



Simulation methods in Physics:

Core concepts

Luís Marques, Marta M. D. Ramos

Computational and theoretical physics group

University of Minho, Department and Centre of Physics,

Campus de Gualtar, Braga, Portugal



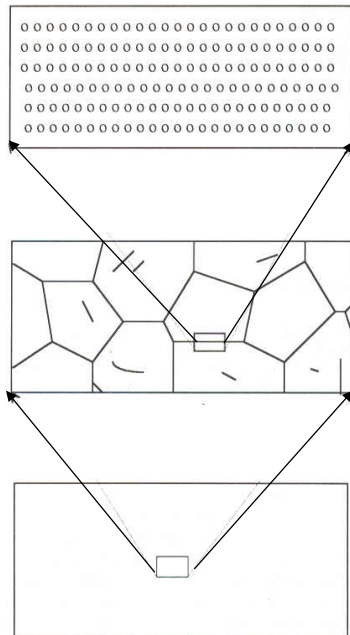
Outline

- 1 – Introduction
- 2 – Computational quantum mechanical techniques
- 3 – Dynamical relaxation techniques: quantum and classical molecular dynamics methods
- 4 – Monte Carlo methods
- 5 – Particle methods for kinetic equations



1 – Introduction

Materials manifests properties that can be investigated over a wide range of length scales:



Scales

Microscopic (< 1nm)

Describe the regime of discrete atoms

Mesoscopic (1nm – 1mm)

Describe the whole range of intermediate length scales between microscopic and macroscopic scales

Macroscopic (> 1mm)

Describe the regime where the internal structure of the material is suppressed entirely

Computational techniques

Quantum mechanical methods

Classical and quantum molecular dynamics

Generalised Monte-Carlo methods

Continuum theoretical methods

Pantelides, S.T., (1994), "Frontiers in computational materials science", Comput. Mater. Sci., 2, 149-155.

1 – Introduction

- Atomic-scale calculations, such as quantum molecular dynamics (working for systems with thousand of atoms – length scale $\leq 5\text{nm}$; time scale $\leq \text{ps}$) and classical molecular dynamics (working for systems with hundred million of atoms – length scale $\leq 100\text{nm}$; time scale $\leq \text{ns}$) describe the properties of local regions.
- The properties of nanocomposites, especially electrical and mechanical, are determined by the collective properties of the mesoscopic structure.
- Generalised Monte-Carlo methods, with input parameters obtained by atomic-scale calculations, can provide the collective properties of the mesoscopic structure at time mesoscopic structure at time scales that many processes in nanocomposites occur.
- By suitable statistical averaging of the mesoscopic properties, one can obtain the fundamental laws of continuum theories without any empirical postulates whatever.
- We advocate a systematic link from microscopic theories through the mesoscopic regime to the macroscopic continuum. Such an approach can form the basis for a first-principles theory of electrical and mechanical properties of nanocomposites.

2 – Computational quantum mechanical techniques

2.1 – The Schrödinger equation of molecular systems

- The starting point of any theoretical description of the electronic structure of molecular systems is the time-dependent Schrödinger equation.
- When the time-dependent inter-particle interactions can be neglected, we can use the time-independent Schrödinger equation.
- According to quantum mechanics the complete description of the movement of N electrons and M nuclei of a system requires the solution of the Schrödinger equation:

$$\hat{H} \Psi(q_i, q_A) = E \Psi(q_i, q_A) \quad (1)$$

where

$\hat{H} \rightarrow$ Hamiltonian of the system

$\Psi(q_i, q_A) \rightarrow$ Wave function of the system in a state with energy E

$q_i (i = 1, 2, \dots, N) \rightarrow$ Electrons coordinates

$q_A (A = 1, 2, \dots, M) \rightarrow$ Nuclei coordinates

The Schrödinger equation (1) can not be solved without using several approximations.

2 – Computational quantum mechanical techniques

2.2 – The basic approximations

2.2.1 – Non-relativistic Hamiltonian

Neglecting all the relativistic effects (such as spin-orbital and spin-spin interactions), the non-relativistic Hamiltonian of the system (in SI units) is given by:

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} \quad (2)$$

where

$$\hat{T}_n = -\sum_{A=1}^M \frac{\hbar^2}{2M_A} \nabla_A^2 \rightarrow \text{kinetic energy operator for nuclei}$$

$$\hat{T}_e = -\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 \rightarrow \text{kinetic energy operator for electrons}$$

$$\hat{V}_{ee} = \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \rightarrow \text{potential energy operator for electronic repulsions}$$

$$\hat{V}_{en} = -\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_A|} \rightarrow \text{potential energy operator for nuclear- electronic attractions}$$

$$\hat{V}_{nn} = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B e^2}{4\pi\epsilon_0 |\vec{R}_A - \vec{R}_B|} \rightarrow \text{potential energy operator for nuclear repulsions}$$

$\vec{R}_A, M_A, Z_A, e \rightarrow$ position vector, mass e charge of nucleus A

$\vec{r}_i, m_e, e \rightarrow$ position vector, mass and charge of electron i

2 – Computational quantum mechanical techniques

2.2 – The basic approximations

2.2.2 – The Born-Oppenheimer approximation

➤ This approximation is based on the fact that $M_A \gg m_e$ and, for this reason, electrons move much faster than the nuclei. Therefore, the electronic density distribution will be able to adjust almost instantaneously to any nuclear motion.

➤ According to the Born-Oppenheimer approximation we can solve the Schrödinger equation for the electrons and consider the nuclei fixed in their mean positions. After the electronic problem has been solved, it is possible to consider the motion of the nuclei under the same approximation.

➤ Within this approximation, the electronic Hamiltonian (in atomic units) can be written as:

$$\hat{H}_e = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (3)$$

where

$$r_{ij} = \left| \vec{r}_i - \vec{r}_j \right|$$

$$r_{iA} = \left| \vec{r}_i - \vec{R}_A \right|$$

2 – Computational quantum mechanical techniques

2.2 – The basic approximations

2.2.2 – The Born-Oppenheimer approximation

➤ Within the Born-Oppenheimer approximation, the electronic wave function of the system, for a certain geometric configuration of the nuclei, satisfies the Schrödinger equation involving the electronic Hamiltonian

$$\hat{H}_e \Psi_e = E_e \Psi_e \quad (4)$$

➤ In calculating the internal energy of the system for stationary nuclei we need to add the nuclear repulsion energy to the electronic energy:

$$E = E_e + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (5)$$

where

$$R_{AB} = \left| \vec{R}_A - \vec{R}_B \right|$$

2 – Computational quantum mechanical techniques

2.3 – *Ab initio* Molecular Orbital Theories (MO)

2.3.1 – Obtained from the theory of Hartree-Fock (HF)

Additional approximations in the electronic calculations:

↳ Independent-electron approximation:

Each electron is moving in the potential of the nuclei and the average potential of the other electrons.

According to this approximation, the one-electron wave function, called spin-orbital, is given by

$$\psi(\vec{r}\sigma) = \chi(\vec{r})\sigma \quad (6)$$

Pauli exclusion principle

The simplest many-electron wave function that satisfies this requirement is the Slater determinant of spin-orbitals

$$\Psi_e(\vec{r}_1\sigma_1, \dots, \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1\sigma_1) & \dots & \psi_N(\vec{r}_1\sigma_1) \\ \vdots & & \vdots \\ \psi_1(\vec{r}_N\sigma_N) & \dots & \psi_N(\vec{r}_N\sigma_N) \end{vmatrix} \quad (7)$$

$\chi(\vec{r}) \rightarrow$ Function of electron spatial coordinates

$\sigma \rightarrow$ Function of spin (α or β)

2 – Computational quantum mechanical techniques

2.3 – *Ab initio* Molecular Orbital Theories (MO)

2.3.1 – Obtained from the theory of Hartree-Fock (HF)

The electronic energy of the system is given by

$$E_e[\Psi_e] = \frac{\langle \Psi_e | \hat{H}_e | \Psi_e \rangle}{\langle \Psi_e | \Psi_e \rangle} \quad (8)$$

Including equations (3) and (7) in equation (8), we obtain

$$E_e = \langle \Psi_e | \hat{H}_e | \Psi_e \rangle = \sum_{i=1}^N H_{ii} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) \quad (9)$$

where

$$H_{ii} = \langle \psi_i | \hat{h} | \psi_i \rangle = \int d^3r \chi_i^*(\vec{r}) \left(-\frac{1}{2} \nabla^2 - \sum_{A=1}^M \frac{Z_A}{|\vec{r} - \vec{R}_A|} \right) \chi_i(\vec{r})$$

$J_{ij} = (ij | ij) \rightarrow$ Coulomb integral

$K_{ij} = (ij | ji) \rightarrow$ exchange integral

and

$$\begin{aligned} (ij | kl) &= \langle \psi_i \psi_j | \hat{v} | \psi_k \psi_l \rangle = \\ &= \delta_{\sigma_i \sigma_k} \delta_{\sigma_j \sigma_l} \iint d^3r d^3r' \chi_i^*(\vec{r}) \chi_k(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \chi_j^*(\vec{r}') \chi_l(\vec{r}') \end{aligned}$$

$$H_{ii} = \int d^3r \chi_i^*(\vec{r}) \left(-\frac{1}{2} \nabla^2 - \sum_{A=1}^M \frac{Z_A}{|\vec{r} - \vec{R}_A|} \right) \chi_i(\vec{r}) \quad (3)$$

$$\Psi_e(\vec{r}_1\sigma_1, \dots, \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1\sigma_1) & \dots & \psi_N(\vec{r}_1\sigma_1) \\ \vdots & & \vdots \\ \psi_1(\vec{r}_N\sigma_N) & \dots & \psi_N(\vec{r}_N\sigma_N) \end{vmatrix} \quad (7)$$

2 – Computational quantum mechanical techniques

2.3 – *Ab initio* Molecular Orbital Theories (MO)

2.3.1 – Obtained from the theory of Hartree-Fock (HF)

- In order to obtain the wave function Ψ_e that minimize the electronic energy of the system, we need to use the variational principle

$$\delta \left(\frac{\langle \Psi_e | \hat{H}_e | \Psi_e \rangle}{\langle \Psi_e | \Psi_e \rangle} \right) = 0 \quad (10)$$

- To introduce variations in Ψ_e , we have to change each spin-orbital, $\psi_i(\vec{r}\sigma)$
- We have to minimize the electronic energy with respect to the spin-orbitals $\psi_i(\vec{r}\sigma)$ subject to the condition that they remained normalized $\langle \psi_i | \psi_i \rangle = 1$. This problem can be solved using the Lagrange's multiplier method and we obtain:

$$\delta \left(\langle \Psi_e | \hat{H}_e | \Psi_e \rangle - \sum_{i=1}^N E_i \langle \psi_i | \psi_i \rangle \right) = 0 \quad (11)$$

$E_i \rightarrow$ Lagrange's multiplier

2 – Computational quantum mechanical techniques

2.3 – *Ab initio* Molecular Orbital Theories (MO)

2.3.1 – Obtained from the theory of Hartree-Fock (HF)

- If we include equation (9) in equation (11), we obtain

$$\sum_{i=1}^N \left\{ \langle \delta \psi_i | \hat{h} | \psi_i \rangle + \sum_{j \neq i}^N \left[\langle \delta \psi_i | \psi_j | \hat{v} | \psi_i \psi_j \rangle - \langle \delta \psi_i | \psi_j | \hat{v} | \psi_j \psi_i \rangle \right] - E_i \langle \delta \psi_i | \psi_i \rangle \right\} = 0 \quad (12)$$

where

$$\hat{h} = -\frac{1}{2} \nabla^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \quad \hat{v} = \frac{1}{r_{ij}}$$

- As $\delta \psi_i$ is an arbitrary quantity, then equation (12) leads to the Hartree-Fock equations

$$\hat{F} | \psi_i \rangle = E_i | \psi_i \rangle \quad (13)$$

Where the matrix elements associated to the Fock operator, \hat{F} , are given by

$$F_{ij} = H_{ij} + \sum_{k=1}^N \left[(ik | jk) - (ik | kj) \right] \quad (14)$$

- Since $E_i = \langle \psi_i | \hat{F} | \psi_i \rangle$ and comparing the equation (14) with the equation (9), we see that the electronic energy of the system can be written as

$$E_e = \sum_{i=1}^N E_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N [J_{ij} - K_{ij}] \quad (15)$$

$$E_e = \langle \Psi_e | \hat{H}_e | \Psi_e \rangle = \sum_{i=1}^N H_{ii} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) \quad (9)$$

$$\delta \left(\langle \Psi_e | \hat{H}_e | \Psi_e \rangle - \sum_{i=1}^N E_i \langle \psi_i | \psi_i \rangle \right) = 0 \quad (11)$$



2 – Computational quantum mechanical techniques

2.3 – *Ab initio* Molecular Orbital Theories (MO)

2.3.1 – Obtained from the theory of Hartree-Fock (HF)

□ If we build the molecular orbitals χ_i as a linear combination of the atomic orbitals Φ_μ we obtain

$$\chi_i = \sum_{\mu} C_{\mu i} \Phi_{\mu} \quad (16)$$

□ The application of the variational principle to the electronic function, where the molecular orbitals χ_i are linear combination of atomic orbitals Φ_μ and the coefficients are the variational parameters, leads to the following system of homogeneous equations

$$\sum_{\nu} C_{\nu i} (F_{\mu\nu} - E_i S_{\mu\nu}) = 0 \quad (17)$$

where

$$S_{\mu\nu} = \langle \Phi_{\mu} | \Phi_{\nu} \rangle$$

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda} \sum_{\rho} P_{\lambda\rho} \left[(\mu\nu | \lambda\rho) - \frac{1}{2} (\mu\rho | \lambda\nu) \right]$$

and

$$P_{\lambda\rho} = \sum_i^N C_{\lambda i}^* C_{\rho i}$$

$$(\mu\nu | \lambda\rho) = \int \int \Phi_{\mu}^*(\vec{r}) \Phi_{\nu}(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \Phi_{\lambda}^*(\vec{r}') \Phi_{\rho}(\vec{r}') d^3r d^3r'$$



2 – Computational quantum mechanical techniques

2.3 – *Ab initio* Molecular Orbital Theories (MO)

2.3.1 – Obtained from the theory of Hartree-Fock (HF)

□ Since the Hartree-Fock equations are not linear, we have to use the iterative method to solve the equations (17) and calculate the coefficients $C_{\nu i}$.

□ Once we know the values of $C_{\nu i}$ and the corresponding density matrix $P_{\mu\nu}$, the electronic energy of the system can be calculated by the expression

$$E_e = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\rho} P_{\mu\nu} P_{\lambda\rho} \left[(\mu\nu | \lambda\rho) - \frac{1}{2} (\mu\rho | \lambda\nu) \right] \quad (18)$$

$$\sum_{\nu} C_{\nu i} (F_{\mu\nu} - E_i S_{\mu\nu}) = 0 \quad (17)$$



2 – Computational quantum mechanical techniques

2.4 – Approximations involved in semi-empirical Molecular Orbital Theories

2.4.1 – The zero-differential overlap approximation

✓ This approximation is based on the fact that the differential overlap $\Phi_\mu(\vec{r})\Phi_\nu(\vec{r})$ is very small unless $\mu = \nu$ and, consequently the integrals involving these overlaps are also very small.

✓ According to this approximation the two-electron integrals which depend on the overlap of charge distribution of different orbitals are neglected, so that:

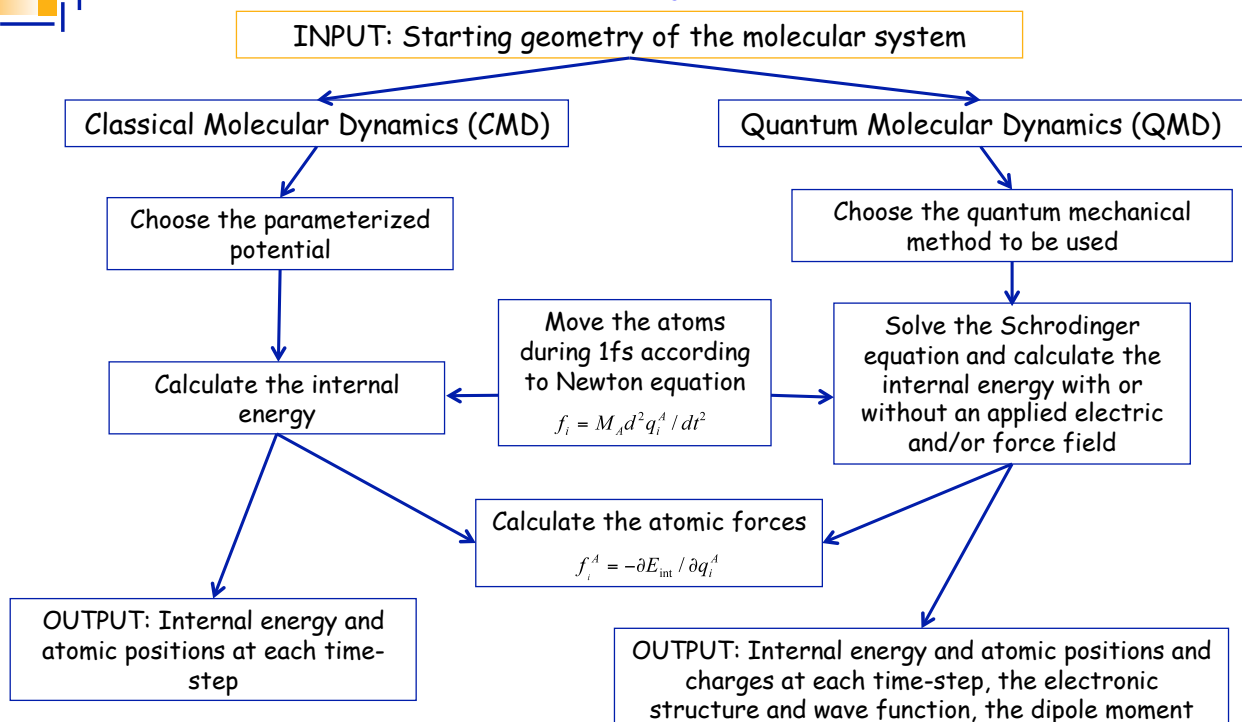
$$(\mu\nu | \lambda\rho) = (\mu\mu | \lambda\lambda) \delta_{\mu\nu} \delta_{\lambda\rho} \quad (29)$$

$$S_{\mu\nu} = \int \Phi_\mu^*(\vec{r})\Phi_\nu(\vec{r})d^3r = 0 \quad \text{para } \mu \neq \nu$$

$H_{\mu\nu} \rightarrow$ These integrals can not be neglected because they will affect the ability of bonding between different atoms in the system. Therefore, these integrals are replaced by semi-empirical parameters.

3 – Dynamical relaxation techniques

3.1 – Quantum and classical molecular dynamics methods



3 – Dynamical relaxation techniques

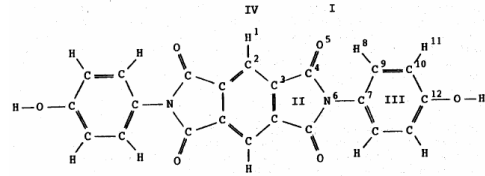
3.1 – Quantum and classical molecular dynamics methods

3.1.1 – Examples of application of QMD: adhesion between metals and polymers

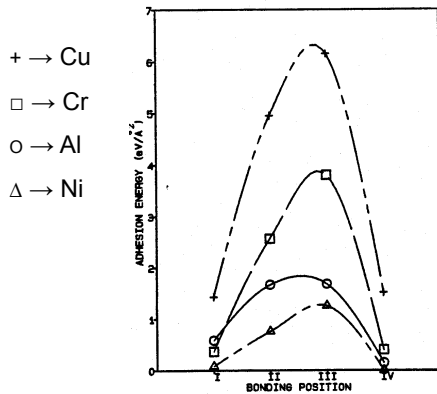
Experimental results:

The deposition of metal atoms on PMDA-ODA substrates revealed changes in XPS and HREELS line profiles associated with the carbonyl group of polyimide, which were attributed to metal bonding at carbonyl site.

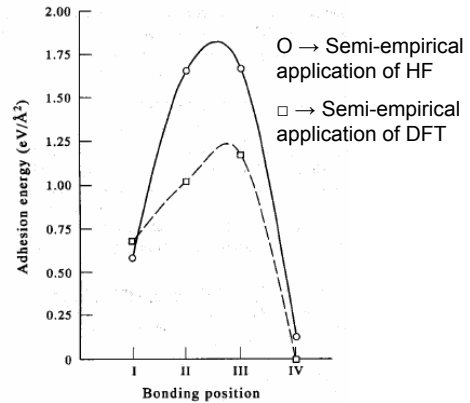
System studied:



Results obtained:



Effects of CNDO parametrization in the results obtained for Al



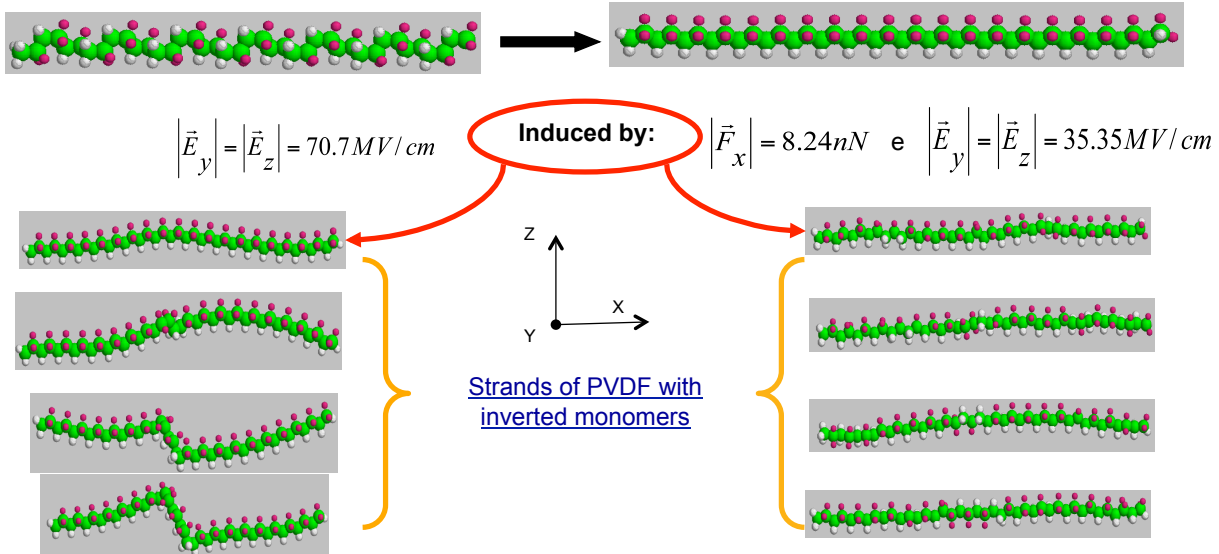
Ramos, M.M.D., (2002), "Theoretical study of metal-polyimide interfacial properties", Vacuum, 64, 255-260.

Ramos, M.M.D., Stoneham, A.M., Sutton, A.P., (1993), "Aluminum Polyimide Adhesion", Acta Metall. Mater., 41, 2105-2111.

3 – Dynamical relaxation techniques

3.1 – Quantum and classical molecular dynamics methods

3.1.1 – Examples of application of QMD: Transformation of α -PVDF in β -PVDF



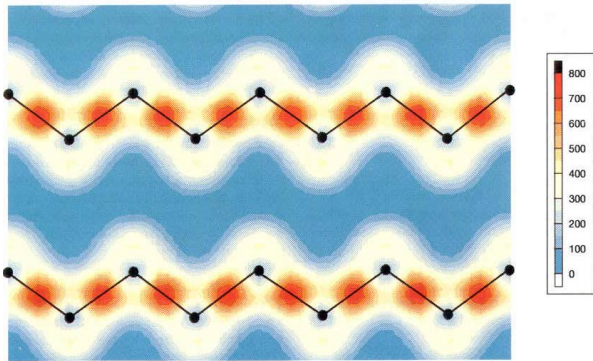
Ramos, M.M.D., Correia, H.M.G., Lanceros-Mendez, S., (2005), "Atomistic modelling of processes involved in poling of PVDF", Comput. Mater. Sci., 33, 230-236.



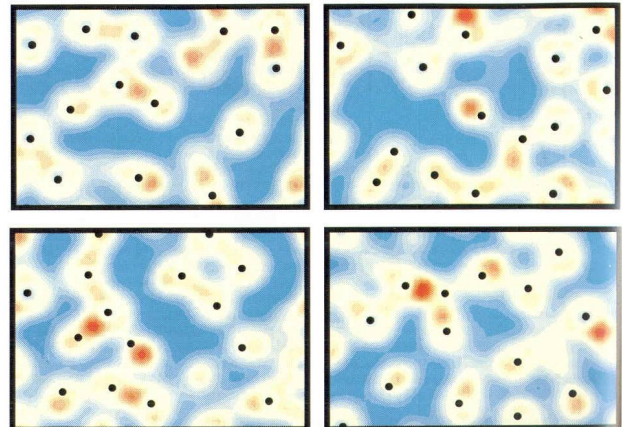
3 – Dynamical relaxation techniques

3.1 – Quantum and classical molecular dynamics methods

3.1.1 – Examples of application of QMD: the effect of temperature on charge density distribution



Charge density map for crystalline silicon. This map correspond to a (110) plane in the 64-atom simulation cell. The charge is normalized to 256 electrons in the unit cell. The atoms are shown by the black dots.



Charge density map for liquid silicon at four different times.

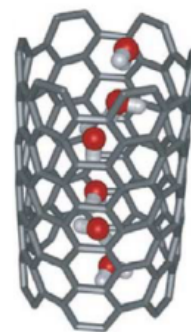
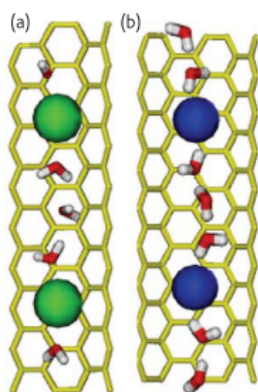
Chelikowsky, J.R., Binggeli, N., (1994), "Doing materials science with a supercomputer: on the road to 1000 atom systems", Comput. Mater. Sci., 2, 111-126.



3 – Dynamical relaxation techniques

3.1 – Quantum and classical molecular dynamics methods

3.1.1 – Examples of application of CMD: simulations of ion and water transport in charged CNTs



MD simulations of water and proton transport in CNTs

MD simulations of the ion transport in CNTs.

- (a) Snapshot of water molecules and K^+ ions in a negatively charged (5,5) CNT.
- (b) Snapshot of water molecules and Cl^- ions in a positively charged (6,6) nanotube

Noy, A., Park, H.G., Fornasiero, F., Holt, J.K., Grigoropoulos, C.P., Bakajin, O., (2007), "Nanofluidics in carbon nanotubes", Nano Today, 2, 22-29.

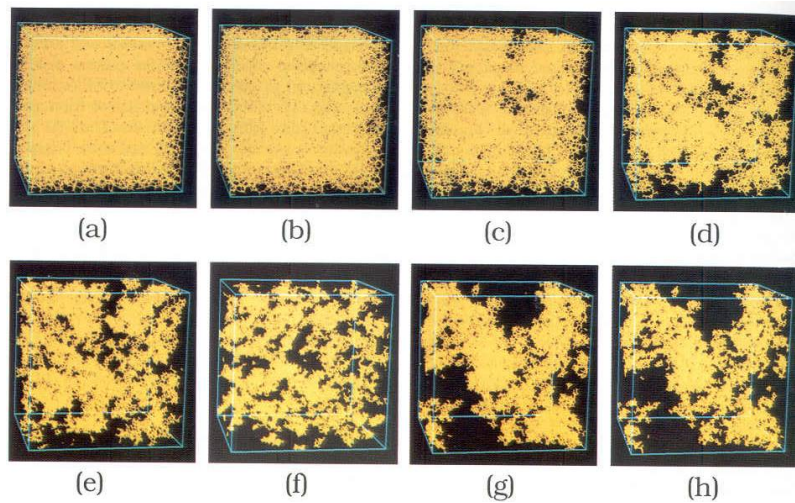




3 – Dynamical relaxation techniques

3.1 – Quantum and classical molecular dynamics methods

3.1.1 – Examples of application of CMD: time evolution of porous Silica glasses at different densities and temperatures



(a) 2.2, (b) 1.6, (c) 0.8, (d) 0.4, (e) 0.2 and (f) 0.1g/cm³ prepared at 300K, and (g) 0.2 and (h) 0.1g/cm³ prepared at 1000K. Lines represent Si–O bonds.

Vashishta, P., Kalia, R.K., de Leeuw, S.W., Greenwell, D.L., Nakano, A., Jin, W., Yu, J., Bi, L., Li, W., (1994), "Computer simulation of materials using parallel architectures", *Comput. Mater. Sci.*, 2, 180-208.



4 – Monte Carlo modelling

If you cannot do the direct dynamics, you can use statistical mechanics instead.

You consider a macroscopic state as a collection of microscopic states that you could fluctuate in between

The probability for each of these microscopic states is proportional to $e^{-\beta E_i}$ and $\beta = 1/kT$.

$$P_i = \frac{\exp[-\beta E_i]}{Q} \longrightarrow \text{Probability to be in a given state } i$$

where the partition function Q is defined as the sum of the un-normalized probability terms:

$$Q = \sum_i \exp[-\beta E_i] \longrightarrow \text{Partition Function}$$

The partition function Q is hard to find since it implies we have to sum over all configurations.



4 – Monte Carlo modelling

In general we can write the time evolution of the probability of finding a state using the “Master equation “,

$$P_k(t + 1) = P_k(t) + \sum_{l \neq k} (w_{l \rightarrow k} P_l(t) - w_{k \rightarrow l} P_k(t)).$$

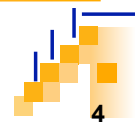
This is a restricted class of master equation as the configuration or probability at time t+1 only depends on the probability at time t. Processes of this type are called **Markov systems**.

One way to fulfill this equation is to require **detailed balance, i.e., the net probability flux** between every pair of states in equilibrium is zero,

$$P_k(t + 1) = P_k(t) = P_k^{eq}$$

which gives the detailed balance condition,

$$\frac{w_{l \rightarrow k}}{w_{k \rightarrow l}} = \frac{P_k^{eq}}{P_l^{eq}} = e^{-(E_k - E_l)/k_B T}.$$



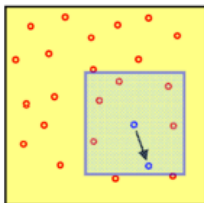
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4.1 – Monte Carlo modelling. Metropolis sampling.



- 1 Start from initial (random) configuration R_0 .
- 2 Randomly displace one (or more) of the particles.
- 3 Compute energy difference between two states:
 $\Delta E = V(R_{i+1}) - V(R_i)$.
- 4 Evaluate the transition probability which satisfies the detailed balance:

$$v(\mathbf{R}_i, \mathbf{R}_{i+1}) = \frac{p_B(\mathbf{R}_{i+1})}{p_B(\mathbf{R}_i)} = \min [1, e^{-\beta \Delta E}]$$



- $\Delta E \leq 0$: always accept new configuration.
 - $\Delta E > 0$: accept with prob. $p = e^{-\beta \Delta E}$
- 5 Repeat steps (2)–(4) to obtain a final estimation:
 $\bar{A} = \langle A \rangle \pm \delta A$, with the error: $\delta A = \sqrt{\tau_A \sigma_A^2 / M}$.



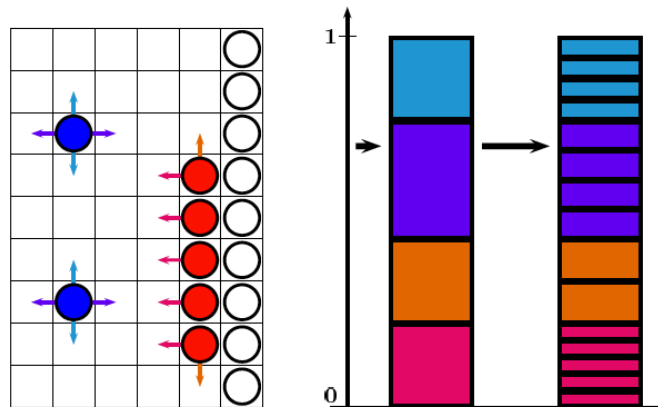
4.1 – Kinetic Monte Carlo modelling.

In a MC simulation, we may count the simulation steps. However, the foundation of the method lies in *equilibrium statistical physics*. Once equilibrium is reached, *time* has no physical meaning.

In order to address *kinetics*, i.e. to make a statement how fast a system reaches equilibrium, we need to go beyond that, and take into account for the role of time.

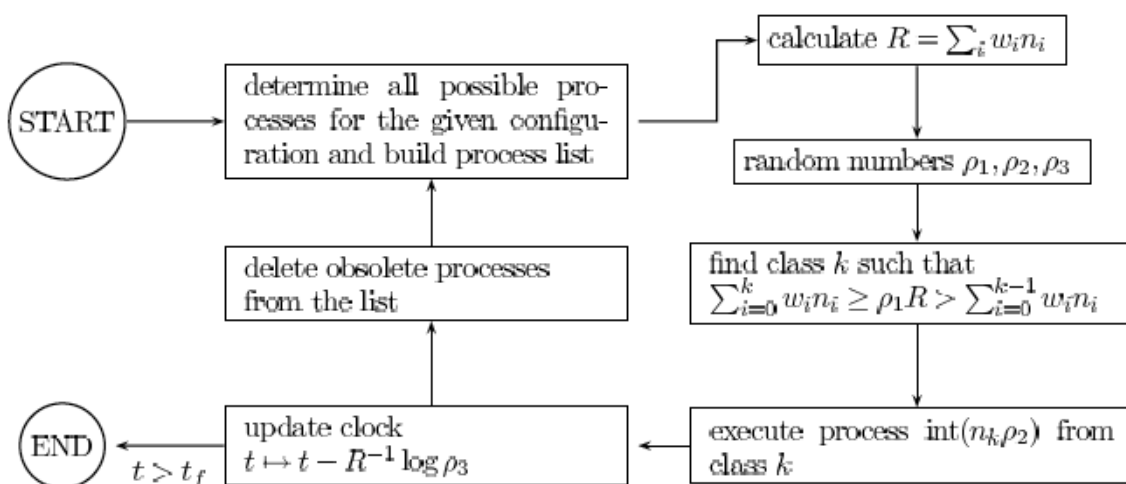
To do that, we need to provide as input the rates of all relevant individual processes.

The best way for getting values for the individual rates is by performing molecular dynamics simulations, possibly with first-principles electronic structure methods.



4.1 – Kinetic Monte Carlo modelling.

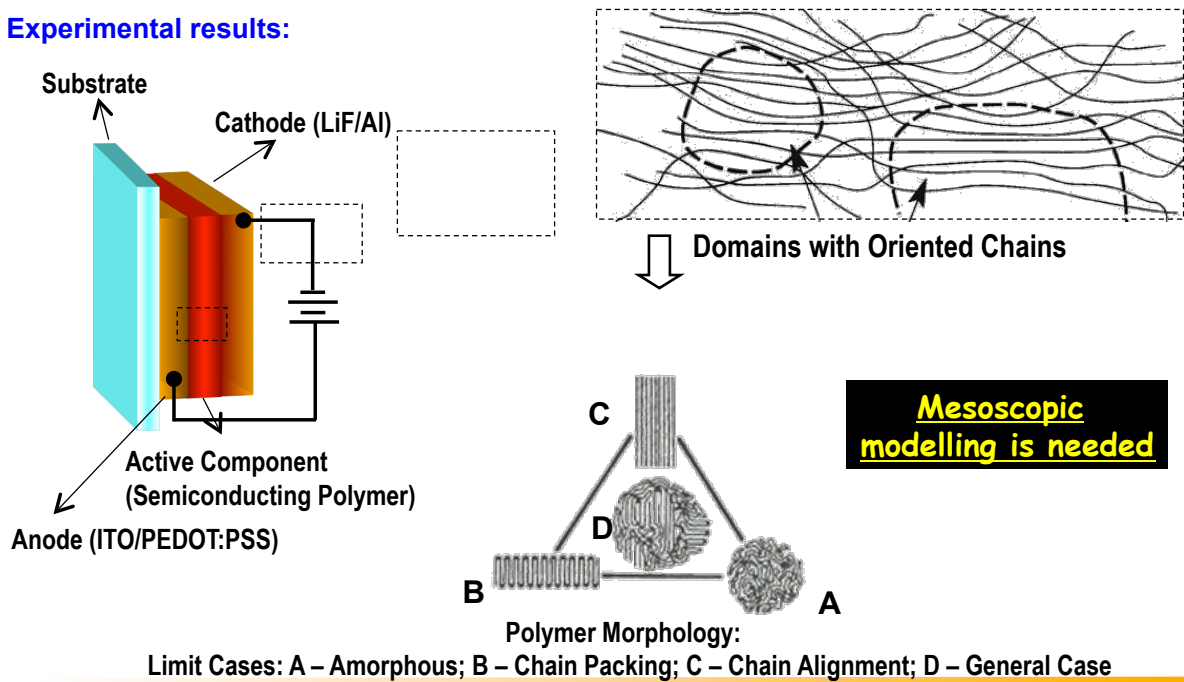
Flow chart for the process-type list algorithm.



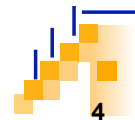
4.2 – Kinetic Monte Carlo modelling: a case study

4.2.1 – Motivation: the effects of molecular arrangement and properties on the functioning of single-layer polymer-based devices

Experimental results:



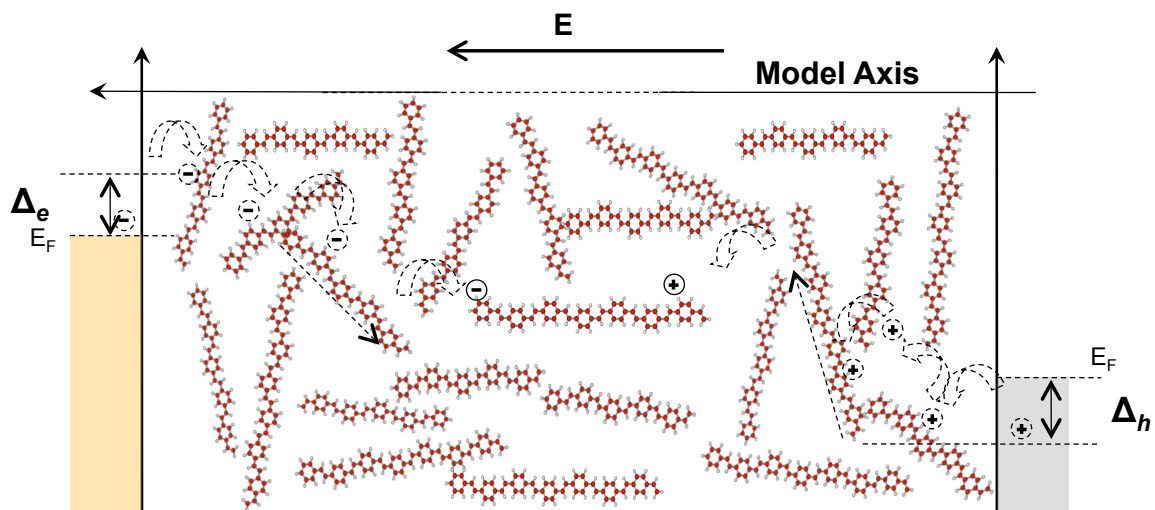
Jain SC et al, "Conducting Organic Materials and Devices", vol. , Academic Press (2007) .
 Dover D., "An Introduction to polymer physics", Cambridge University Press (2002)



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4.2 – Kinetic Monte Carlo modelling: a case study

4.2 – Electronic Processes Considered in the Mesoscopic Modelling of the case study (Polymer Diodes)



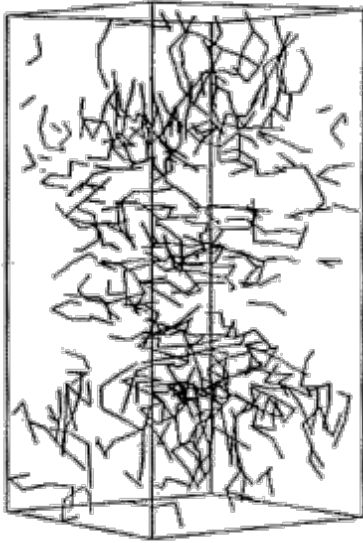
1. Charge Injection (Collection).
2. Intermolecular Charge Transport (Charge Hopping).
3. Intramolecular Charge Transport.
4. Charge Recombination.

Barbosa, H.M.C., (2009), "Study the Factors That Influence the Efficiency of Organic Electronic Devices by Computational Simulation", PhD thesis, Universidade do Minho, Braga, 2009.



4.2 – Kinetic Monte Carlo modelling: a case study

4.2.3 – Mesoscopic model of the polymer film



The mesoscopic structure of the polymer film is built using a generalised Monte Carlo method, which creates the long polymer chains as a sequence of self-avoiding straight conjugated segments, taken from a Gaussian distribution of lengths, separated by kinks.

Stoneham, A.M., Ramos, M.M.D., Almeida, A.M., Correia, H.M.G., Ribeiro, R.M., Ness, H., Fisher, A.J., (2002), "Understanding electron flow in conducting polymer films: injection, mobility, recombination and mesostructure", J. Phys.-Condes. Matter, 14, 9877-9898.

4.2 – Kinetic Monte Carlo modelling: a case study

4.2.4 – Mesoscopic model and simulation of charge injection and transport in the polymer film

- Charge (electron or hole) injection occurs by hopping from an electrode position, chosen randomly to the polymer strand monomer with the greatest hopping probability.
- After charge injection occurs, it moves along the polymer strand (intra-molecular charge transport) to the most energetically favourable position during the time given by

$$\tau_{\text{int}} = \frac{d}{\mu E_p}$$

where:

d - distance that the charge moves along the polymer strand

μ - charge mobility along the polymer strand

E_p - the strength of the local electric field along the molecular axis

Pereira, A., Barbosa, H.M.C., Correia, H.M.G., Marques, L., Ramos, M.M.D., (2010), "Theoretical study of the influence of salt doping in the functioning of OLEDs", Journal of Materials Chemistry, 20, 9470-9475.

4.2 – Kinetic Monte Carlo modelling: a case study

4.2.4 – Mesoscopic model and simulation of charge injection and transport in the polymer film

- After the intra-molecular charge transport occurs, it can hop to a monomer in a neighbouring strand or to one of the electrodes.
- The hopping rates for charge injection/collection from/by the electrode and intermolecular charge transport are given by

$$w_{ij} = w_o \exp\left(\frac{R_{ij} - R_o}{R_o}\right) \begin{cases} \cos \theta, \text{ for } -\frac{\pi}{2} \leq \theta \leq \frac{\pi}{2} \\ 0, \text{ for } -\frac{\pi}{2} > \theta > \frac{\pi}{2} \end{cases} \begin{cases} \exp\left(-\frac{\Delta E_{ij}}{k_B T}\right), \text{ for } \Delta E_{ij} > 0 \\ 1, \text{ for } \Delta E_{ij} \leq 0 \end{cases}$$

where:

w_o – the attempt-to-jump frequency

θ – the angle between the electric force vector on the charge and the jumping vector

R_{ij} – the jumping distance between hopping site i and j

R_o – minimum inter-strand distance given by the atomistic calculations

k_B – the Boltzmann constant

T – the simulation temperature

ΔE_{ij} – energetic barrier that the charge has to overcome during the jump (taking into account the electron affinity and ionization potential given by the atomistic calculations and the effect of the local electric field)

Pereira, A., Barbosa, H.M.C., Correia, H.M.G., Marques, L., Ramos, M.M.D., (2010), "Theoretical study of the influence of salt doping in the functioning of OLEDs", Journal of Materials Chemistry, 20, 9470-9475.

4.2 – Kinetic Monte Carlo modelling: a case study

4.4 – Mesoscopic model and simulation of charge injection and transport in the polymer film

- The hopping probability is defined by

$$P_{ij} = \frac{w_{ij}}{\sum_{i \neq j} w_{ij}}$$

and for each charge the only hopping process that takes place is the one with the greatest hopping probability if that probability is larger than 10^{-5} .

- The time of occurrence of all charge hopping processes is given by

$$\tau_{hop} = -\frac{\ln(x)}{w_{ij}}$$

where x is a random number uniformly distributed between 0 and 1.

- Charge recombination occurs whenever two charges of opposite sign meet on the same polymer strand if the local electric field does not prevent it.
- The electronic process with the smallest time of occurrence takes place at each computer iteration

Pereira, A., Barbosa, H.M.C., Correia, H.M.G., Marques, L., Ramos, M.M.D., (2010), "Theoretical study of the influence of salt doping in the functioning of OLEDs", Journal of Materials Chemistry, 20, 9470-9475.

5 – Particle methods for kinetic equations.

Boltzmann transport equation .

$$\frac{\partial F}{\partial t} + \vec{v} \cdot \vec{\nabla} F + \frac{\vec{X}}{m} \cdot \frac{\partial F}{\partial \vec{v}} = \left(\frac{\partial F}{\partial t} \right)_c$$

Rate of change of F in time
in configuration space
in velocity space
due to collisions
Force acting on particles

The **particle distribution function** $F(\mathbf{r}, \mathbf{v}, t)$ represents the number of particles per unit volume of phase space (\mathbf{r}, \mathbf{v}) , at time t .

The number of particles per unit volume of configuration space, at position \mathbf{r} and time t , with velocity components between V_x and $V_x + dV_x$, V_y and $V_y + dV_y$, and V_z and $V_z + dV_z$ is

$$F(x, y, z, v_x, v_y, v_z, t) dv_x dv_y dv_z$$

The main problem in kinetic theory ...

$$F(\vec{r}, \vec{v}, t) = ?$$

5.1 - Particle Simulation approach

- Particle simulation techniques attempt to model many-body systems by solving the equations of motion of a set of particles .
- Tracking particle trajectories enables us to explore physical effects which are inaccessible to other modeling techniques.
- The method employs the fundamental equations without much approximation, allowing it to retain most of the physics.



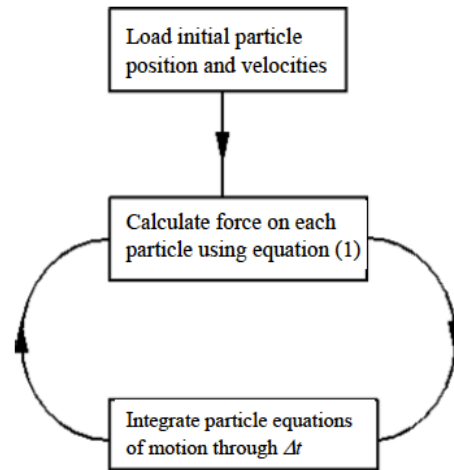
5.1 - Particle Simulation approach

Particle-Particle Method

$$F_i = q_i \sum_{j=1, \neq i}^{N_p} q_j \frac{x_i - x_j}{|x_i - x_j|^3} \quad (1)$$

$$\frac{dx_i}{dt} = v_i \quad (2)$$

$$\frac{dv_i}{dt} = \frac{F_i}{m_i} \quad (3)$$



1. Buneman O 1959 Dissipation of currents in ionized media *Phys. Rev.* **115** 503–17
2. Dawson J M 1962 One-dimensional plasma model *Phys. Fluids* **5** 445–59



5.1 - Particle Simulation approach

- The severe limitations: the number of arithmetic operations required in the force evaluation scales as Np^2 .
- *In a 1D simulation the interaction between 2 particles requires approximately 10 floating point operations.*
- *For a code running for Nt timesteps, the force evaluation requires roughly $10 \cdot Nt \cdot Np^2 / 2$ floating point operations.*
- On one processor of a PentiumIV CPU, which has a clock speed of 0.25 nanoseconds, a 2000 time-step calculation using a modest 5×10^6 particles would last more than 13 days.
- This approach is proper for a system with a small ($< 10^6$) particle number.
- Otherwise, we need to reduce the scaling of the operation count in the force evaluation below order Np^2 .



5.1 Particle Simulation approach

- **Tree Code** – the key idea is to replace the particle–particle interactions by particle–cluster interactions. The scaling of the operation count in the force evaluation below order $Np \ln Np$.

Refer to : J. Barnes and P. Hut, “A hierarchical $O(N \log N)$ force-calculation algorithm,” *Nature*, vol. 324, pp. 446–449, 1986.

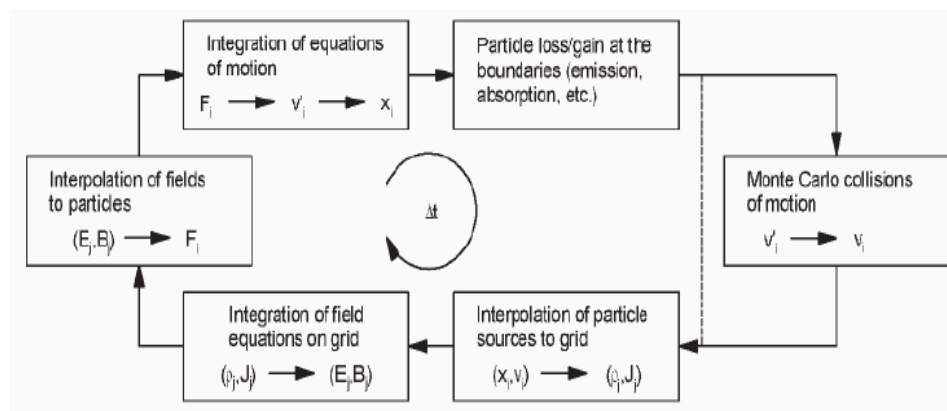
- **Particle-Mesh Technique** – the key idea is to replace the particle–particle interactions by particle–mesh interactions.

A numerical mesh is added to more effectively compute the forces acting on particles.

The force equation is replaced with an evaluation based on continuum representations of the charge density and electric field. (Cloud-in-Cell or Particle-in-Cell)

Particle In Cell with Monte Carlo collisions

Particle-In-Cell plus Monte Carlo: Full cycle, one time step



1. Verboncoeur J P, Langdon A B and Gladd N T 1995 An object-oriented electromagnetic PIC code, *Comput. Phys. Commun.* **87** 199–211.
2. Verboncoeur J P, 2005 Particle simulation of plasmas: review and advances, *Plasma Phys. Control. Fusion* **47** A231–A260.



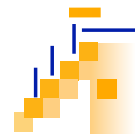
5.2 Particle In Cell

Integration of Equations of Motion

The conventional wisdom is that the simple second order leapfrog achieves the best balance between accuracy, stability and efficiency.

$$\begin{aligned} \frac{dx_i}{dt} &= v_i \\ \frac{dv_i}{dt} &= \frac{F_i}{m_i} \\ &\downarrow \\ m_i \frac{v_i^{n+1/2} - v_i^{n-1/2}}{\Delta t} &= F_i^n \\ \frac{x_i^{n+1} - x_i^n}{\Delta t} &= v_i^{n+1/2} \end{aligned}$$

For an electrostatic case, if $\omega p \Delta t \leq 2$, the leap frog scheme is stable.



5.2 Particle In Cell

Integration of Field Equations

$$\frac{\partial^2 \phi}{\partial x^2} = -\rho(x)$$

$$E_x = -\frac{\partial \phi}{\partial x}$$

Finite
Difference

$$\frac{\phi_{g+1} - 2\phi_g + \phi_{g-1}}{\Delta x^2} = -\rho_g$$

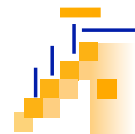
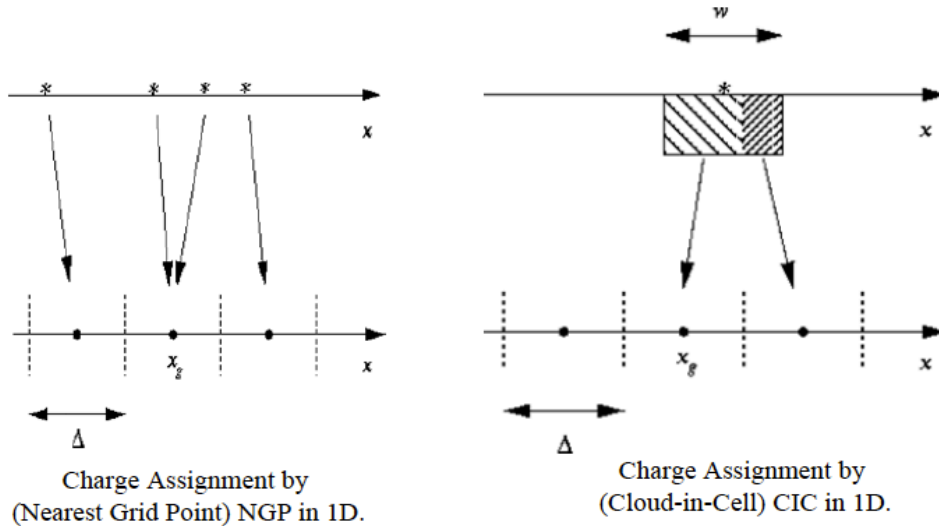
$$E_g = \frac{\phi_{g+1} - \phi_{g-1}}{2\Delta x}$$



5.2 – Particle In Cell

Charge Assignment and Force Interpolation

Once we introduce the grid we can no longer view the particles as point particles, this leads naturally to the idea of a finite sized particle.



5.2 - Particle In Cell

Charge Assignment and Force Evaluation by Cloud-in-Cell in 1D

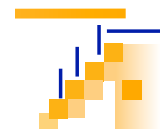
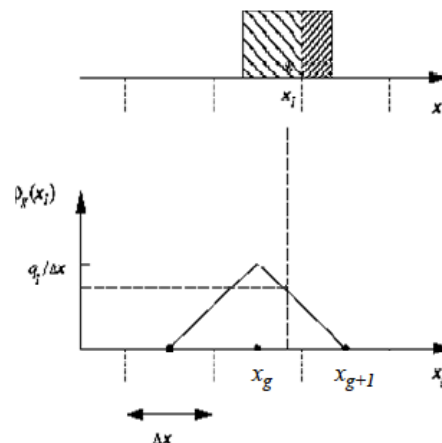
To ensure momentum conservation, the same interpolation scheme is used to compute the force on a particle as was used to perform the assignment of the particles charge to the mesh.

$$\rho_g = q_i \frac{x_{g+1} - x_i}{\Delta x}$$

$$\rho_{g+1} = q_i \frac{x_i - x_g}{\Delta x}$$

$$F_i = q_i \left(\frac{x_{g+1} - x_i}{\Delta x} E_g + \frac{x_i - x_g}{\Delta x} E_{g+1} \right)$$

where $x_g \leq x_i \leq x_{g+1}$





Particle-in-Cell (PIC) Algorithms

PIC codes have low computational intensity (2-3 FLOPs/memory access)

- 2D Electrostatic code has 55 FLOPs/particle update (11 for deposit, 34 for push)
- Memory access is still the bottleneck. FLOPs are cheap

PIC codes can implement a streaming algorithm by keeping particles constantly sorted.

- Minimizes global memory access since field elements need to be read only once.
- Cache is not needed, no gather/scatter.
- Deposit and updating particles can have optimal stride 1 access.
- Single precision can be used for particles

Challenge: optimizing particle sort

