SCIENCES Master Physique Informatique

Practicing Molecular Simulations

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The philosophy we'll follow…

"I hear and I forget,

I see and I remember,

I do and I understand."

Confucius
Chinese Teacher and Philosopher
(551 BC – 479 BC)

The outline of lectures.

1. Introduction:
   - why molecular simulations?
   - interdisciplinary & multiscale approach;
   - our working case.

2. Physics and chemistry of interfaces. Physical adsorption.

3. Force Fields: interactions & forces in modeling.

4. Monte Carlo: theory, code structure, code's building blocks.

5. Simulation's output: what can we learn?

6. Analysis of error; traps (numerical and physical) in computer simulations.

.

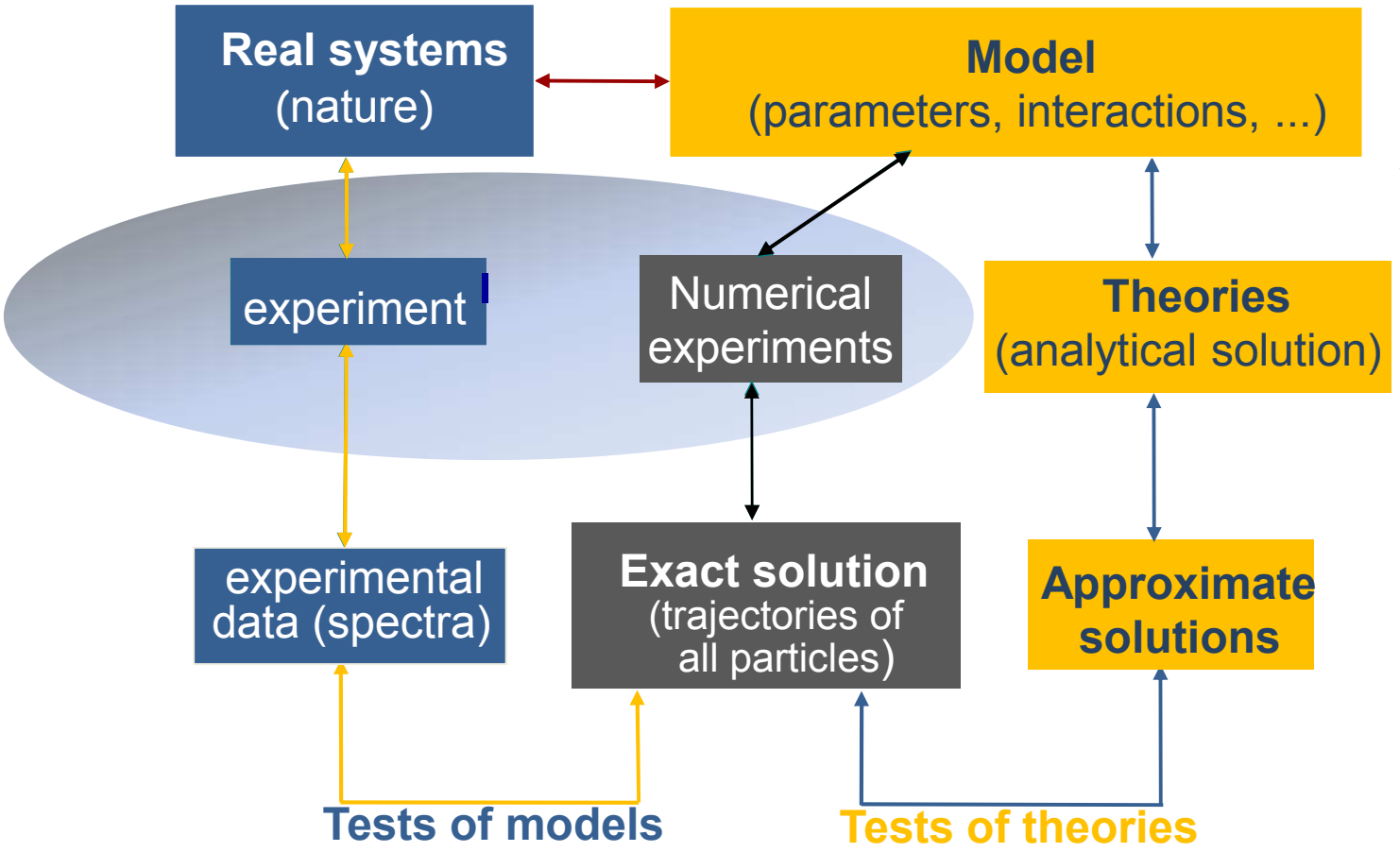
Course output = project.

The knowledge is not compartmentalized…

"… the depth of science has increased dramatically, and Alfred Nobel would be astonished by the changes. **Now in the 21st century, the boundaries separating chemistry, physics and medicine have become blurred,** and as happened during the Renaissance, scientists are following their curiosities even when they run beyond the formal limits of their training……"

From Peter Agre's Nobel Banquet Speech (2003)

Why simulations?



1. Fundamental studies, e.g. to determine range of validity of Kelvin's equation, Fick's law of diffusion, Newton's law of viscosity, etc.

2. **Test** theories by comparing theory and simulation

3. **Test** model by comparing simulated and experimental properties. Then use model in further simulations to carry out "experiments" **not possible** in the laboratory, e.g. critical points for molecules that decompose below T_c, properties of molten salts, long-chain hydrocarbon properties at very high pressures, properties of confined nano-phases, etc.

Why industry is using computer modeling methods?

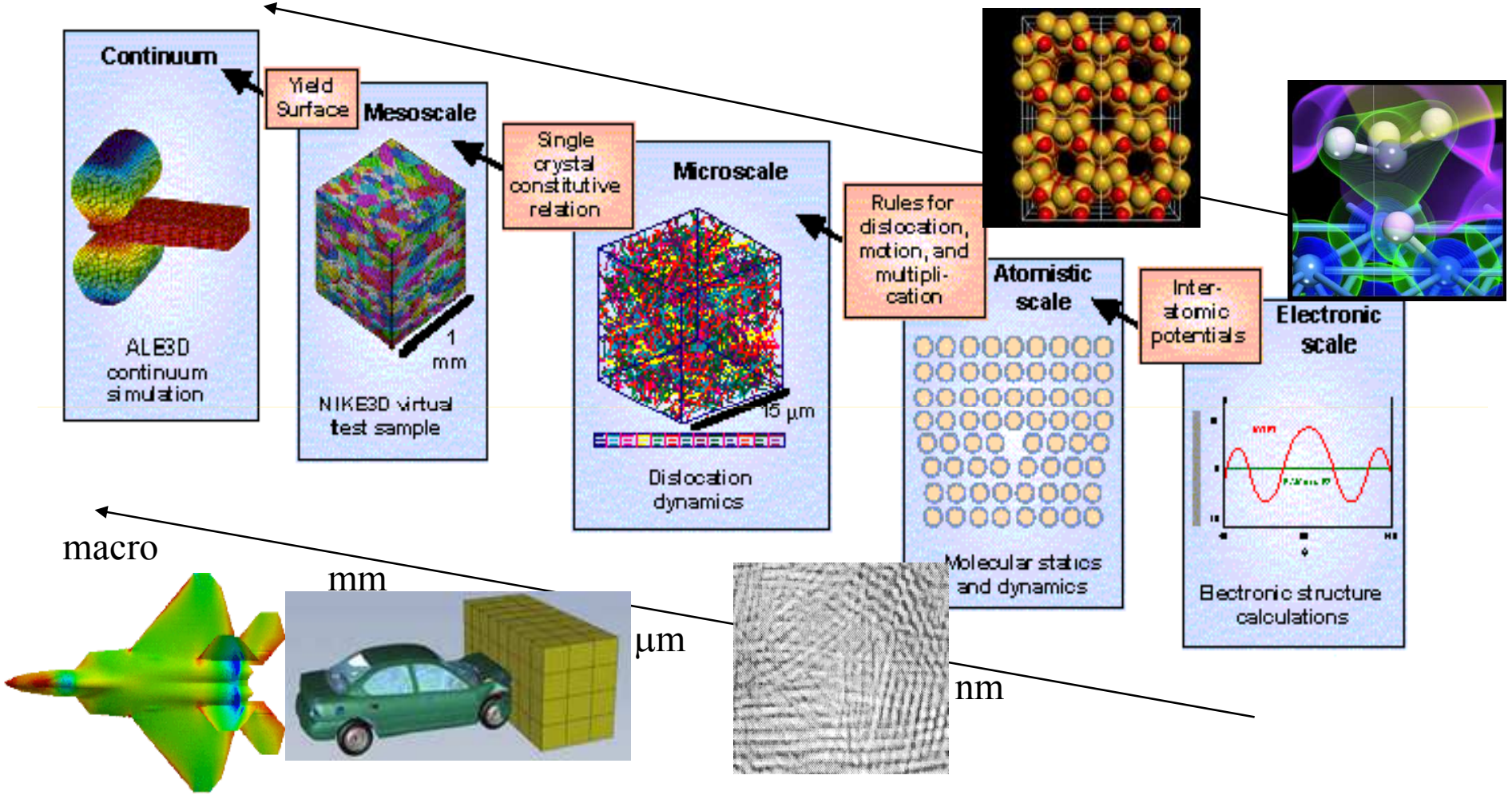
- **Reduction of the time and the price** of development
  (new technologies and materials)
- **Providing the important information at the initial stage of studies**
  - elimination of non physical projects
  - guiding the experiments
- **Cheaper than experiments**
  - increase of experimental effectiveness.
  - financial profit due to the shorter time of development.
  - better managing of risk

(*)Example: Using, at the same time, experimental and numerical methods of development, Toyota has reduced the time needed to make a new product by 30 - 40 %

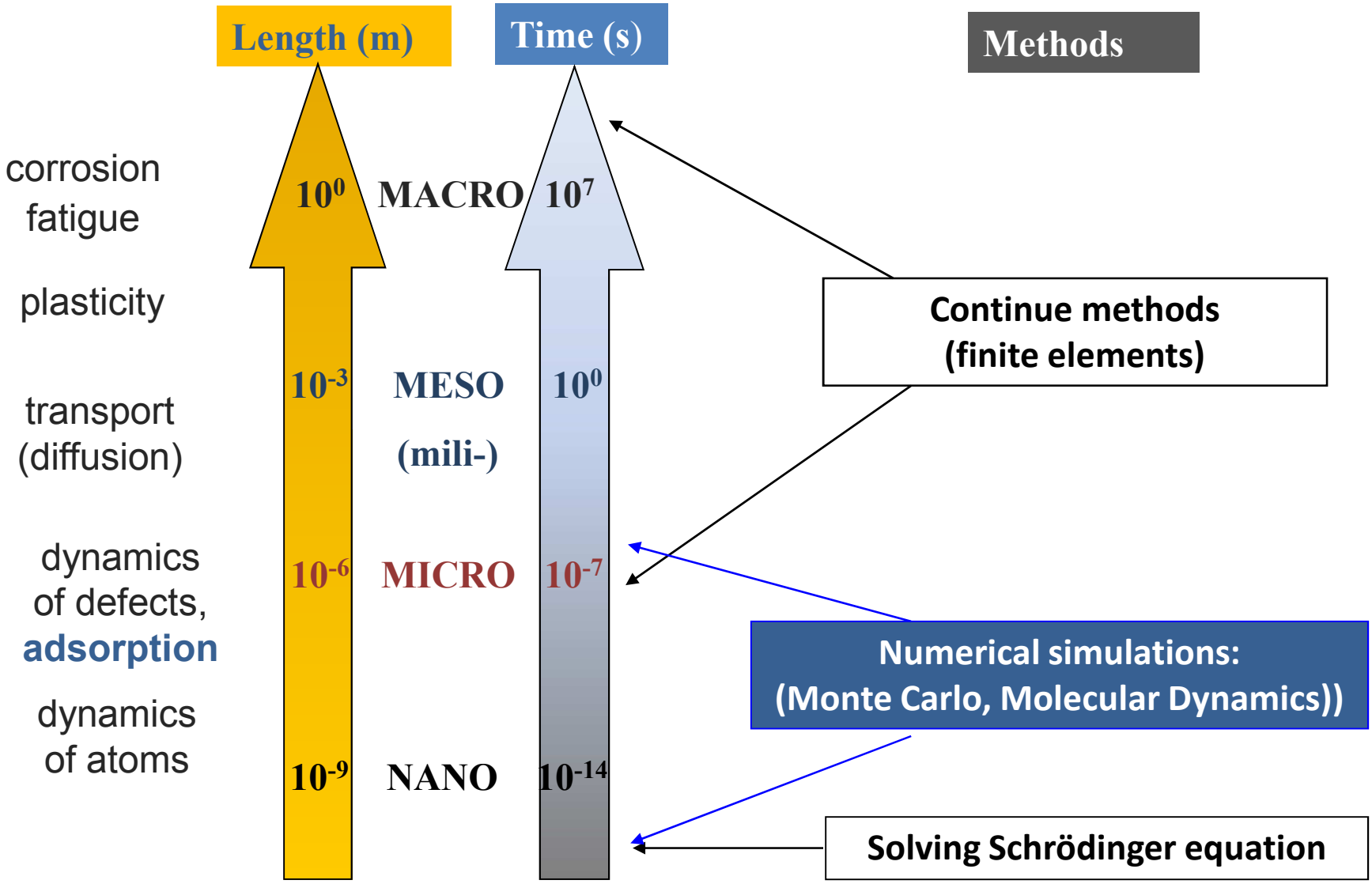
For each dollar invested in simulations and modeling (software & hardware), $3 to $9 return to entreprise as a profit or saving:

(S. Tomke, Enlightened Experimentation, Harvard Business Reviews, 2001)*

Simulation scales – goals and reality



Modeling and simulation: at which scale?



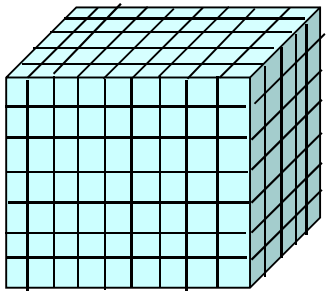
Limitations of computer simulations: why?

Limitations are mainly due to the finite speed and the finite memory capacity of computers

1. discrete character of variables, (Δx, Δt) – defined by the problem
2. **constant** number of independent variables

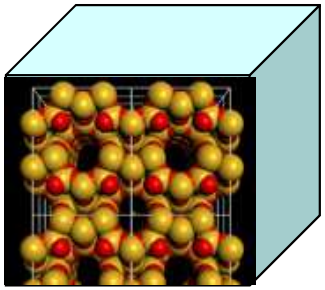
If N – number of independent variables
(electrons, atoms or finite elements)

N finite elements



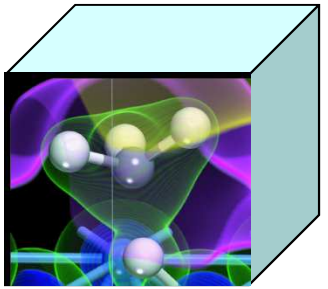
$\geq \mu$ m

N atoms



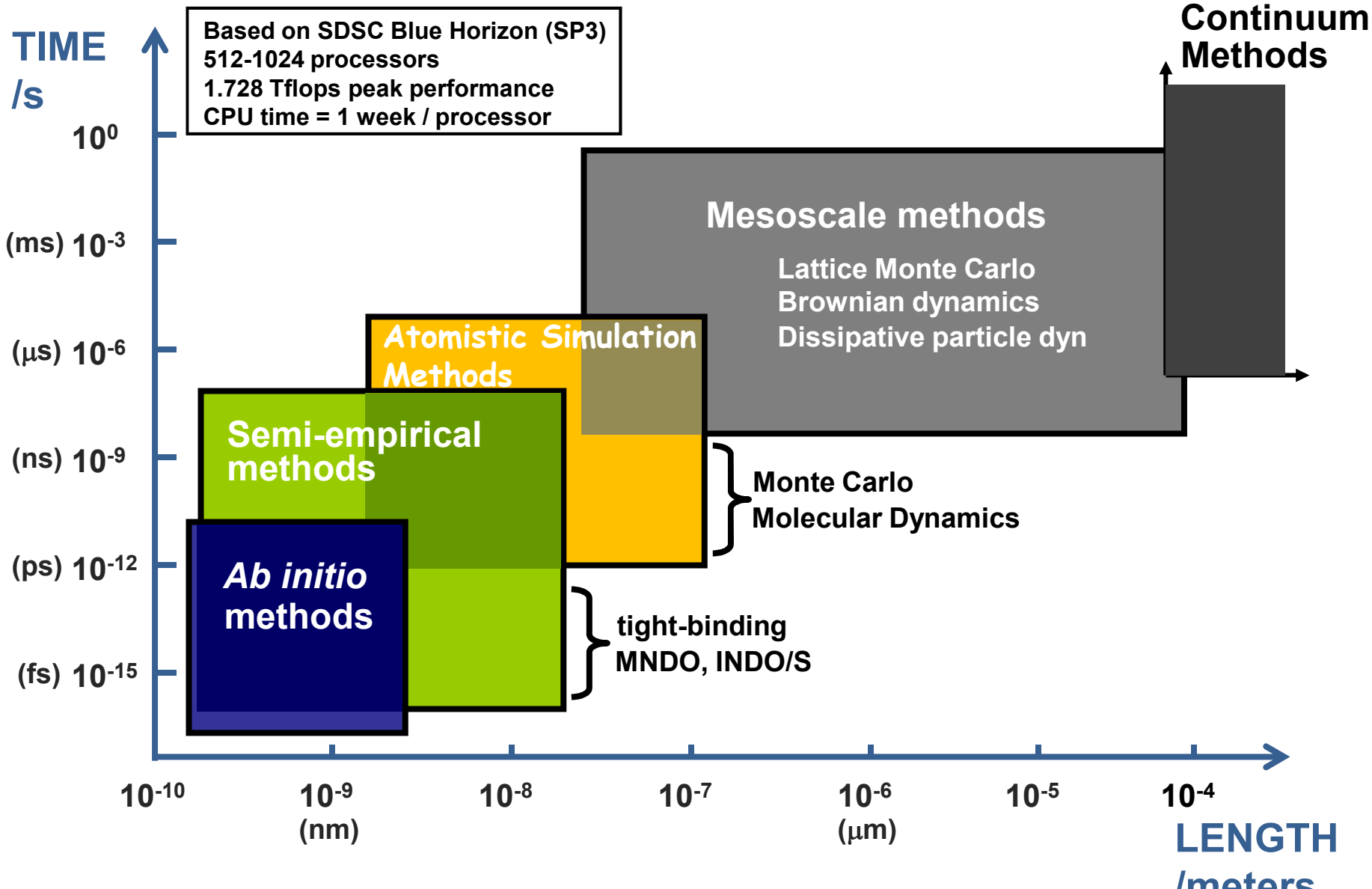
μ m –nm

N electrons

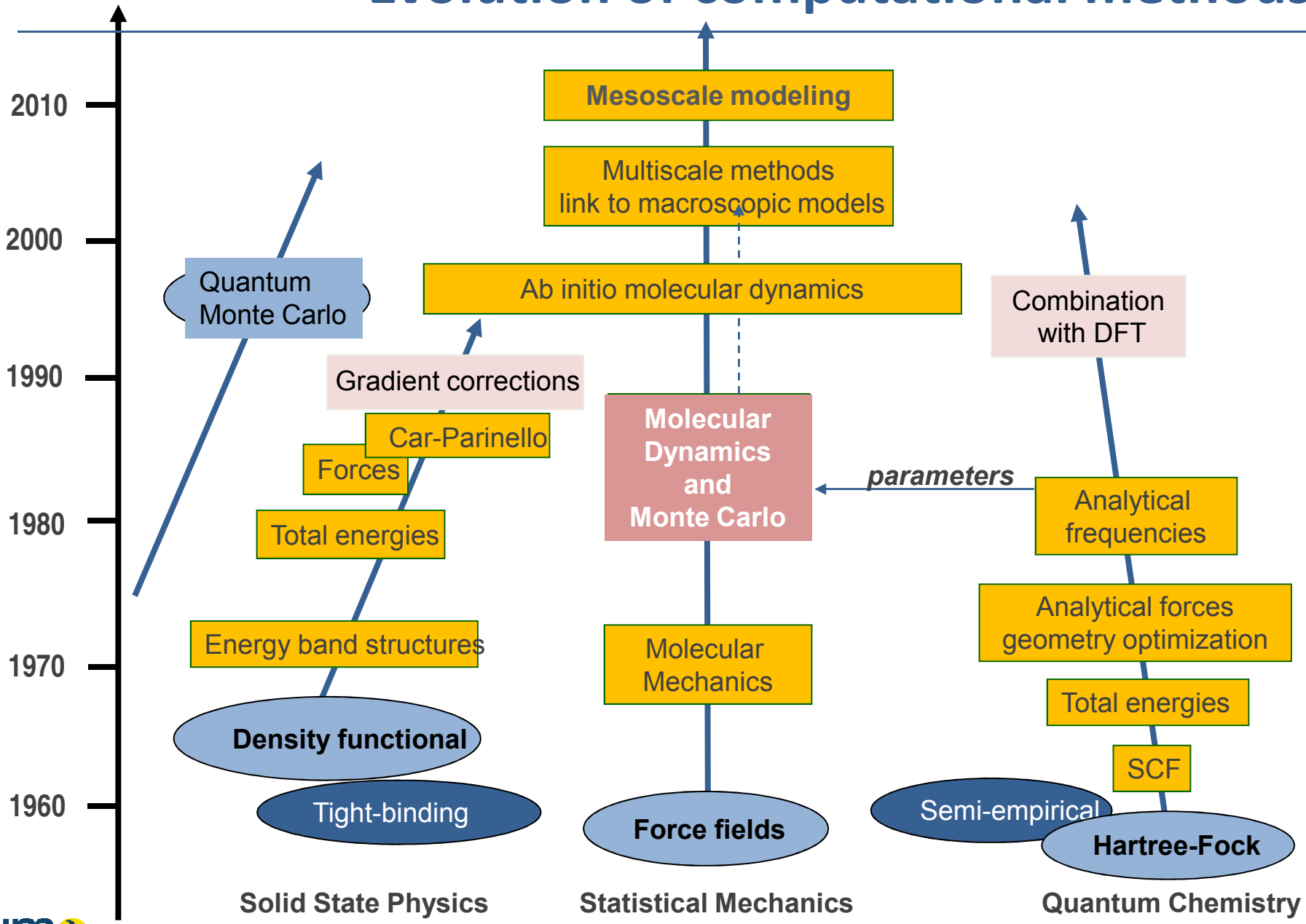


nm

Theory and simulations scales.



Evolution of computational methods.



Which computational method?

Hypothèse ergodique

$\langle A(\mathbf{r}(t), \mathbf{p}(t))\rangle_{time} = \langle A(\mathbf{r}, \mathbf{p})\rangle_{states}$

Molecular Dynamics

Exploration of the energy surface in a dynamic way, by solving the Newton equation of motion

$$\dot{r}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{m_i}$$

$$\dot{p}_i = -\frac{\partial H}{\partial r_i} = -\frac{\partial U}{\partial r_i} = F_i(r_i,...,r_N)$$

Choice of Δt: it has to be relatively small in comparison with the typical oscillation time of the studied phenomenon

Monte Carlo

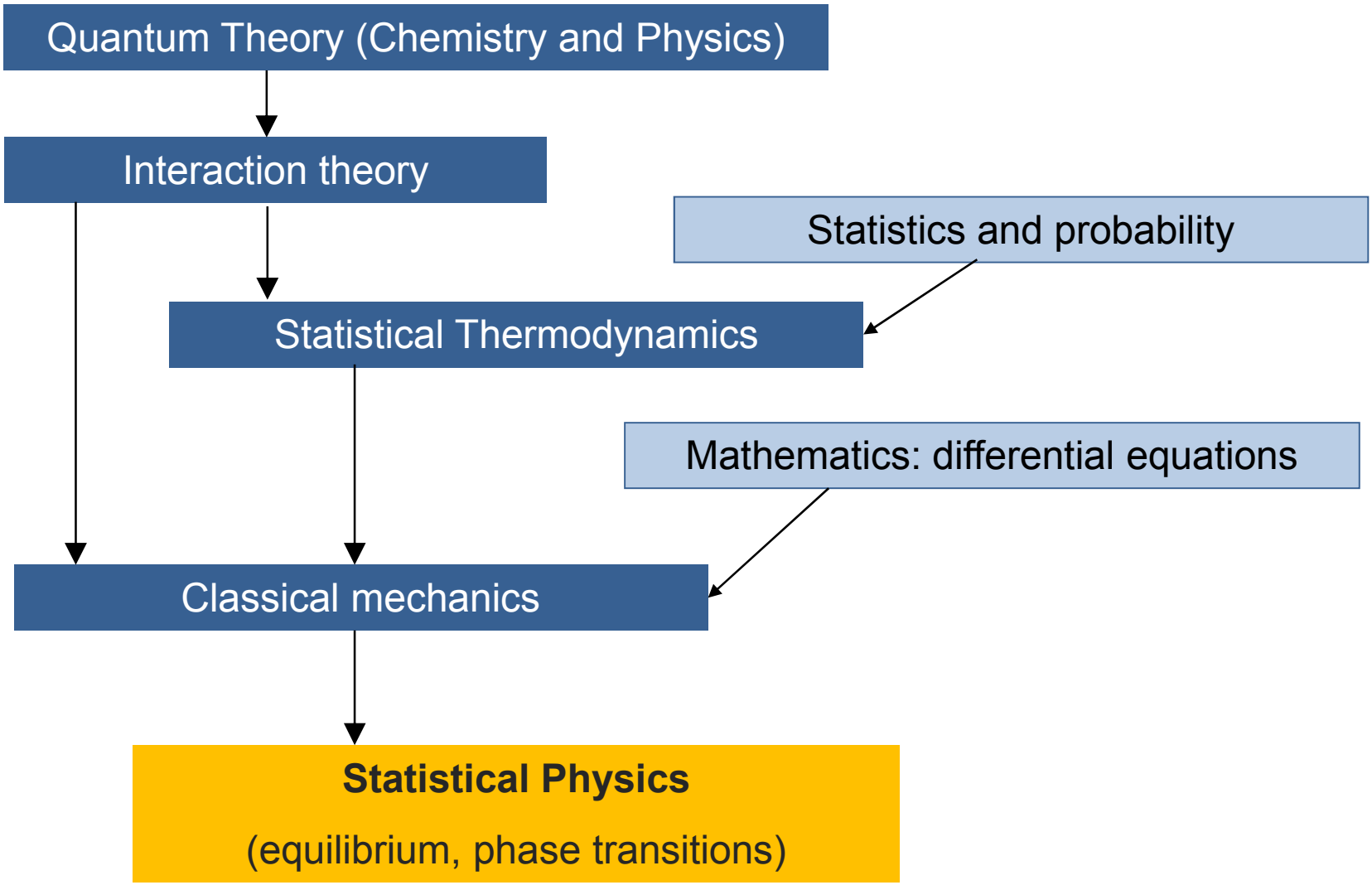
Stochastic generation of microstates with probability :

$$p_k = C\exp(-\frac{E_k}{k_B T})$$

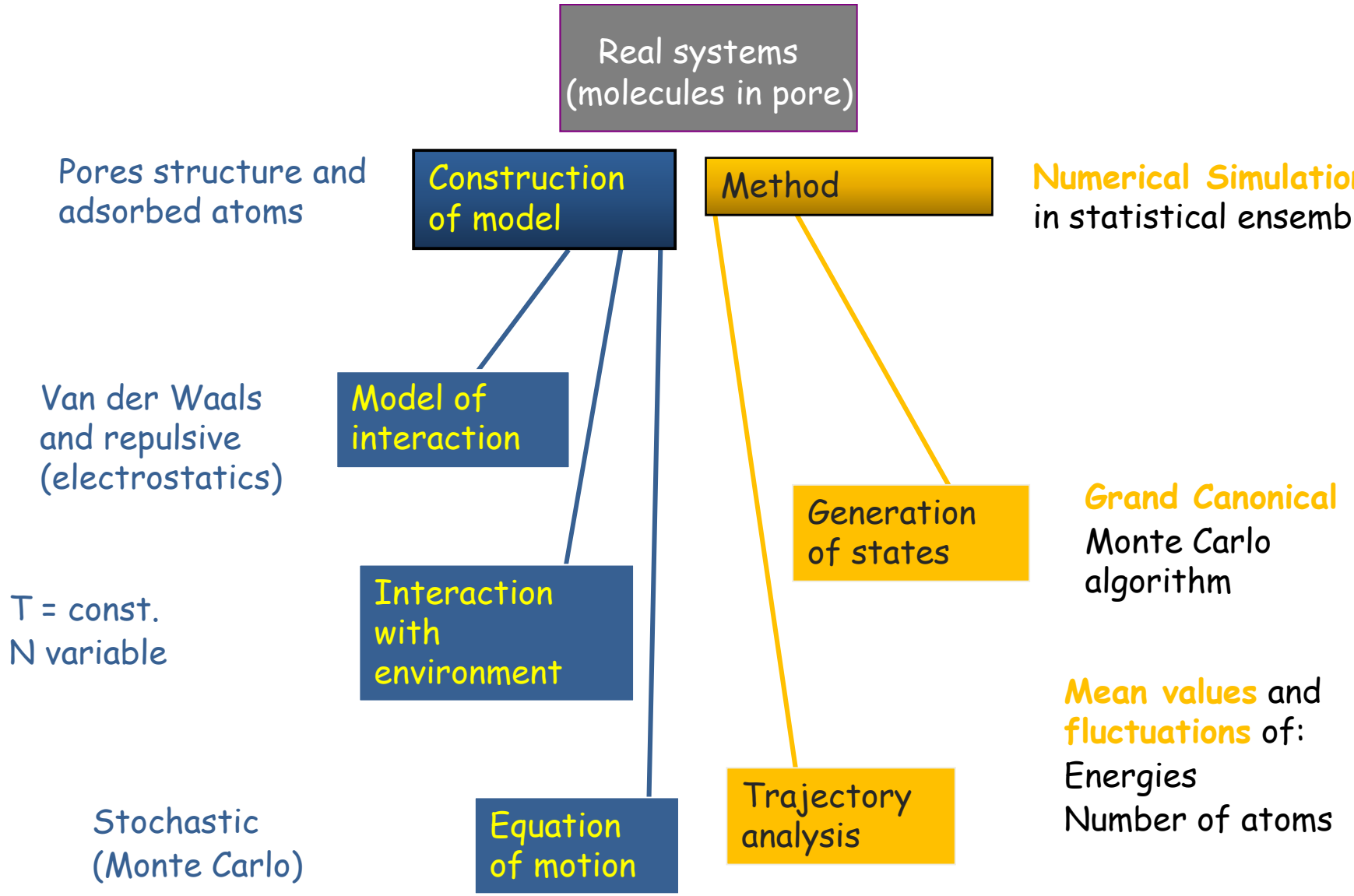
where E_k – potential energy (NVT)
potential energy +pV (NpT)
...

Choice of p_k: it has to avoid trapping in unphysical metastable states.

Numerical modeling.



Numerical simulations: how?



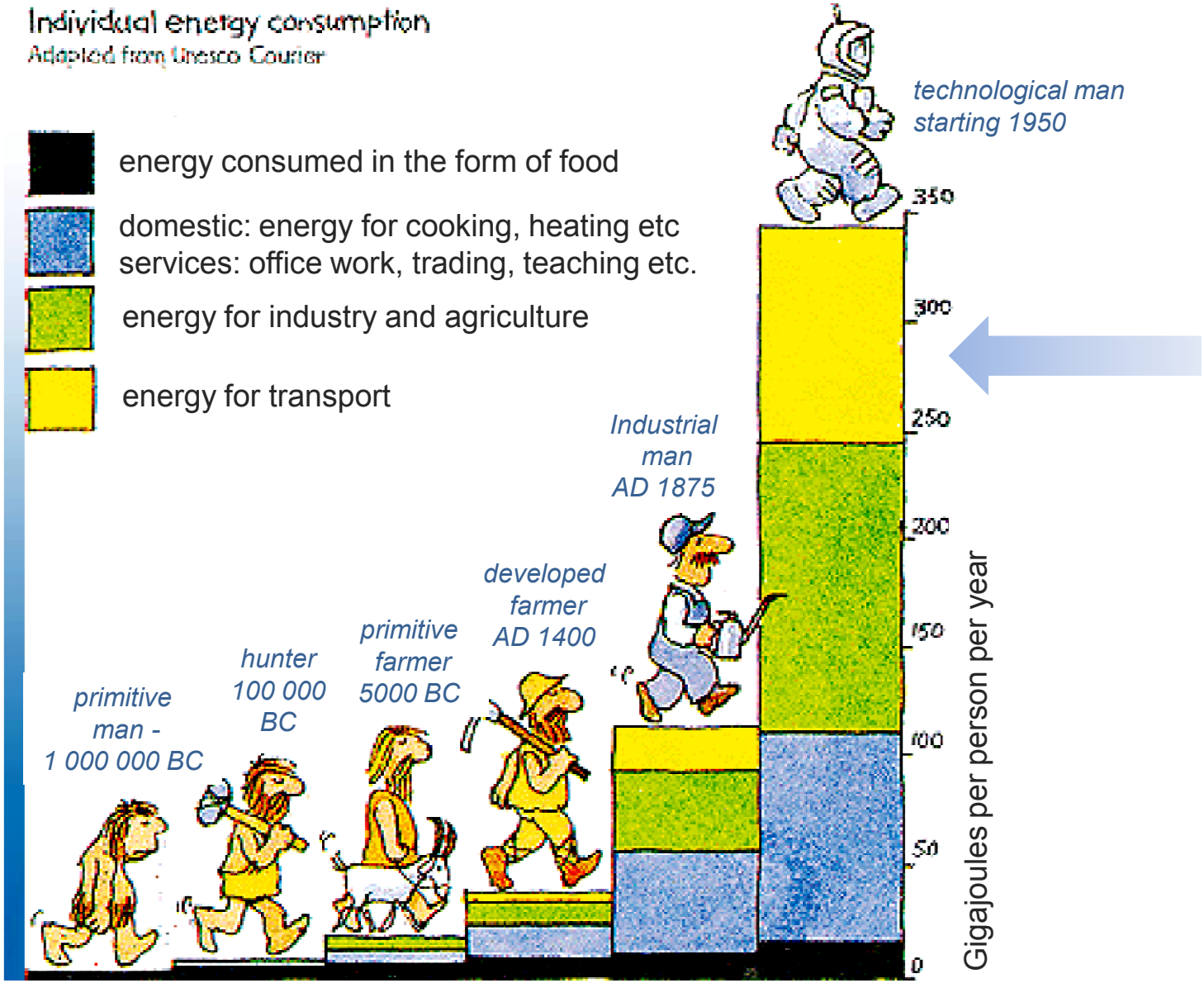
Working case.

Simulations of gas storage in a porous material

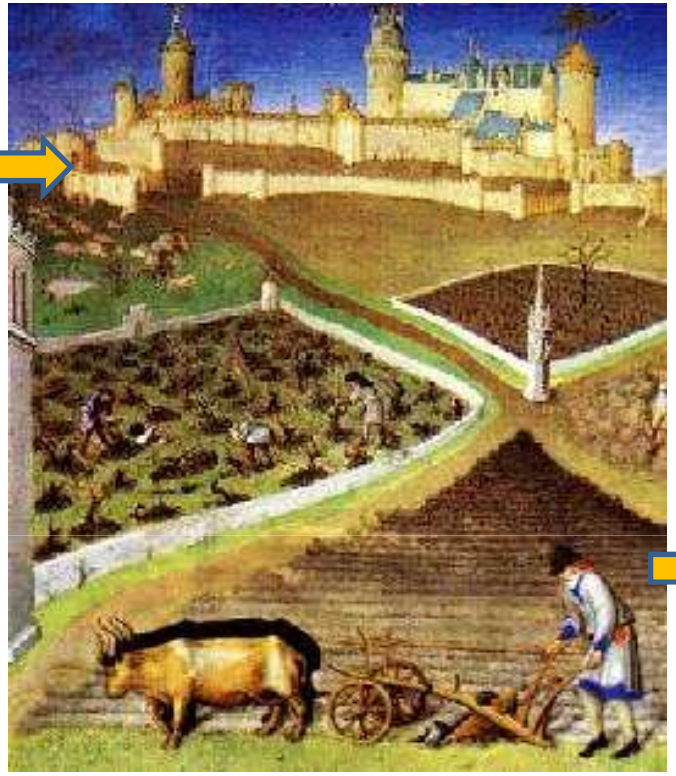
(goal: fuel storage for vehicular applications)

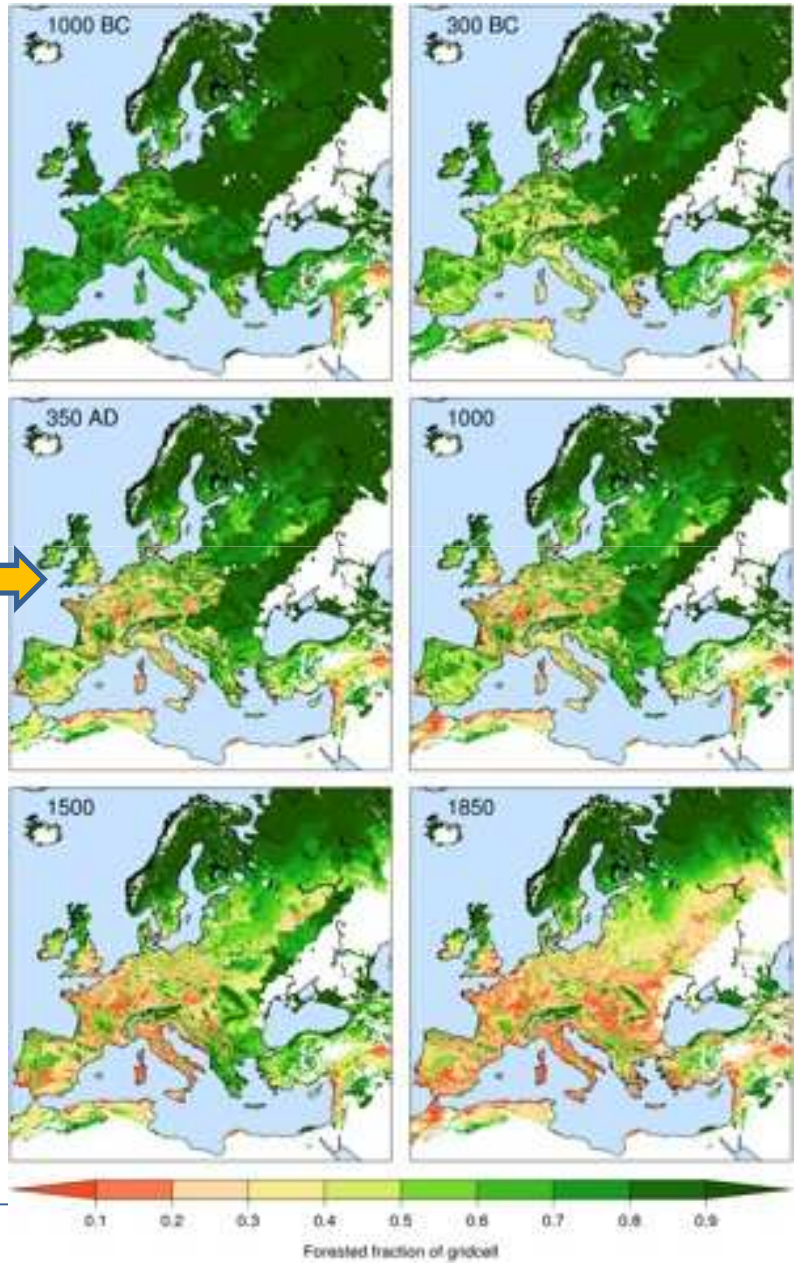
Saudi saying:
My father rode a camel,
I rode a car,
my son rides jet airplanes…
His son will ride a camel.

Context: energy consumption.



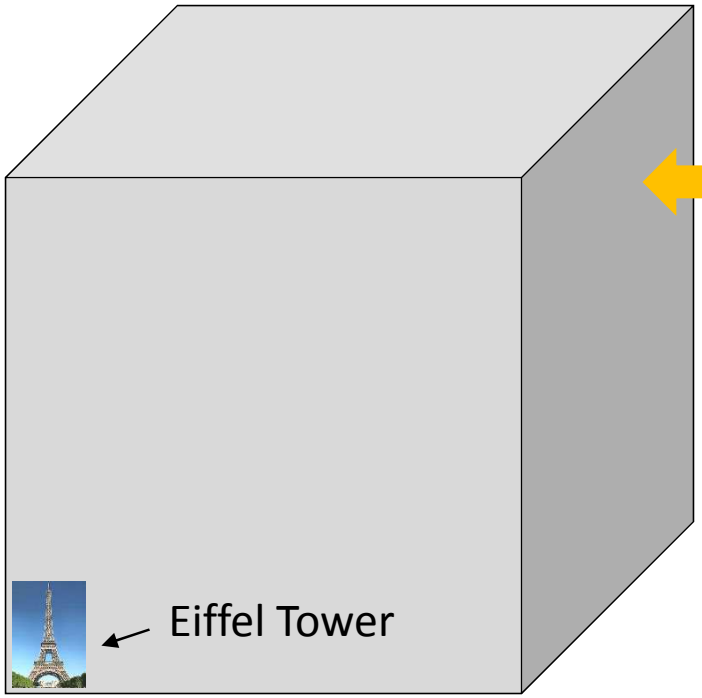
Natural resources depletion 1: preindustrial era.





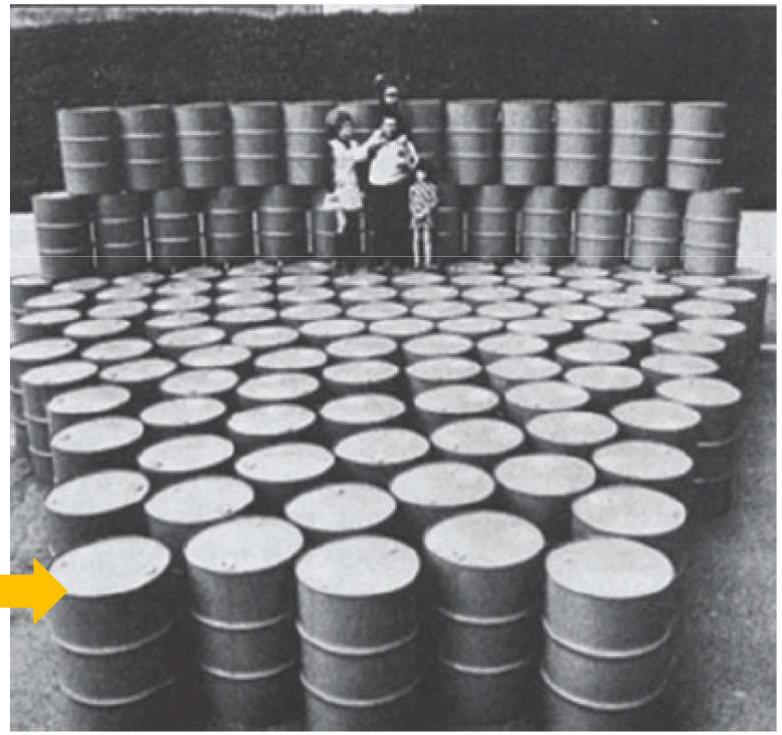
Almost 90% of Europe was once covered by forests; the majority was cut-down for fuel and/or for agricultural use.

Natural resources depletion 2: today (fossil fuels).



In 2008 the world 'gobbled up'
~ 1 cubic mile (4.2 km^3) of oil.
Approx. 1,000 barrels/second!

An american family surrounded by the oil it consumed annually in the 1970's (currently 40% higher).

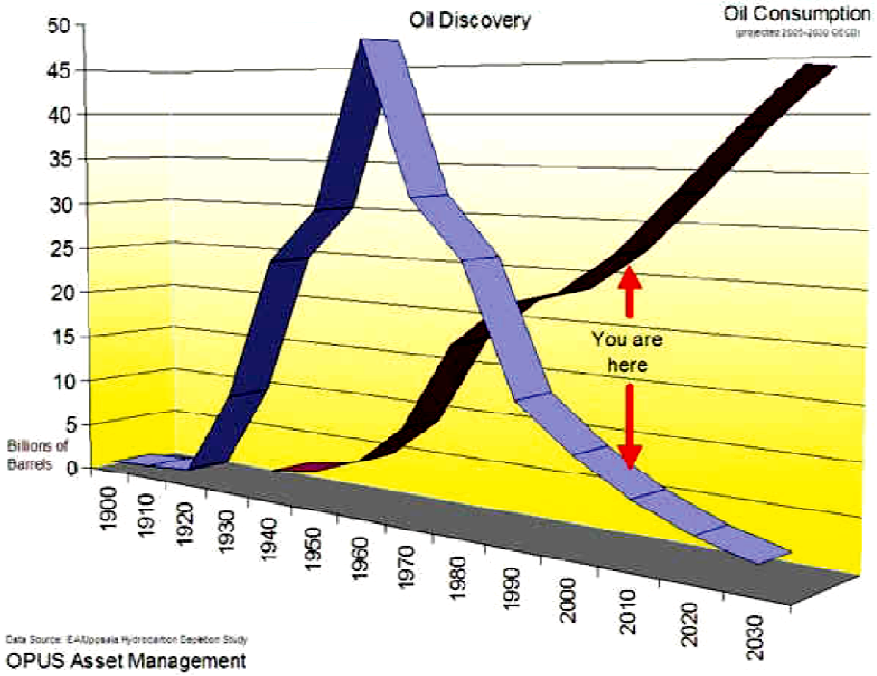


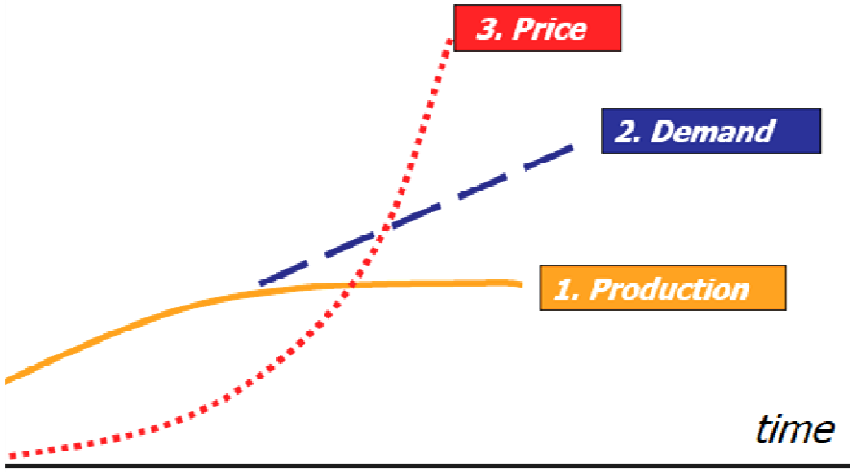
The Future of Energy Supply: Challenges and Opportunities
N. Armaroli, V. Balzani, Angew. Chem. Int. Ed. **46**, 52 (2007).

Natural resources depletion 3: tomorrow.

Presently we are 'finding' one new barrel of oil for every four we use.

What will happen
when demand exceeds supply?





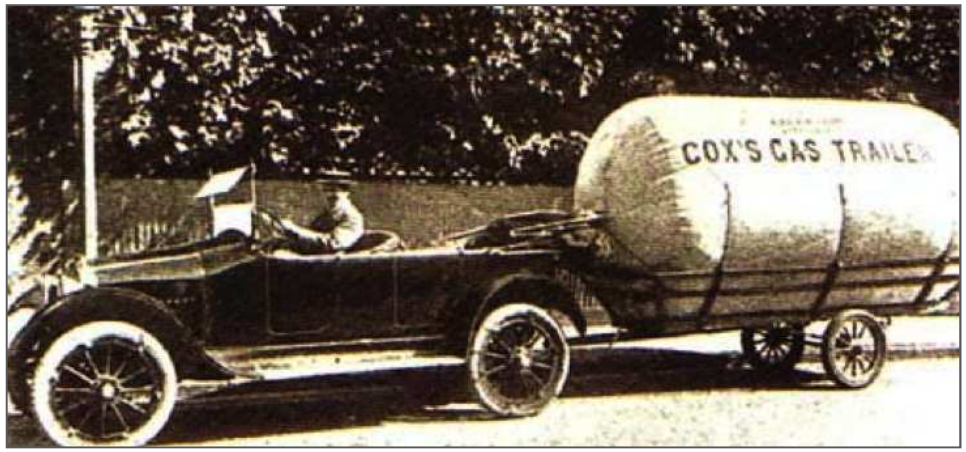
Alternative for vehicular applications.

Some numbers

Substance	MJ/l	MJ/kg
Gasoline	40	50
Ethanol	25	30
Methanol	18	20
Diesel	40	45
CH_4	25	55
Propane (C_3H_8)		50
H_2		121

Gas storage: past and present

First NG vehicle, 1910, USA



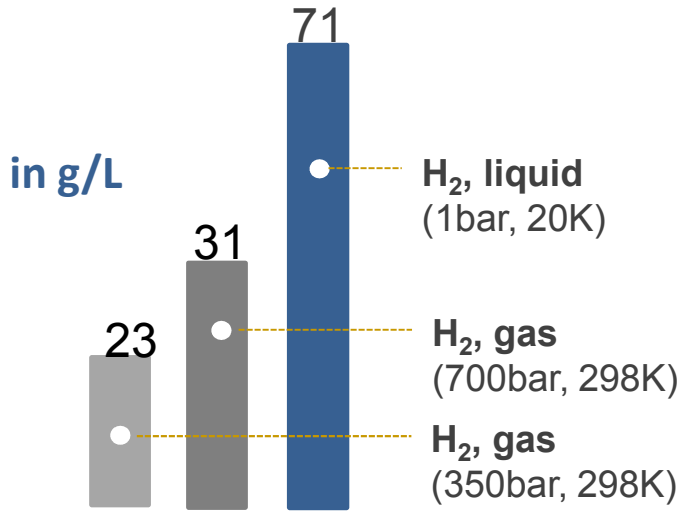
~1930, France

Current NG vehicle
with high-pressure tank in trunk
Problem: Trunk space is gone!

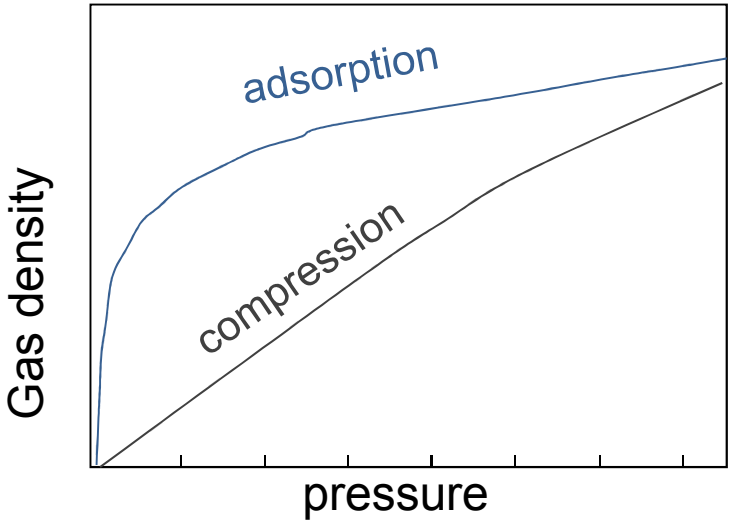
CNG ~200 bar

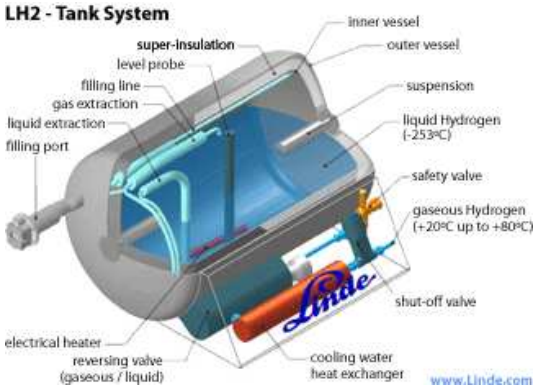
Gas storage: how?

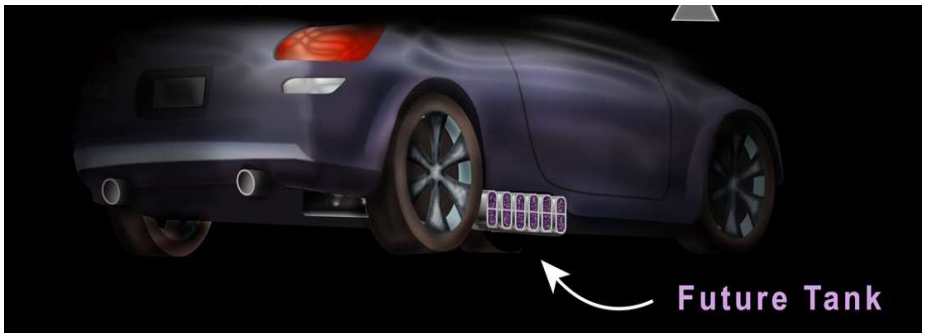
Compression and liquefaction



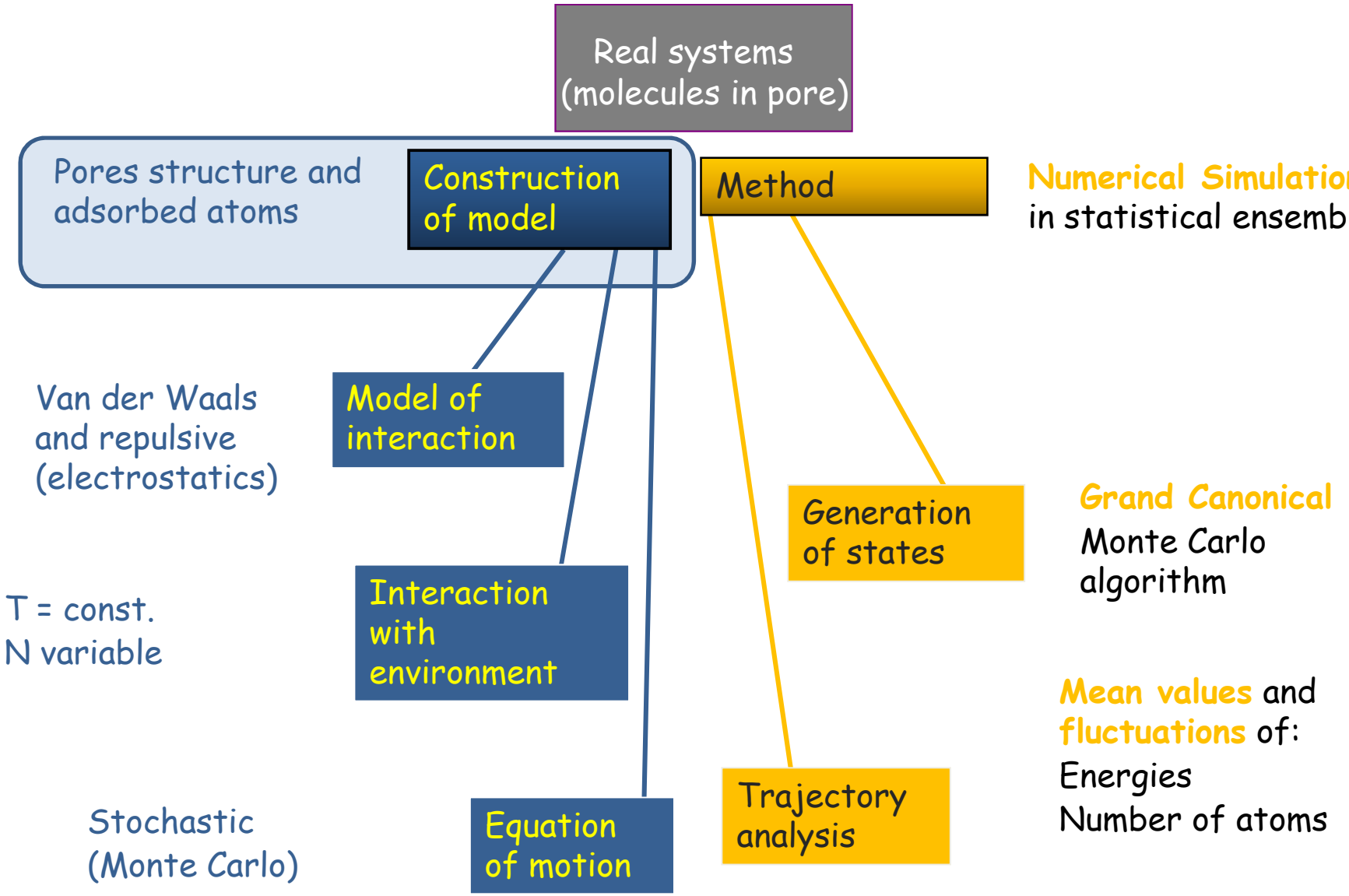
Physisorption







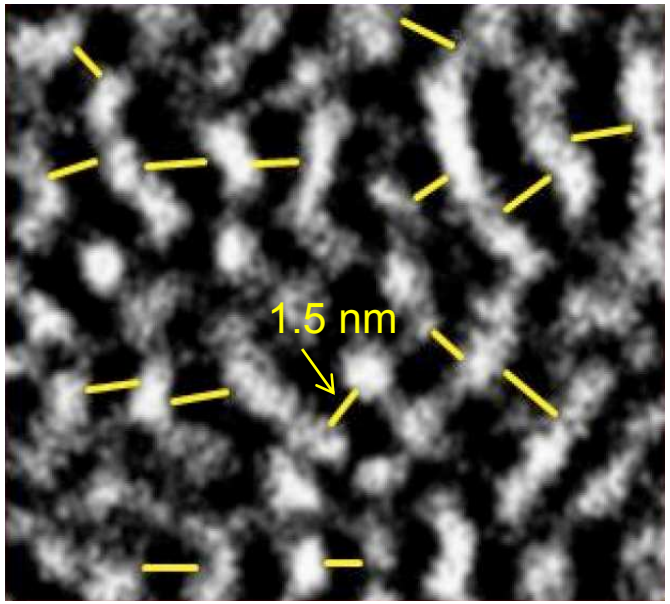
Numerical simulations: how?



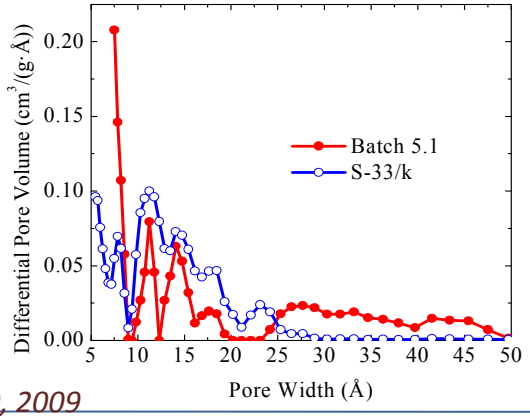
Porous carbons.

- can be prepared from
  - almost any organic precursor (polymers, carbides etc.)
  - almost any agriculture waste (corncobs, coco, cacao or peanut shells….)

Corncob – derived activated carbon.



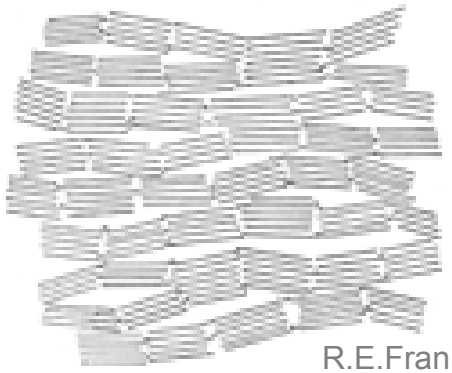
- are almost totally micro- and mezoporous (no macroporosity)



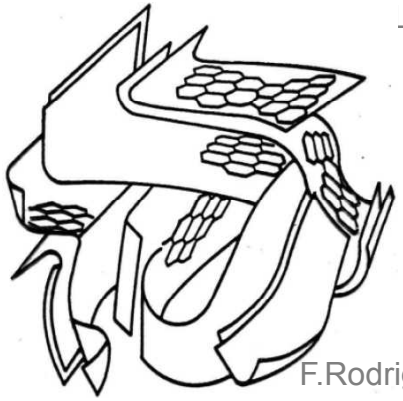
Nanotechnology 20, 2009

Models of porous carbons.

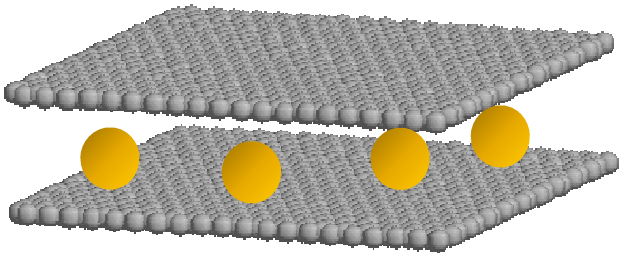
more or less locally parallel graphite-like structures

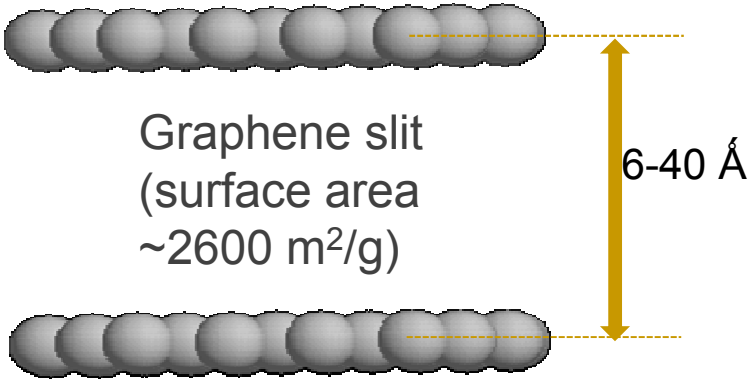


R.E.Franklin, Proc.Roy. London 209. 1951



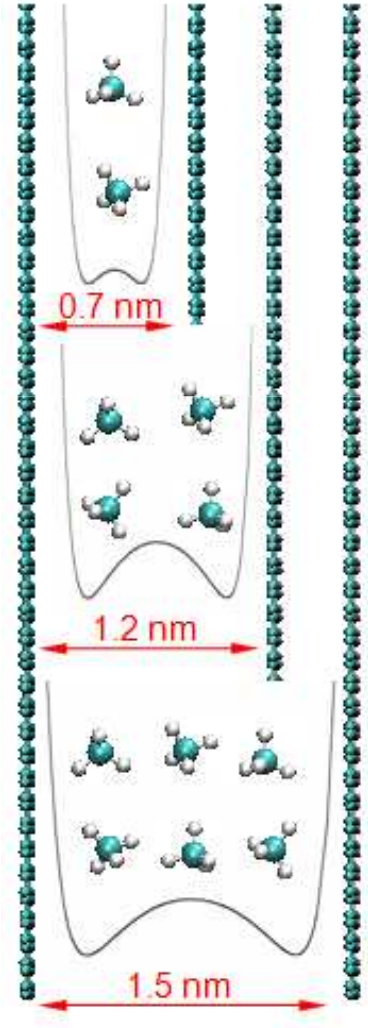
F.Rodriguez Reinoso, 2007





J.Romanos,APS 2010

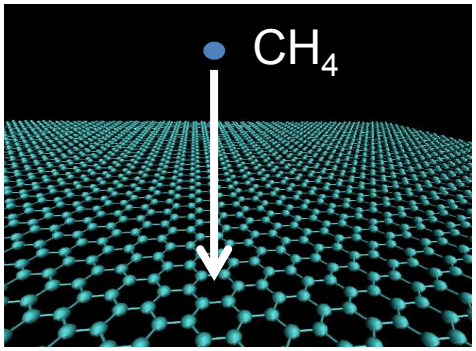
Models of porous carbons



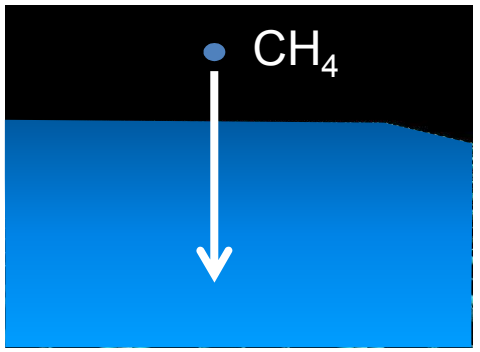
our model:

1. pore wall = rigid (no wall deformation allowed)
2. wall structure atomically resolved
   (or not, we will check if such precision is necessary)

atomic wall

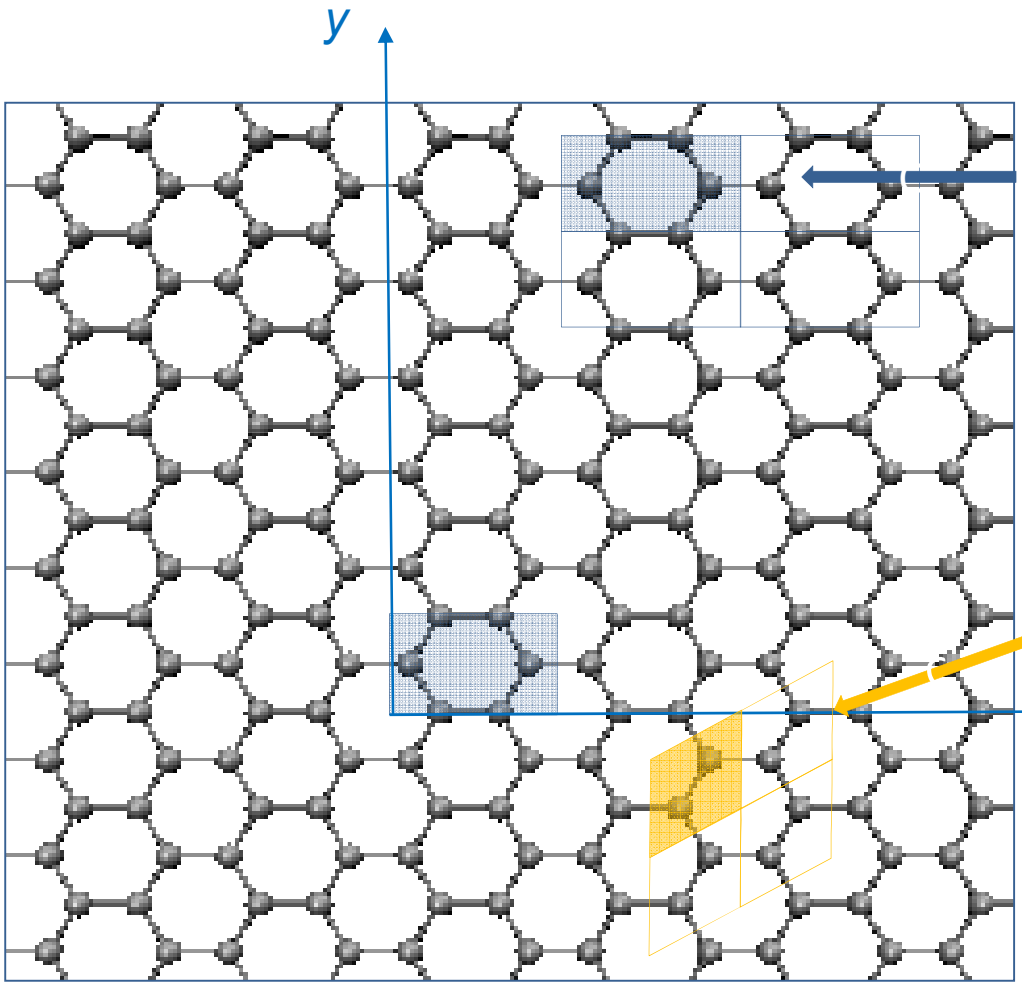


smooth wall



1 step: building graphene surface.

Basic information: C-C distance *d* = 1.42 Å

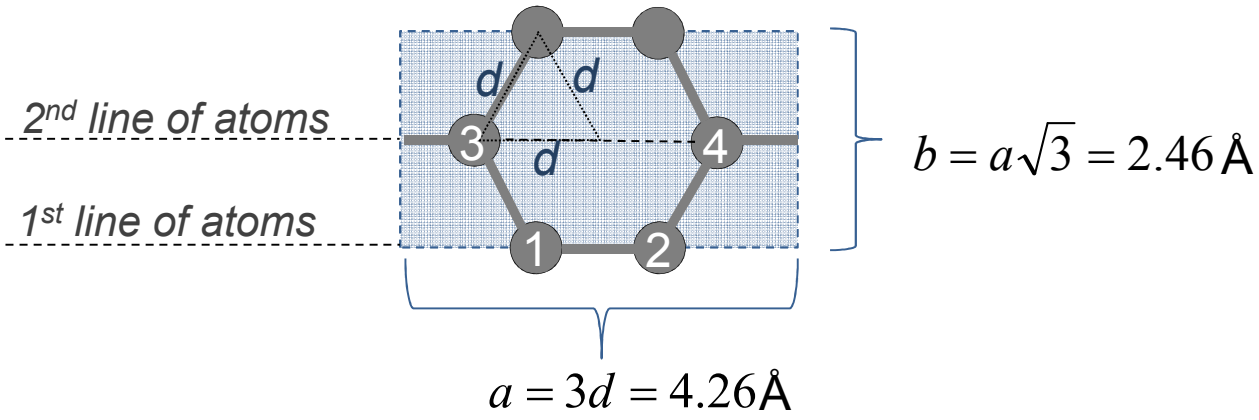


"simulations" unit cell: orthogonal (if possible)

crystallographic unit cell: minimal number of atoms (here, 2)

1 step: building graphene surface.

Basic information: C-C distance *d* = 1.42 Å



Carbon coordinates:

1st line: $x_{1c} = 1.42 + (n_x\text{-}1)\cdot 4.26$
$x_{2c} = 2.84 + (n_x\text{-}1)\cdot 4.26$
$y_{1c} = y_{2c} = 0$

2nd line: $x_{3c} = 0.71 + (n_x\text{-}1)\cdot 4.26$
$x_{4c} = 3.55 + (n_x\text{-}1)\cdot 4.26$
$y_{3c} = y_{4c} = 1.23$

To do for the next time:

1. write the code generating the surface of graphite of given dimension;

2. generate slit pores of the surface 10 x 20 graphene unit cells of 4 different widths: 10 Å, 15 Å, 20 Å et 25 Å;

3. visualize the slits (gnuplot, origin, vmd, rasmol….).

```
      Program Substrate_Generation
* *** **************************************************
*  Generates  surfaces and slit pores of graphene
*        You need to:  1. choose the number of unit cells to generate
*                      2. choose the pore width
* *** **************************************************
```

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