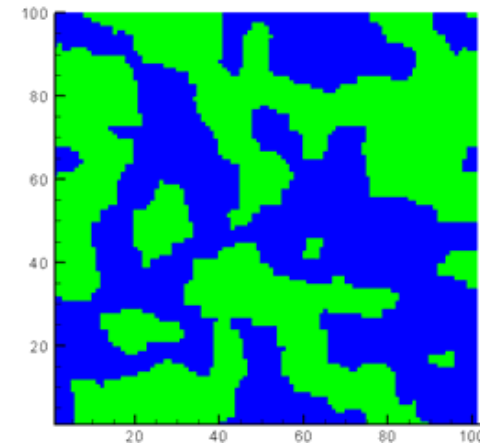
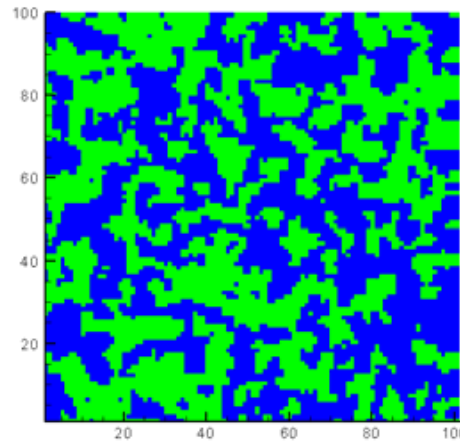
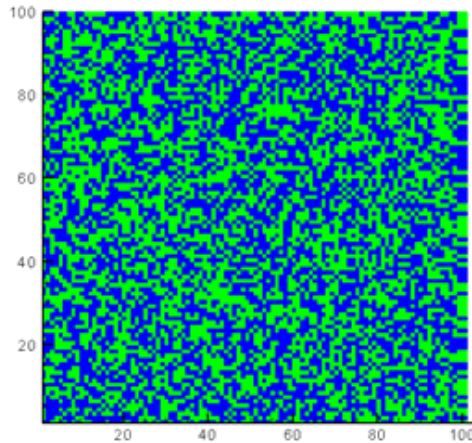
# Metropolis Monte Carlo: Example

MSE 6270 homework: Metropolis Monte Carlo simulation of 2D binary alloys

Interatomic energies are  $E_{AA} = E_{BB} = -0.05$  eV,  $E_{AB} = -0.25$  eV  $\rightarrow \Delta H_{\text{mix}} < 0$ ;  $T = 50$  K



Interatomic energies are  $E_{AA} = E_{BB} = -0.05$  eV,  $E_{AB} = -0.01$  eV  $\rightarrow \Delta H_{\text{mix}} > 0$ ;  $T = 50$  K





# Kinetic Monte Carlo: kinetics of atomic rearrangements

**Kinetic Monte Carlo** – can address kinetics. The main idea behind KMC is to use transition rates that depend on the energy barrier between the states, with time increments formulated so that they relate to the microscopic kinetics of the system.

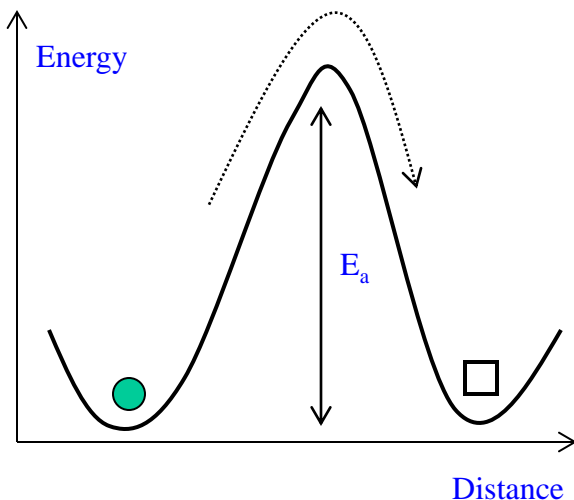
Before starting kMC simulation we have to make **a list of all possible events that can be realized during the simulation** and calculate rates for each event.

Input to KMC:      Fast processes – MD simulations  
                         Slow processes – transition state theory, experiments

*For example*, diffusion on the surface is determined by the energy barriers for the breaking the adatom-substrate bonds,  $E_a = E_{\text{saddle}} - E_{\text{min}}$ , and the rate constant for diffusion can be calculated using a simplified transition state theory:

$$k_{\text{TST}} = n_p v \exp \left( - \frac{E_a}{kT} \right)$$

$n_p$  is the number of possible jump directions  
 $v$  is the harmonic frequency.



For atoms adjacent to an island/step, additional (Ehrlich-Schwoebel) barriers/rates should be specified for breaking bonds with the atoms of the island. As the system becomes more complex, the number of possible events becomes larger...



# Example: Growth of fractal structures in fullerene layers

Monte Carlo simulation by Hui Liu (term project for MSE 627)

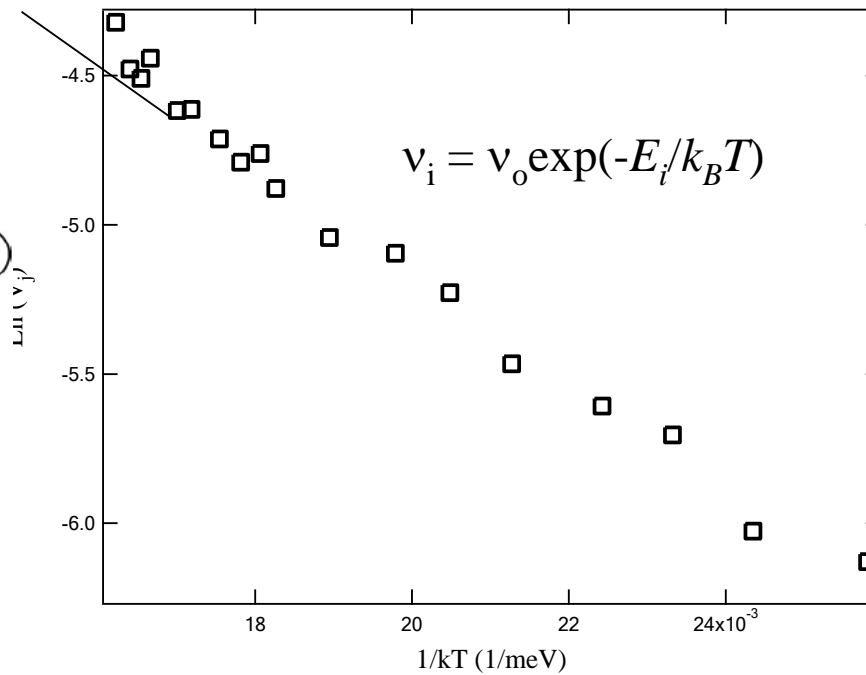
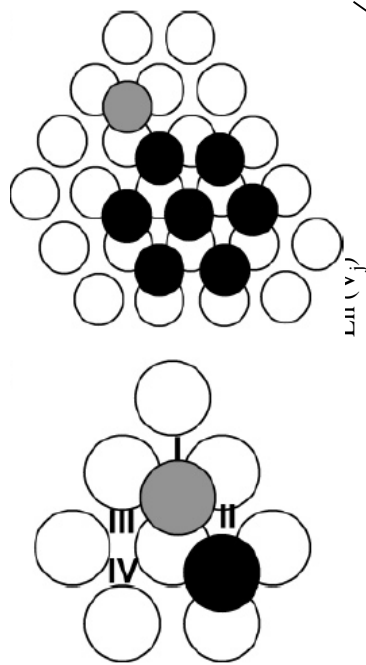


STM images of  $C_{60}$  film growing on graphite

Boundary	Jump to I	Jump to II	Jump to III
	$P_j^I = 45. \pm 1 \%$	$P_j^{II} = 10.0 \pm 0.5 \%$	$P_j^{III} = 45. \pm 1 \%$
	$P_{jII}^I = 99.97 \pm 0.03 \%$	$P_{jII}^{II} = 0.03 \pm 0.03 \%$	$P_{jII}^{III} = 0\%$
	$P_{jIII}^I = 50 \%$		
	$E_{jIV}^I = 207 \pm 4$ $v_{jIV}^I = 0.29 \pm 0.01$	$E_{jIV}^{II} = 354 \pm 53$ $v_{jIV}^{II} = 0.3 \pm 0.05$	$E_{jIV}^{III} = \infty^\dagger$
<b>j2</b> (two or more neighbors)	$E_{j2} = \infty^\dagger$	$E_{j2} = \infty^\dagger$	$E_{j2} = \infty^\dagger$

All possible thermally-activated events have to be considered

Terrace	Jump to I Energy barrier (meV) Attempt frequency ( $\times 10^{12} s^{-1}$ )	Jump to II Energy barrier (meV) Attempt frequency ( $\times 10^{12} s^{-1}$ )	Jump to III Energy barrier (meV) Attempt frequency ( $\times 10^{12} s^{-1}$ )
<b>0</b> (without neighbors - basic movement)	$E_0 = 178 \pm 4$ $v_0 = 0.2 \pm 0.03$	$E_0 = 178 \pm 4$ $v_0 = 0.2 \pm 0.03$	$E_0 = 178 \pm 4$ $v_0 = 0.2 \pm 0.03$
	$E_{1I}^I = 429 \pm 57$ $v_{1I}^I = 0.65 \pm 0.09$	$E_{1I}^{II} = \infty^\dagger$	$E_{1I}^{III} = 185 \pm 6$ $v_{1I}^{III} = 0.25 \pm 0.04$
		$\sim 50\%^\dagger$	$P_{12}^{III} = 0 \%$
	$E_{2I}^I = 354 \pm 63$ $v_{2I}^I = 0.06 \pm 0.01$	$E_{2I}^{II} = 354 \pm 63$ $v_{2I}^{II} = 0.06 \pm 0.01$	$E_{2I}^{III} = \infty^\dagger$
	$E_{3I} = \infty^\dagger$	$E_{3I} = \infty^\dagger$	$E_{3I} = \infty^\dagger$
	$P_{2II}^I = 98.24 \pm 0.3 \%$	$P_{2II}^{II} = 0.88 \pm 0.15\%^\dagger$	$P_{2II}^{III} = 0.88 \pm 0.15\%^\dagger$
	$E_{2II}^I = \infty^\dagger$	$E_{2II}^{II} = \infty^\dagger$	$E_{2II}^{III} = \infty^\dagger$
	$P_{2II}^I = 99.86 \pm 0.1 \%$	$P_{2II}^{II} = 0.14 \pm 0.1 \%$	$P_{2II}^{III} = 0 \%$
	$E_{2II}^I = \infty^\dagger$	$E_{2II}^{II} = \infty^\dagger$	$E_{2II}^{III} = \infty^\dagger$
	$E_{2II}^I = \infty^\dagger$	$E_{2II}^{II} = \infty^\dagger$	$E_{2II}^{III} = \infty^\dagger$
<b>3</b> (three or more neighbors)	$E_3 = \infty^\dagger$	$E_3 = \infty^\dagger$	$E_3 = \infty^\dagger$



MD simulations – finding the energy barriers, attempt frequencies, and probabilities of diffusion jump events

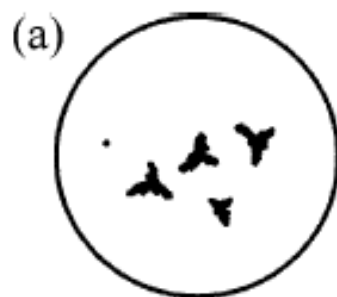


## Example: Growth of fractal structures in fullerene layers

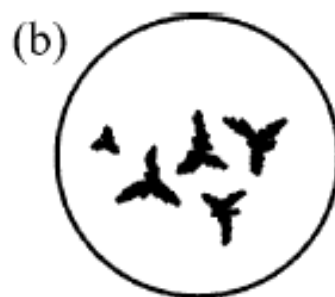
Monte Carlo simulation by Hui Liu (term project for MSE 627)



STM images of C<sub>60</sub> film  
growing on graphite



0.02 ML



0.05 ML



0.09 ML



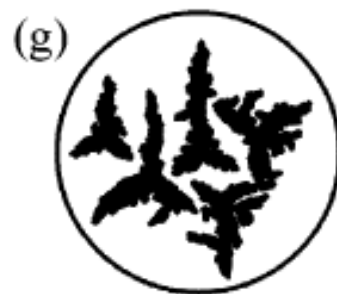
0.12 ML



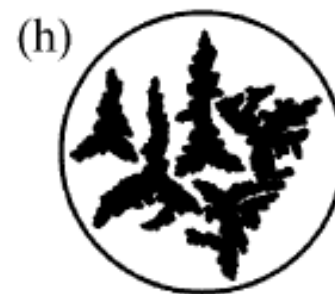
0.16 ML



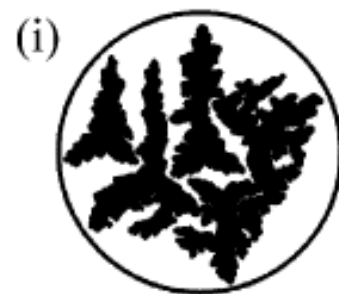
0.20 ML



0.25 ML



0.29 ML



0.34 ML

## Kinetic Monte Carlo: limitations

One (main?) problem in kMC is that we have to specify all the barriers/rates in advance, before the simulation.

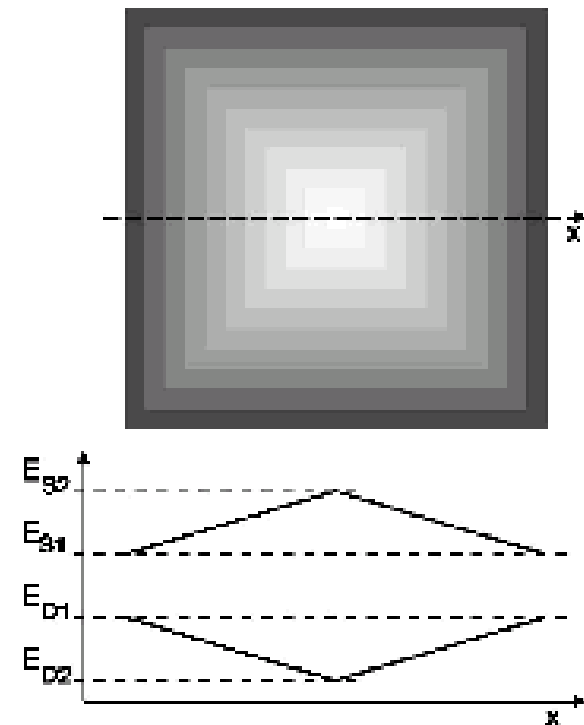
But what if we have a continuous variation of the activation energies in the system? What if the activation energies are changing during the simulation?

**Example:** strain on the surface can affect the diffusion of adatoms and nucleation of islands.

There could be many possible origins of strain, e. g. buried islands, mesas, dislocation patterns in heteroepitaxial systems. One can try to introduce the effect of strain on the activation energies for the diffusion of adatoms. For example, Nurminen et al., *Phys. Rev. B* **63**, 035407, 2000, tried several approaches.

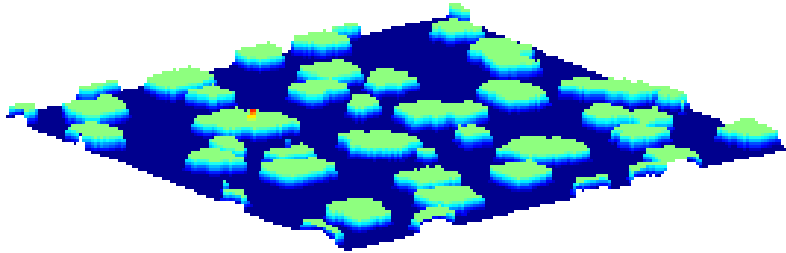
In one approach, they introduced a spatial dependence of the adatom-substrate interaction on a patterned surface,  $E = E_S(x,y) + nE_N$ , where  $E$  is the diffusion activation energy,  $E_S$  is the contribution due to the interaction with substrate, and  $E_N$  is the energy of interaction with other adatoms.

In another approach, an additional hop-direction dependent diffusion barrier  $E_D$  is introduced to describe the long-range interaction between adatom and domain boundaries,  $E = E_S + nE_N + E_D$ .



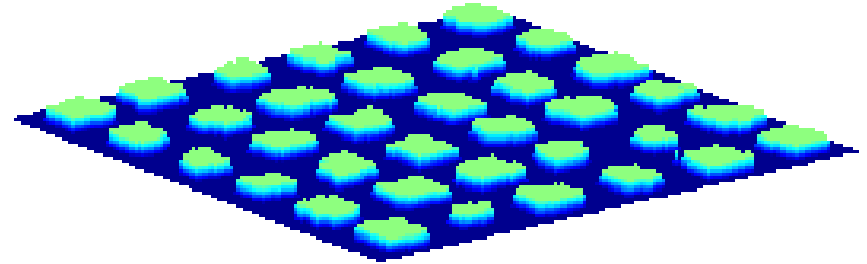
## Kinetic Monte Carlo: example

Kinetic Monte Carlo simulation of island growth on a homogeneous substrate and a substrate with nanoscale patterning (by Nurminen, Kuronen, Kaski, Helsinki University of Technology)



*islands on a homogeneous substrate*

Blue denotes the substrate  
and green the deposited atoms.



*islands on a substrate with nanoscale patterning  
(a checkerboard structure)*

<http://www.lce.hut.fi/publications/annual2000/node22.html>

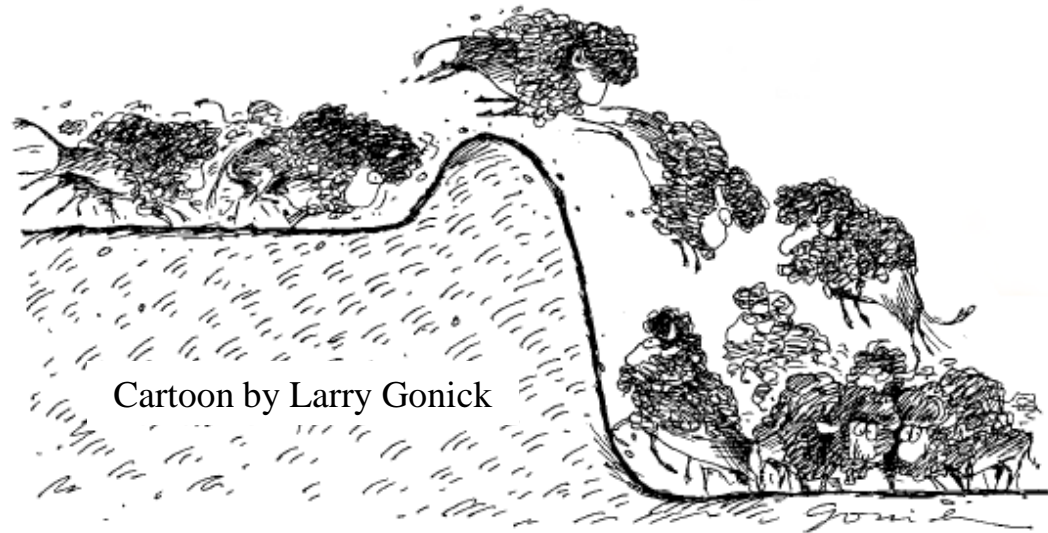
The growing heteroepitaxial islands by themselves can locally modify diffusion barriers. Relaxation of nanostructures introduces local strains that constantly change the energy landscape and corresponding probabilities of Monte Carlo events. Modified approach based on the locally activated Monte Carlo techniques (Kaukonen et al. *Phys. Rev. B*, **61**, 980, 2000) has been proposed to account for local strains.

# Molecular dynamics, Metropolis Monte Carlo and kinetic Monte Carlo

With MD we can only reproduce the dynamics of the system for  $\leq 100$  ns. Slow thermally-activated processes, such as diffusion, cannot be modeled. An alternative computational techniques for slow processes are Monte Carlo methods.

Monte Carlo method is a common name for a wide variety of stochastic techniques. These techniques are based on the use of random numbers and probability statistics to investigate problems in areas as diverse as economics, nuclear physics, and flow of traffic. There are many variations of Monte Carlo methods. In this lecture we will briefly discuss two methods that are often used in materials science - classical Metropolis Monte Carlo and kinetic Monte Carlo.

**Metropolis Monte Carlo** – generates configurations according to the desired statistical-mechanics distribution. There is no time, the method cannot be used to study evolution of the system. Equilibrium properties can be studied.



**Kinetic Monte Carlo** – can address kinetics. The main idea behind KMC is to use transition rates that depend on the energy barrier between the states, with time increments formulated so that they relate to the microscopic kinetics of the system.

## Summary on Atomistic Modeling methods

**Molecular Dynamics** – based on the solution of the equations of motion for all particles in the system. Complete information on atomic trajectories can be obtained, but time of the simulations is limited (up to nanoseconds) – appropriate for fast processes (e.g. FIB local surface modification, sputtering, implantation) or for quasi-static simulations (e.g. stress distribution in nanostructures).

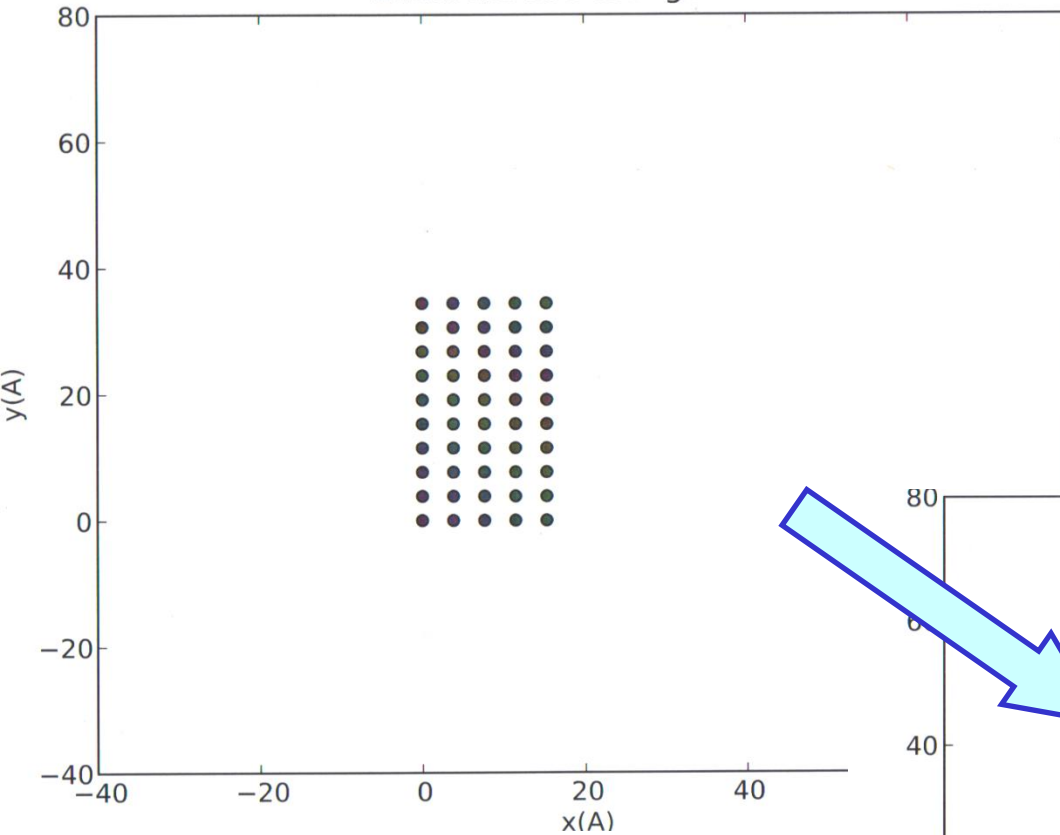
**Metropolis Monte Carlo** – generates random configurations with probability of each configuration defined by the desired distribution  $P(\mathbf{r}^N)$ . This is accomplished by setting up a random walk through the configurational space with specially designed choice of probabilities of going from one state to another. Equilibrium properties can be found/studied (e.g. surface reconstruction and segregation, composition variations in the surface region due to the surface or substrate induced strains, stability of nanostructures).

**Kinetic Monte Carlo** – when the rate constants of all processes are known, we can perform KMC simulation in the time domain. Time increments are defined by the rates of all processes and are formulated so that they relate to the microscopic kinetics of the system. This method should be used when *kinetics rather than equilibrium thermodynamics dominates* the structural and/or compositional changes in the system.

**Kinetic Monte Carlo vs Metropolis Monte Carlo:** in MMC we decide whether to accept a move by considering *the energy difference between the states*, whereas in KMC methods we use *rates* that depend on *the energy barrier between the states*. The main advantages of kinetic Monte Carlo is that time is defined and only a small number of elementary reactions are considered, so the calculations are fast.

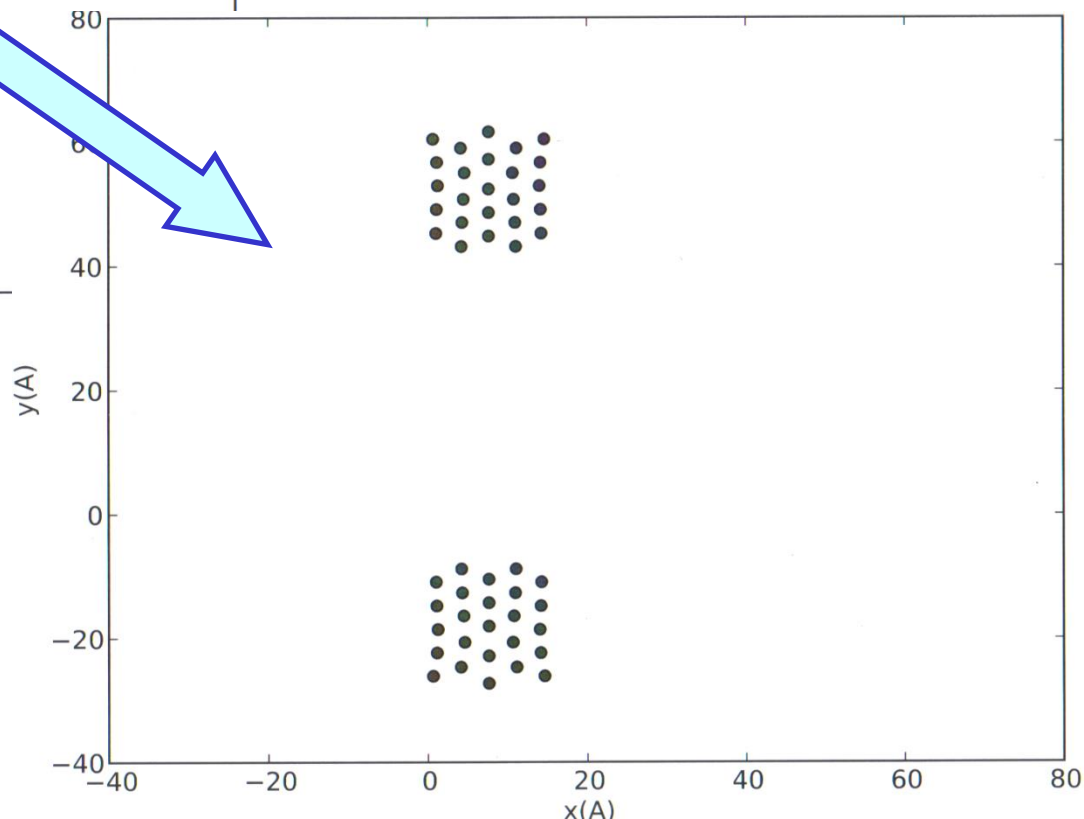
# Homework #1: Atomic configuration

Initial atomic configuration

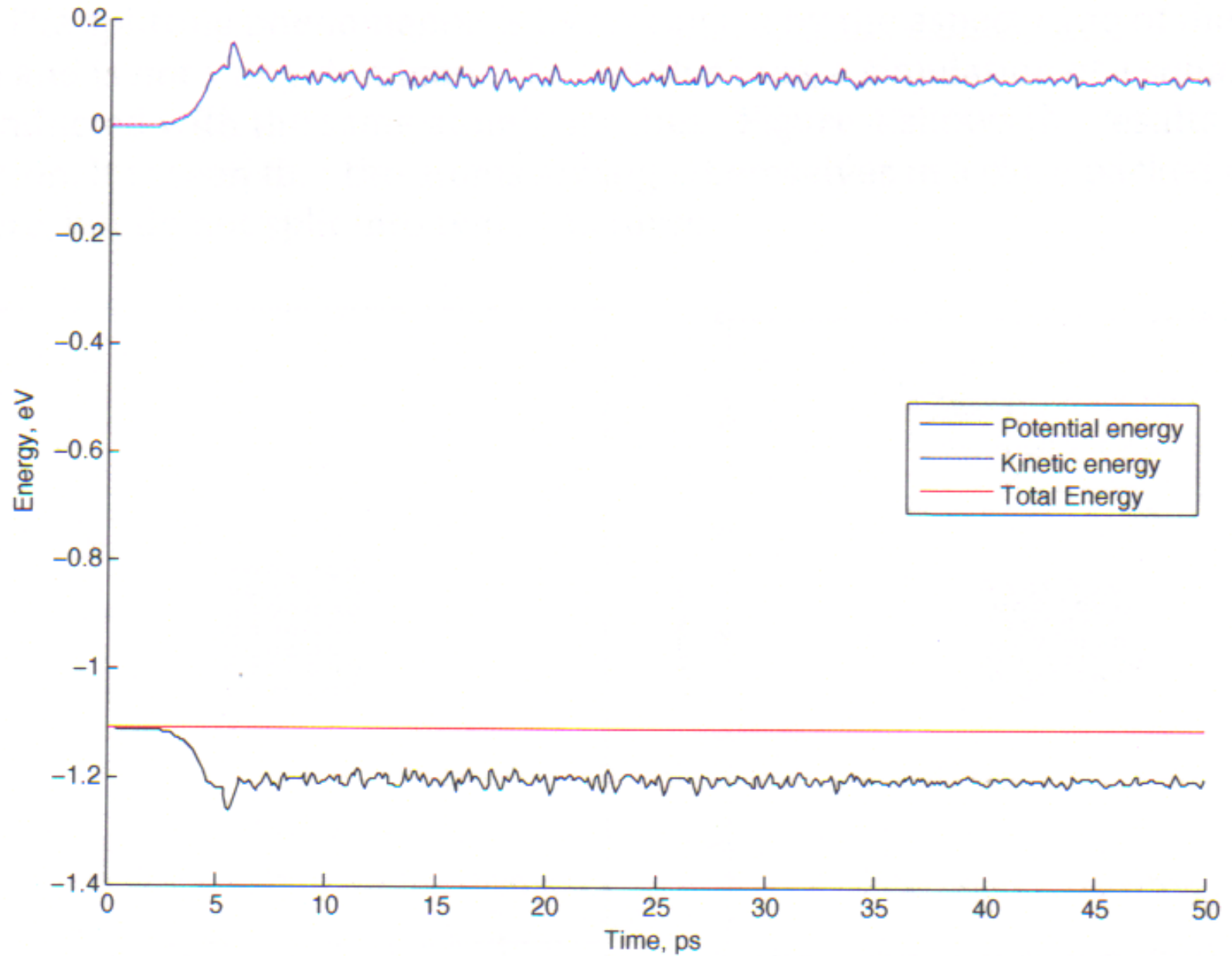


What happens with the initial configuration?

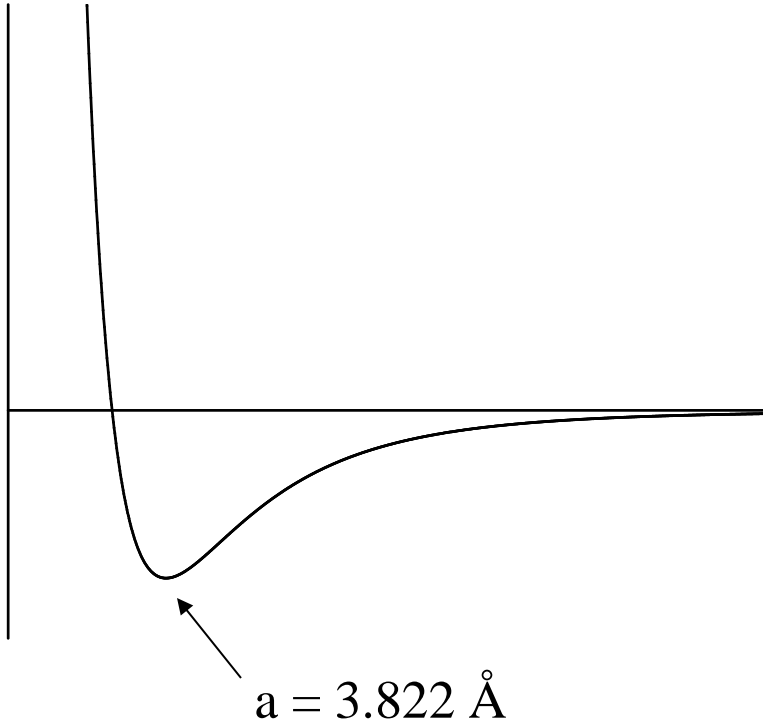
**Why?**



# Homework #1: Energy



## Homework #1



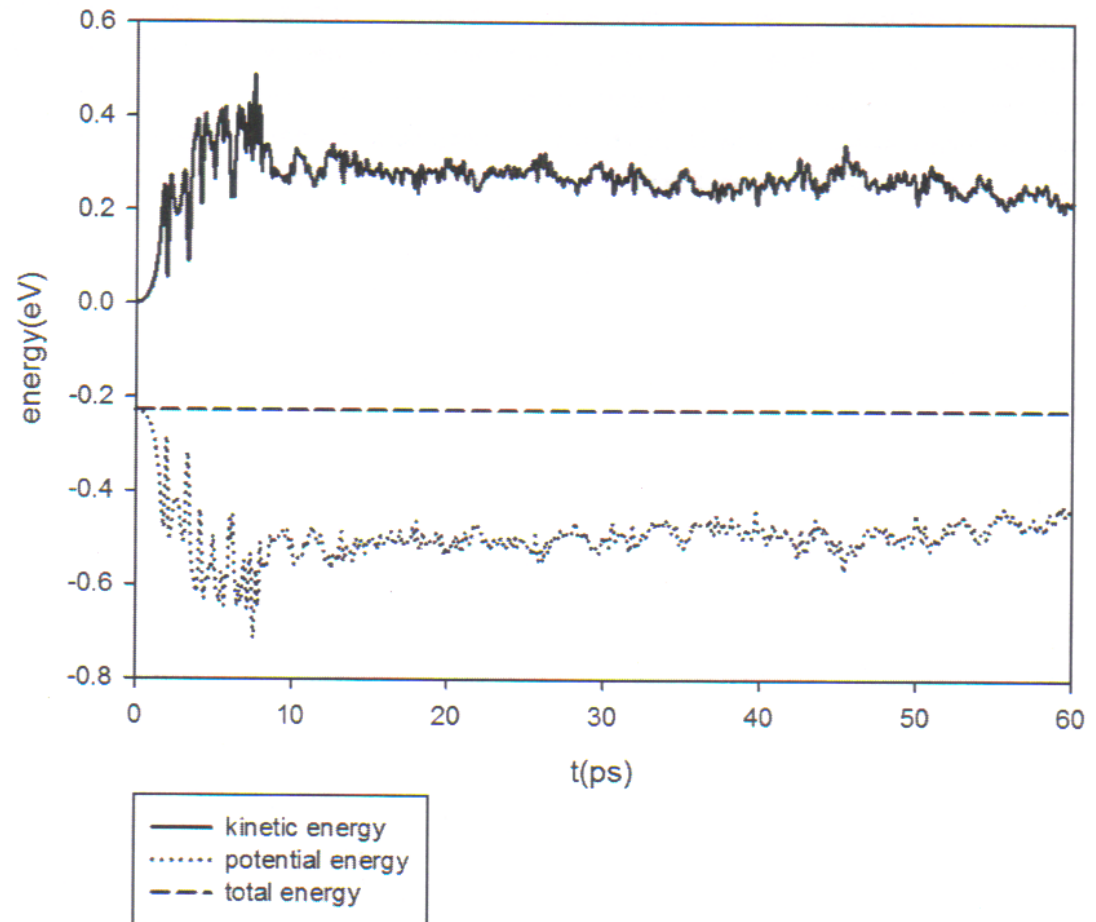
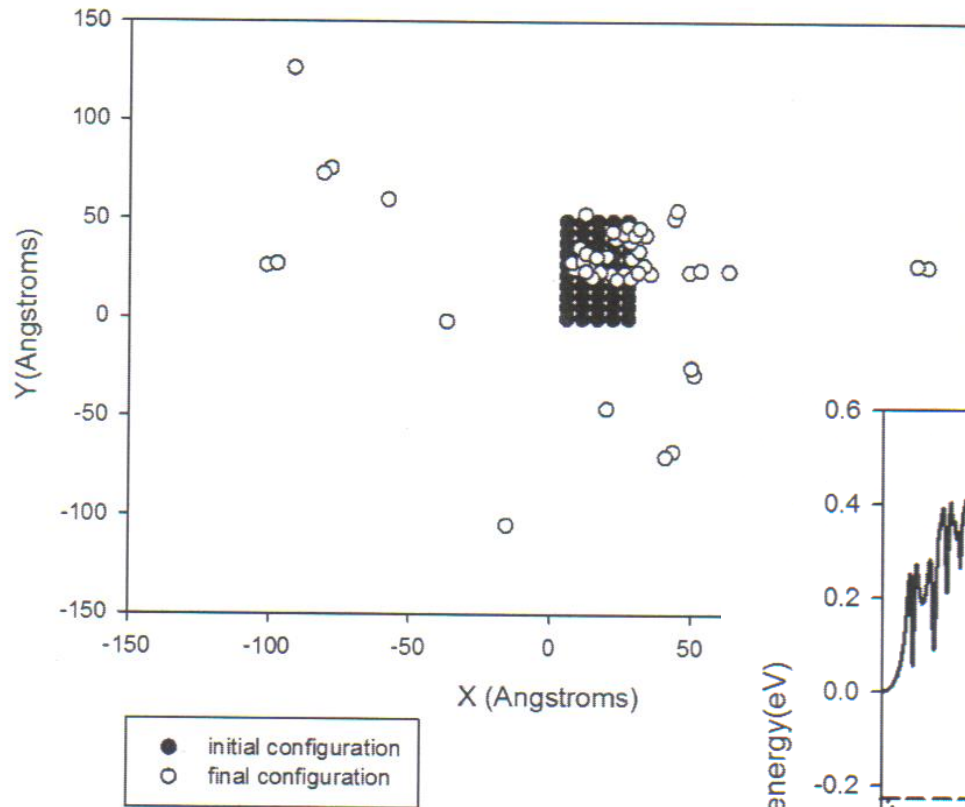
Is this the equilibrium parameter of a crystal lattice?

What values of the kinetic and potential energies of the system should be expected for the initial configuration?

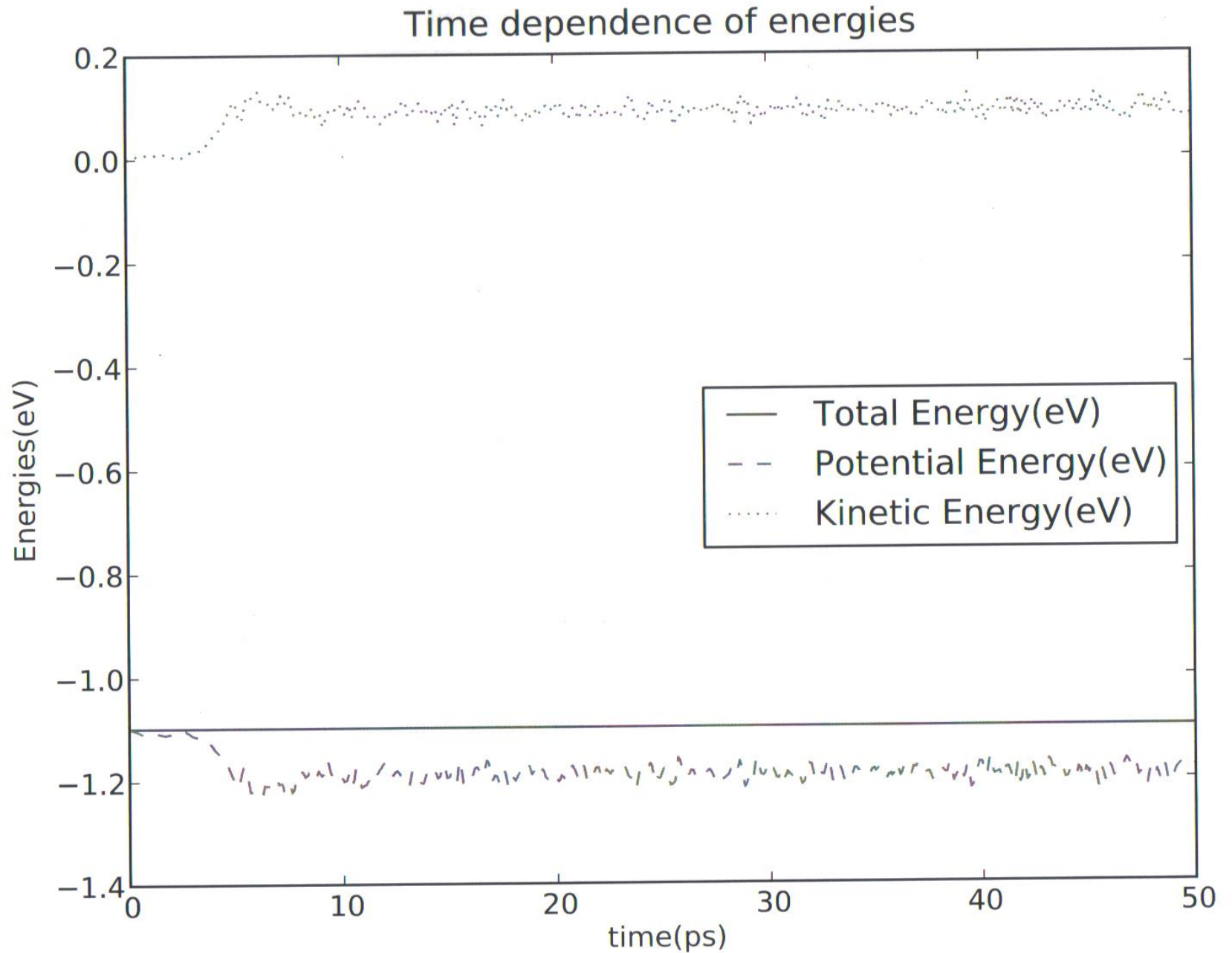


# Homework #1

lattice parameter = 5.431 Å

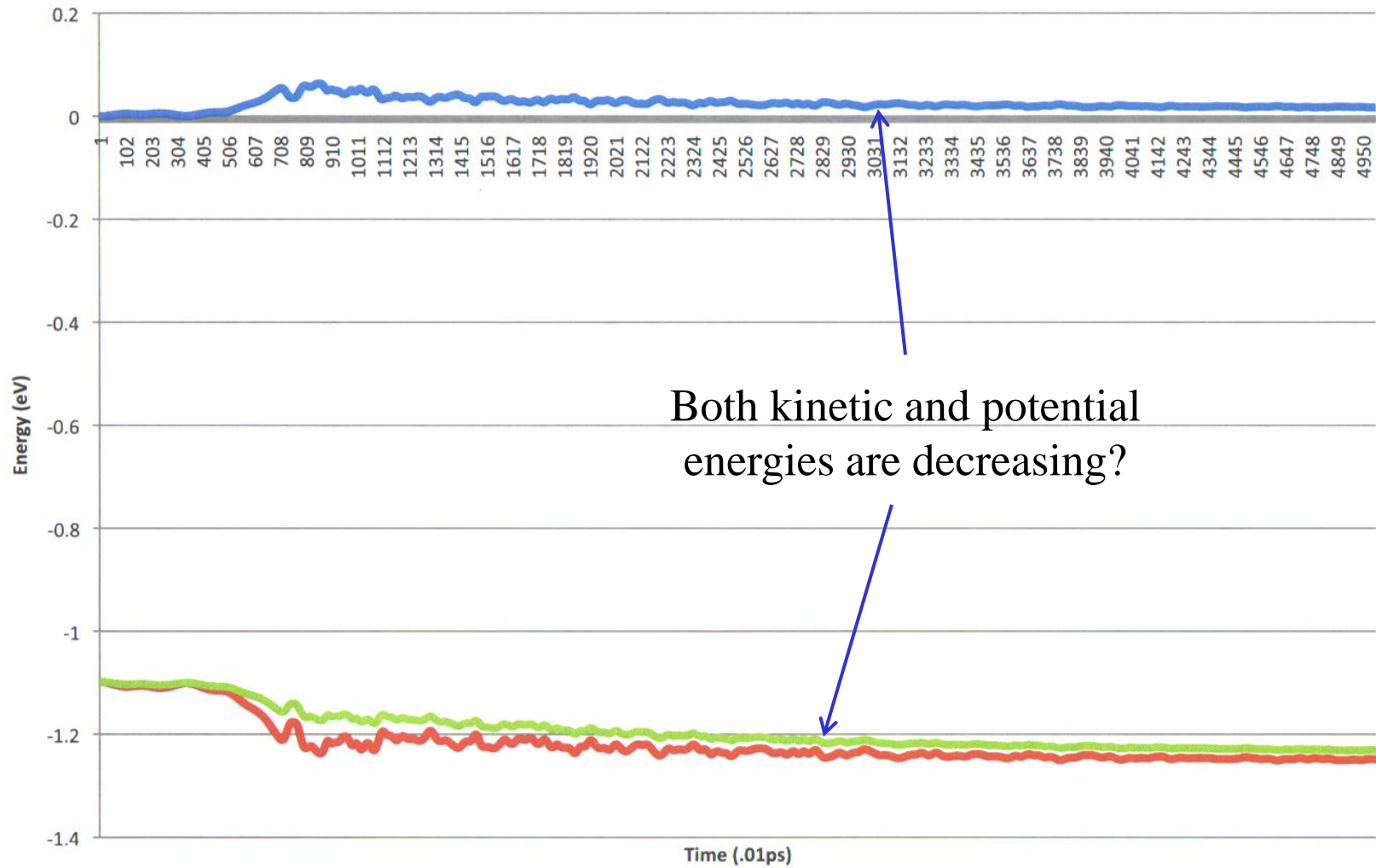


# Homework #1: Energy

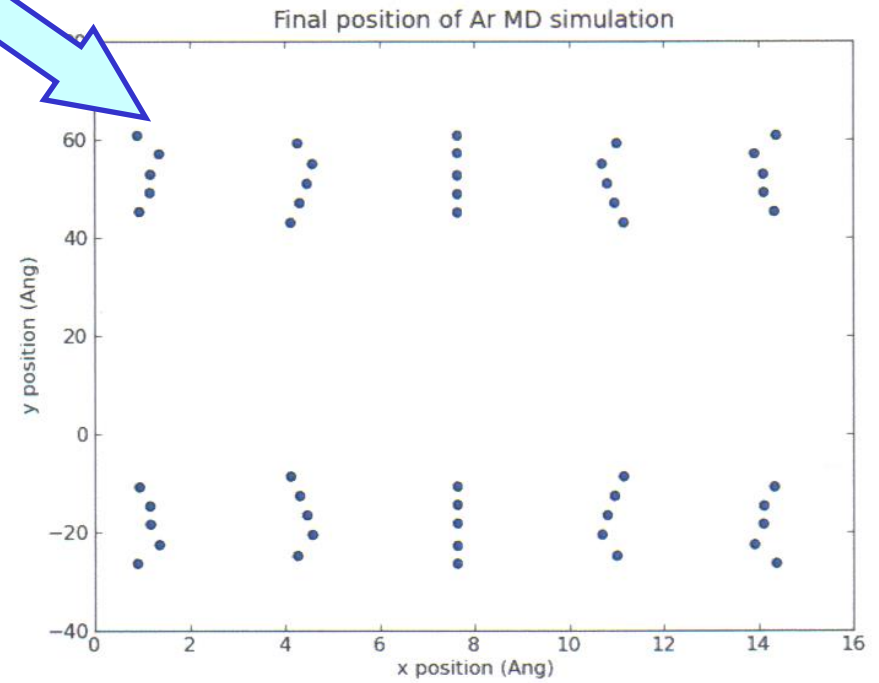
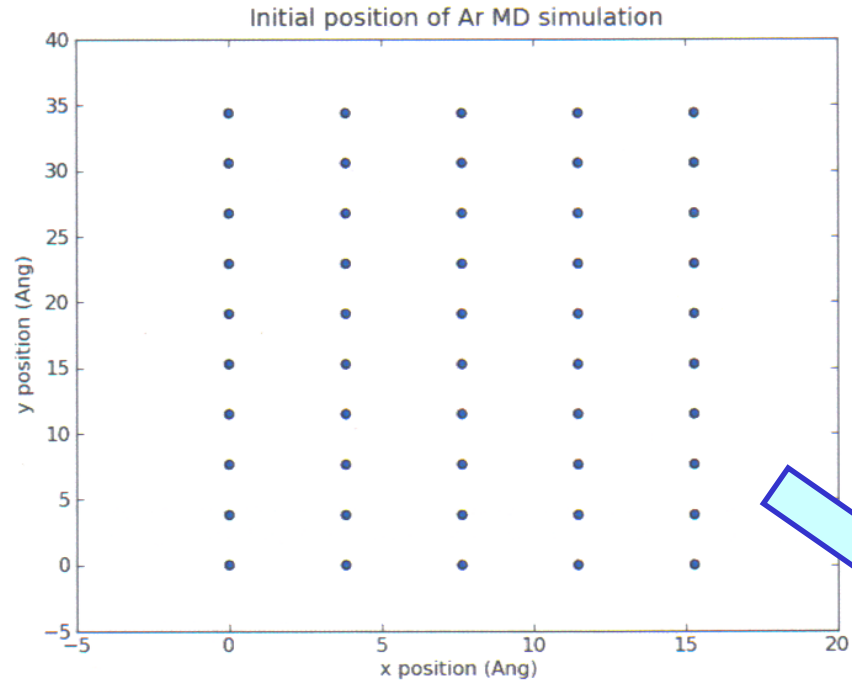


# Homework #1: Energy

Energy Of Simulation

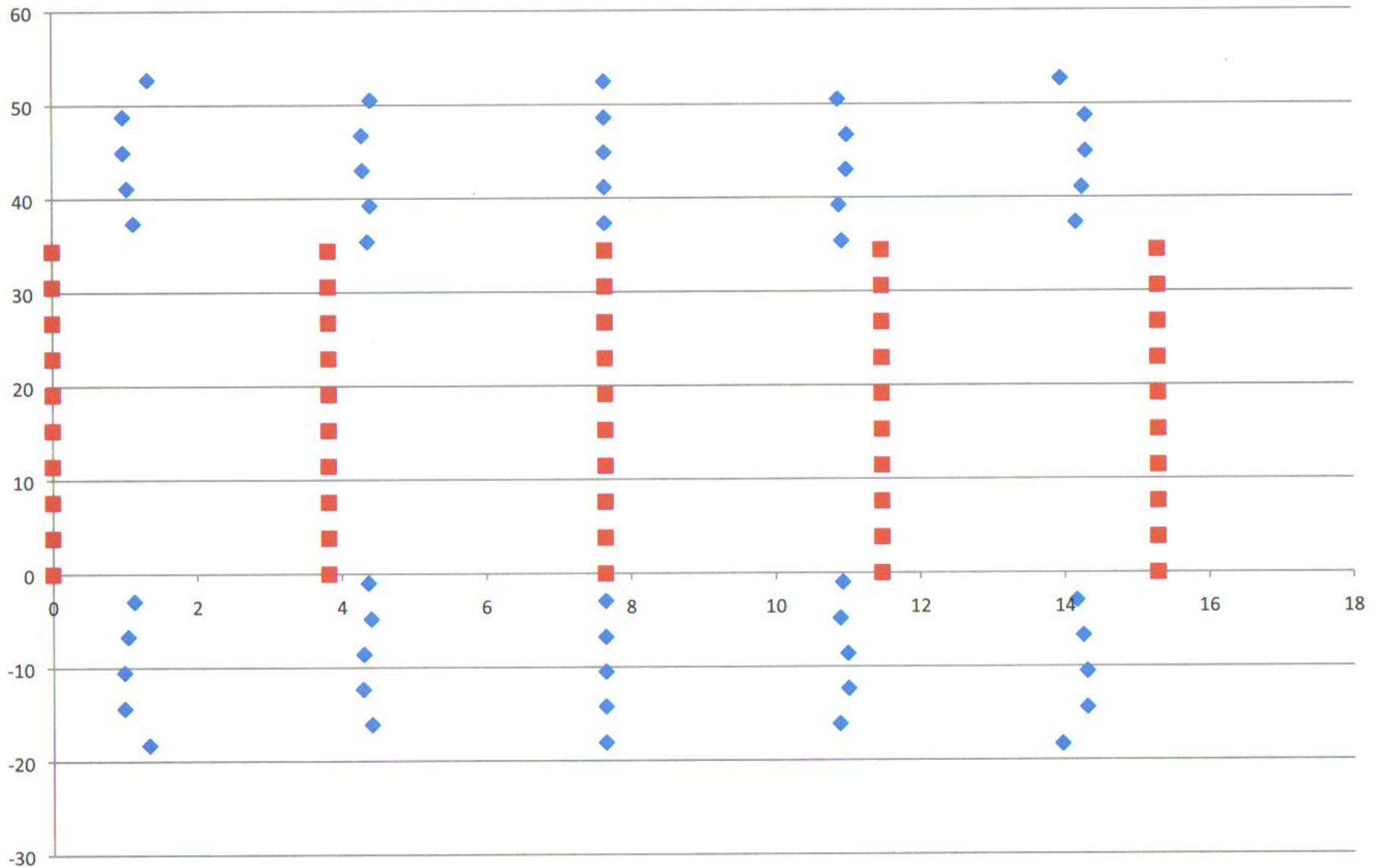


# Homework #1: Atomic configuration

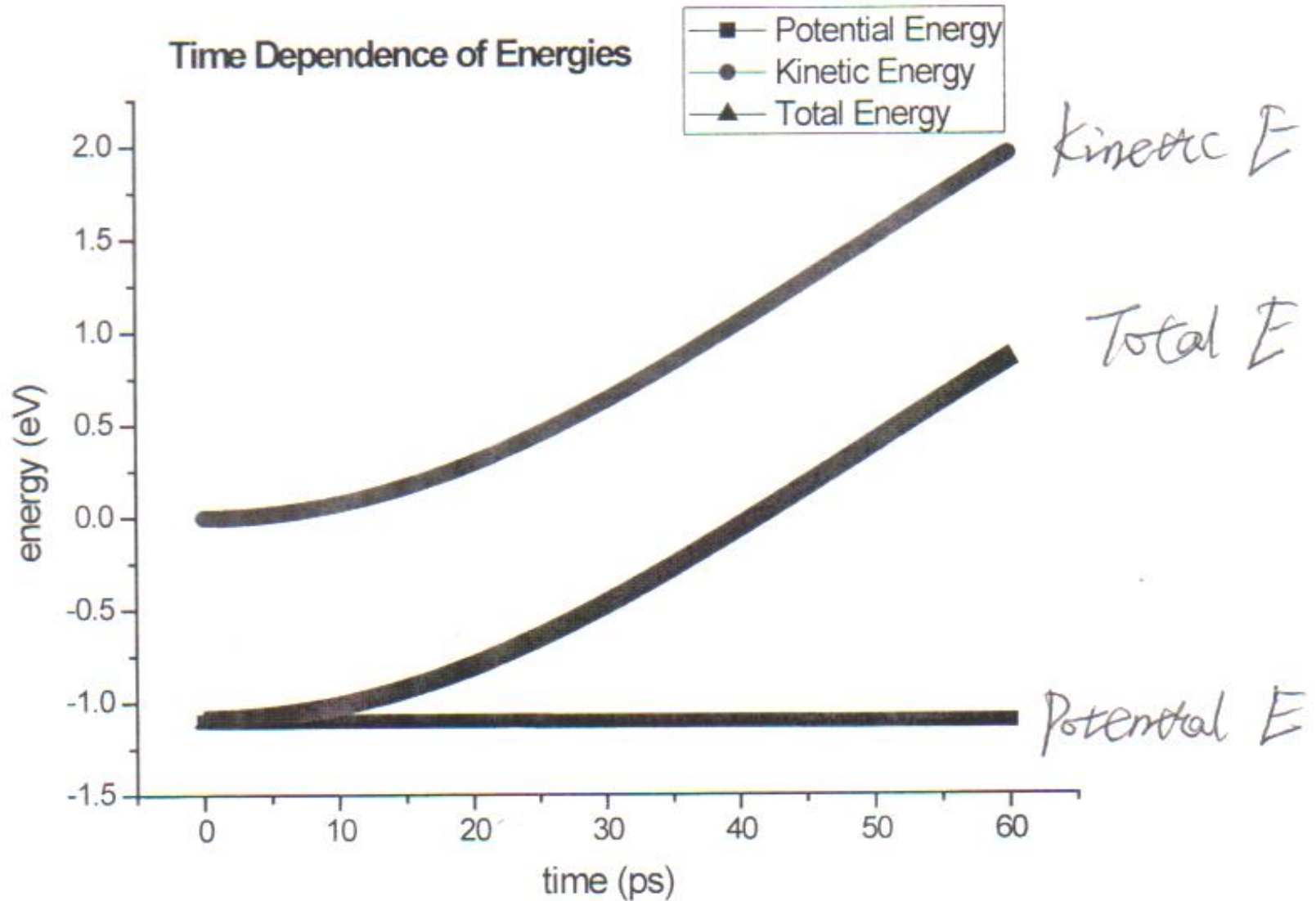


# Homework #1: Atomic configuration

## Beginning Position vs End Position

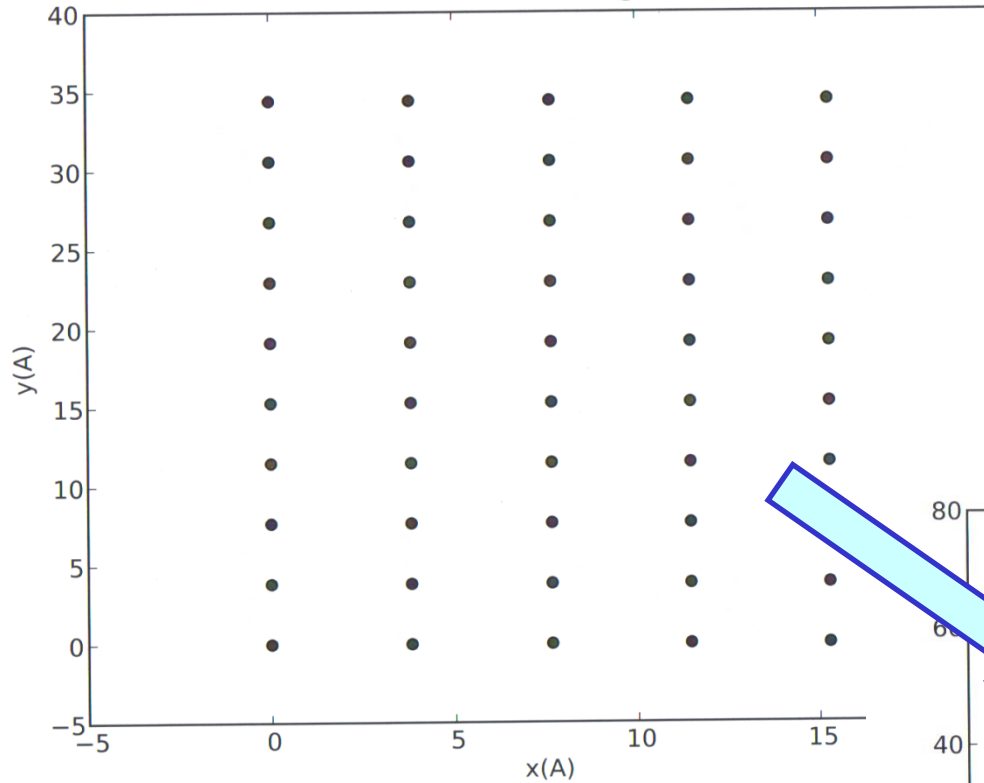


# Homework #1: Energy



# Homework #1: Atomic configuration

Initial atomic configuration



Final atomic configuration

