

MOLECULAR SIMULATION

The State of the Art

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ABSTRACT

Computer simulation methods are now well established and powerful tools for studying very many problems of chemical interest. Phase transitions, electrical and thermal conductivity, surfaces and adsorption, liquid crystals, structure and dynamics of polymers, electrochemical interfaces, metal oxides, chemical reactivity, catalysis and drug design are examples of problems that can be approached by computer simulation.

In this paper we shall focus on computer simulation in Statistical Thermodynamics, namely the Molecular Dynamics and Monte Carlo methods.

The present achievements, future challenges and some applications with interest for Electrochemistry will be reviewed.

Keywords: molecular simulation, computer simulation, molecular dynamics, Monte Carlo

1. Introduction

Science has evolved through the development of theory to explain experimental facts. Experimental observations suggest physico-chemical models expressed by mathematical equations from which theoretical values are drawn and compared with experimental results.

For example, the experiments on the scattering of α -particles, performed by Rutherford, suggested a kind of planetary model for the atom, firstly described by Schrödinger's equation and later by Dirac's equation based on a sounder relativistic basis. In the same way, the experimental work on electrolyte solutions, conducted by Arrhenius and other researchers, firstly led to Debye-Huckel's theory and later to MacMillan-Mayer's theory based on a sounder statistical basis.

Sometimes theory precedes experiment. A well-known example is Einstein's general theory of relativity followed by Eddington's experimental observation of the light deflection by Sun.

In the last fifty years, with the advent of computers, we have at our disposal the powerful computer molecular simulation methods, aiming at the resolution of complex problems in Chemistry, complementing the experimental and theoretical standard methods.

Presently it is possible, for example, to simulate the structure and dynamics of polymers, the electrode/electrolyte interface, the structure and dynamics of solid and liquid electrolytes or to handle, by first principles, the problem of chemical reactivity.

The importance of molecular simulation is two-fold: on one hand the resolution of complex realistic problems in strict connection with experiment; on the other hand the test and improvement of theories by simulating model systems not available at the laboratory. Moreover, there are certain properties that are very difficult or even impossible to obtain experimentally. In such cases, computer simulation is a direct way to measure those properties.

The theoretical basis of computer simulation in Statistical Thermodynamics, namely the Monte Carlo and Molecular Dynamics methods, is the theory of statistical ensembles.

In this article, we shall review the state of the art in this field focusing on the fundamental aspects, possibilities and limitations of the methods. We shall also refer to some applications with interest for Electrochemistry, with emphasis on some research work developed in Portugal.

Finally, some future perspectives of molecular simulation will be drawn.

2. Statistical Ensemble Theory

In the present context, an *ensemble* is a collection of microstates compatible with a pre-defined set of experimental constraints. A microstate, in turn, is defined by the specification of the

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molecular positions and momenta (in the case of a classical description) or the corresponding wave function (in the case of a quantum description) of the system.

The connection between Thermodynamics and Statistical Mechanics can be established through the following postulates [1-4]:

- There exists a function, called the *thermodynamic characteristic function*, CF, which contains all the macroscopic information and depends upon the experimental constraints (*natural variables*) on the system.
- There exists a function, called the *partition function*, PF, which contains all the microscopic information and depends upon the Hamiltonian and the natural variables of the system. The *universal relation* between those functions is:

$$CF(\mathbf{X}) = \ln PF(H; \mathbf{X})$$

where \ln is the logarithmic function, H is the Hamiltonian of the system and \mathbf{X} represents the vector of *natural variables*,

- To change the experimental representation of the functions, that is to say, to change the natural variables (constraints), so that all the information is preserved, appropriate Legendre and Laplace transformations must be performed, respectively, over the characteristic and partition functions.
- Appropriate differential operators obtain the general relations between the thermodynamic and microscopic properties, for a given set of constraints, from the universal relation.

Among the thermodynamic characteristic functions are the *entropic fundamental relations*, which, in the absence of chemical reactions and external electromagnetic fields, can be written, in dimensionless form, as:

$$S_1/k = S_1(E, V, N)/k$$

$$S_2/k = S_2(H, p, N)/k$$

$$S_3/k = S_3(L, V, \mu)/k$$

$$S_4/k = S_4(R, p, \mu)/k$$

where S_n is the entropy, k the Boltzmann constant, E the internal energy, V the volume, N the number of molecules, H the enthalpy, p the pressure, $L = E - \mu N$, the Hill energy, μ the chemical potential and $R = H - \mu N$, the Ray energy.

The Hill and Ray energies are not usually described in textbooks. Indeed, only recently, after the development of the generalised theory of adiabatic ensembles [3, 4], they were shown to be of fundamental interest.

The heat transferred in a thermodynamic process, Δq , is given by:

$$(\Delta E)_{V,N} = (\Delta q)_{V,N} ; (\Delta H)_{p,N} = (\Delta q)_{p,N} ;$$

$$(\Delta L)_{V,\mu} = (\Delta q)_{V,\mu} ; (\Delta R)_{p,\mu} = (\Delta q)_{p,\mu}$$

according to the experimental constraints.

If adiabatic walls are imposed, we are in the field of *adiabatic* or *shell* ensembles. *Adiabatic*, meaning that the systems *do not exchange* heat with the environment and, at equilibrium, they reach the maximum of entropy compatible with the experimental constraints. *Shell*, meaning that, in their time evolution, the systems walk in a shell of the phase-space with *generalised energy* ($GE \pm \Delta GE$). ΔGE is due to the vacuum fluctuations, or weak coupling with external fields, and GE is the internal energy, the enthalpy, the Hill energy or the Ray energy according to the experimental constraints.

The semi-classical partition functions for the adiabatic ensembles can be written, in an unified form, in terms of Dirac's δ -function [3]:

$$Q_n = Z_n \int \delta[X_n - H] d\tau_n$$

H is the classical Hamiltonian of the system:

$$H(\mathbf{p}^N, \mathbf{r}^N) = \sum_i^N \frac{p_i^2}{2m_i} + U(\mathbf{r}^N)$$

where $\mathbf{p}^N \equiv \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N$ and $\mathbf{r}^N \equiv \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ are, respectively, the generalised linear momenta and position vectors of the molecules. $U(\mathbf{r}^N)$ is the potential energy function and the summation term is the kinetic energy.

The generalised Boltzmann's equation is:

$$S_n / k = \ln Q_n$$

The indexed symbols are defined in the following table:

n	S_n	X_n	$d\tau_n$	Z_n
1	$S_1(E, V, N)$	E	$dr^N dp^N$	$\frac{1}{N!h^{3N}}$
2	$S_2(H, p, N)$	$H - pV$	$dr^N dp^N dV$	$\frac{1}{N!h^{3N}}$
3	$S_3(L, V, \mu)$	$L + \mu N$	$dr^N dp^N$	$\sum_{N=0}^{\infty} \frac{1}{N!h^{3N}}$
4	$S_4(R, p, \mu)$	$R - pV + \mu N$	$dr^N dp^N dV$	$\sum_{N=0}^{\infty} \frac{1}{N!h^{3N}}$

where h is the Plank's constant, N! corrects for the indistinguishability of molecules and h^{3N} keeps the observance of Heisenberg's uncertainty principle and makes the partition functions dimensionless

If appropriate Legendre and Laplace transformations are applied to the generalised Boltzmann's equation we shall obtain the formalisms for the remaining four statistical ensembles:

$$\begin{aligned}
 -A(T, V, N)/kT &= \ln Q(H; T, V, N) \text{ - canonical} \\
 -G(T, p, N)/kT &= \ln Q(H; T, p, N) \text{ - isothermal-isobaric} \\
 -pV/kT &= \ln Q(H; T, V, \mu) \text{ - grand-canonical} \\
 0 &= \ln Q(H; T, p, \mu) \text{ - generalised or null}
 \end{aligned}$$

where A is the Helmholtz energy, G the Gibbs energy, T the temperature and $Q(H; X)$ the partition functions.

For example, the semi-classical canonical partition function is the Laplace transform of the microcanonical partition function $Q(E, V, N)$ [4]:

$$Q(T, V, N) = \int_0^{\infty} Q(E, V, N) \exp(-\beta E) dE = (N!h^{3N})^{-1} \iint \exp[-\beta H(p^N, r^N)] dp^N dr^N$$

where $\beta = 1/kT$. Accordingly, the thermodynamic characteristic function of the canonical ensemble,

$$-A/kT = S/k - E(\partial S/\partial E)_{V, N}, \text{ is the Legendre transform of the entropic relation } S(E, V, N)/k \text{ [4].}$$

Additionally, the canonical probability distribution function is:

$$\rho(p^N, r^N; T, V, N) dp^N dr^N = \frac{\exp[-\beta H(p^N, r^N)] dp^N dr^N}{Q(T, V, N)}$$

The corresponding quantum forms are:

$$Q(T, V, N) = \sum_i \exp(-\beta E_i)$$

$$Q(T, V, N) = \sum_v \langle v | \exp(-\beta H) | v \rangle = \text{Tr} \exp(-\beta H)$$

where E_i is the energy of the i th quantum state and H the Hamiltonian operator.

The second form, in terms of the density matrix, is particularly useful for the development of quantum simulation methods, namely the methods based on Feynman's path integral formulation of quantum mechanics [5,6].

The above considerations show that we have at our disposal eight ensembles describing eight experimental situations that can be set up in the laboratory. They are outlined in Fig. 1.

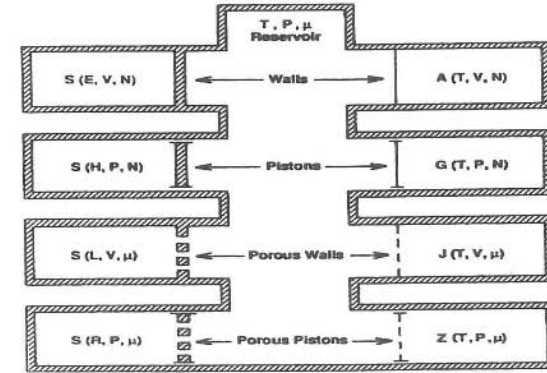


Fig. 1. Eight thermodynamic systems coupled with different reservoirs.

$$\begin{aligned}
 \boxed{k^{-1} S(E, V, N)} & \xrightarrow{\beta E} \boxed{-\beta A(T, V, N)} \\
 = \ln Q(E, V, N) & & = \ln Q(T, V, N) \\
 \\
 \boxed{k^{-1} S(H, p, N)} & \xrightarrow{\beta H} \boxed{-\beta G(T, p, N)} \\
 = \ln Q(H, p, N) & & = \ln Q(T, p, N) \\
 \\
 \boxed{k^{-1} S(L, V, \mu)} & \xrightarrow{\beta L} \boxed{-\beta J(T, V, \mu)} \\
 = \ln Q(L, V, \mu) & & = \ln Q(T, V, \mu) \\
 \\
 \boxed{k^{-1} S(R, p, \mu)} & \xrightarrow{\beta R} \boxed{-\beta Z(T, p, \mu)} \\
 = \ln Q(R, p, \mu) & & = \ln Q(T, p, \mu)
 \end{aligned}$$

Fig. 2. Summary of the Legendre and Laplace transformations.

We can easily move through the different ensembles, in a formal way, by means of appropriate Legendre and Laplace transformations, taking advantage of the experimental situations to be analysed. This is summarised in Fig. 2, where, in the arrows, $\beta=1/kT$ is the parameter of the Laplace transformations and E, H, L or R are the variables to be eliminated from the entropic relations.

The observable macroscopic thermodynamic properties are average values of mechanical properties over the microstates of the system. Therefore, once the partition function or the probability distribution function (note that the partition function is the normalising factor of the distribution function) for a given system are known, all the observable properties can be analytically worked out.

The operational point of view is, however, much more difficult. The analytical treatment of any chosen ensemble implies the resolution of multidimensional integrals or the knowledge of a complete set of wave functions. This is the huge problem of Statistical Thermodynamics, analytically intractable for most of the systems, but very simple or ideal ones. Therefore, the necessity of using numerical methods for molecular simulation is inescapable. These methods are generally designated as Molecular Dynamics (MD) and Monte Carlo (MC) methods.

3. Molecular Dynamics method

The Molecular Dynamics method (MD) was established by Alder and Wainright [7] in the period 1957-59. Firstly, it was applied to a system of hard spheres. Later, in the sixties, the method was extended to realistic potentials by Rahman [8] and by Verlet [9].

The method generates, sequentially in time, an ensemble of microstates by the numerical integration of the Newton's equations of motion, for each molecule in the model:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i$$

where m_i , \mathbf{r}_i and \mathbf{F}_i are, respectively, the mass, the vector position and the total force acting on molecule i .

The time averages of the mechanical properties are calculated over the trajectory of the system in phase space.

The integration starts from a set of initial positions and momenta and takes into account the forces acting on each molecule due to the other molecules in the model.

MD was founded in the context of the microcanonical ensemble: (E, V, N) constants. Apart from a heuristic technique [10] to maintain the temperature constant, until 1980, MD was invariably

carried out in (E, V, N) conditions. Following a master paper by Andersen [11], MD was extended to (H, p, N) [12,13], (T, V, N) [13-15] and (T, p, N) [13, 16-18] ensembles. These were remarkable achievements since those conditions are more appropriate for direct comparisons with experimental results.

Finally, in the present decade, MD has been extended to situations allowing the exchange of molecules of the system with the surroundings, that is to say, to open systems [19-21]. This is, by itself, an important step forward, once the number of molecules is a discrete variable and classical mechanics traditionally deals with continuous variables.

4. Monte Carlo Method

The Monte Carlo method (MC) [22] entered the Statistical Mechanics toolbox through a famous paper by Metropolis et al. [23] in 1953.

The method randomly generates an ensemble of microstates without any time sequence and performs the average of mechanical properties over that ensemble. The calculations start from an initial microstate and take into account the interaction energy of the molecules in the model. Picking up *just one* molecule and giving it a displacement in random directions generates a new microstate.

The generation of microstates is carried out so that they become distributed according to the appropriate probability distribution function for the chosen ensemble, which, as we know, presupposes a pre-defined set of experimental constraints. This is realised by accepting or rejecting a new microstate j , generated from microstate i , with the following transition probability:

$$\pi(i \rightarrow j) = \min \left(1, \frac{\rho_j}{\rho_i} \right)$$

where ρ is the ensemble probability distribution function and **min** is the minimum intrinsic function. When the new microstate j is rejected, the old microstate i is counted as a repeated one.

In the case of the canonical ensemble:

$$\pi(i \rightarrow j) = \min \left(1, \frac{\exp(-\beta U(j))}{\exp(-\beta U(i))} \right)$$

where $U(j)$ is the potential energy of microstate j .

The method was straightforwardly extended to the isothermal-isobaric ensemble [22, 24] and to the grand-canonical ensemble [22, 25] by introducing the appropriate Boltzmann factors in the above transition probabilities. A further important extension of the technique concerns the so-called Gibbs ensemble [26-28] and Gibbs-Duhem integration [29, 30] Monte Carlo methods, which

allow the direct study of phase-equilibria as well as some kinds of chemically reactive and associating systems [31].

A typical characteristic of those methods is the assumption of the separability of the kinetic and potential energies in the Hamiltonian. The kinetic part is analytically integrated in the probability distribution functions and the sampling is only carried out on the configurational space. The extensions of the Monte Carlo method to the microcanonical ensemble [32-35] and other adiabatic ensembles [36, 37], most of them carried out in the present decade, have, however, shown the possibility of also performing the sampling on the momenta space. This is, by itself, a noteworthy achievement, for in such a form the Monte Carlo method turns out as the full nondeterministic counterpart of the Molecular Dynamics method. Their equivalence is a further demonstration that deterministic chaos may be generated by the coupled classical equations of motion.

As far as the equilibrium properties are concerned MC and MD are equivalent. However, as in MC the microstates are not generated in a time sequence, that is to say, there is no integration of motion equations, the dynamic properties are not directly measured by MC, although some kind of stochastic dynamics may be worked out [38]. On the contrary, MD is fully deterministic and the dynamic properties can be calculated from the trajectory of the system in phase space.

5. Limitations

The methods referred to so far presuppose well-defined simultaneous positions and velocities for the molecules. Apparently, this is a paradox, since Heisenberg's uncertainty principle is universally valid, in particular at an atomic level. However, it is well-known that the classical translational motion is approached when the de Broglie's thermal wavelength of a molecule is less than the average distance between neighbouring molecules. This limit is reasonably attained for most of the systems at normal thermodynamic conditions, except for liquids helium and hydrogen at very low temperatures. In the case of molecules with internal degrees of freedom, the classical approximation is also reasonable when the rotational energy spacings are small compared with kT and the molecules are mainly in the ground state vibrational level. On the contrary, vibration is, mainly, a quantum phenomenon and, in general, it demands special quantum simulation approaches [5, 6, 22, 39]. However, in a first approximation, vibration may be treated classically by introducing harmonic potentials between the atoms and integrating the corresponding Newton's equations. This is common practice, for example, in molecular mechanics calculations [40].

The classical simulation methods also presuppose the knowledge of the intermolecular potential energy function, a concept based on the Born-Oppenheimer approximation, where the nuclear and electronic degrees of freedom are supposed to be strongly coupled. In reactive or

metallic systems, that strong coupling does not exist and the concept of a pair potential between two closed shell atoms is no longer useful. Thus, another approach has to be used. A combination of Density Functional Theory and Molecular Dynamics in the Carr-Parrinello method [41] is well suited to study those situations. In what follows we shall be mainly concerned with classical methods.

6. Boundary Conditions

Due to memory and computer time requirements, the number of molecules that is possible to follow, presently, by MD or MC, are typically of the order $10^3 - 10^6$ depending on the computer available and the complexity of the molecules. Those numbers are obviously very small if we are interested in bulk systems, where the number of molecules is of order 10^{23} , for the surface effects can be significant. In such cases, the use of boundary conditions is inevitable in order to attenuate those effects.

Cubic periodic conditions are common in most of the calculations: N molecules are enclosed in a cubic box (simulation box) whose volume, V , is chosen according to a pre-defined density. The simulation box is made to behave as though it were part of an infinite system by surrounding it with periodically repeated images of itself, as illustrated in Fig. 3.

The evaluation of potential energy and forces must consider not only the particles in the simulation box, but also their images in order to eliminate surface effects and to approach a bulk system. When the interactions between molecules are short-ranged, that is to say, when they can be neglected after ~ 3 molecular diameters (the so-called cut-off distance, r_c) the calculation is carried out using the *minimum image approximation with truncation*: given a molecule i , the simulation box is translated so that is centred on i (see Fig. 3). Then the molecule i only interacts explicitly with the molecules or their images within the sphere of radius r_c centred on molecule i . The distance r_c must be less than half of the simulation box side length. After the cut-off distance, it is assumed an uniform distribution of molecules and long range corrections are analytically calculated [22].

The minimum image approximation with truncation is largely used in the study of non-polar systems, in particular, of noble gases. Such an approximation is, however, unsuitable for ionic or highly polar systems where the electrostatic interactions extend over many molecular diameters. All images have, then, to be accounted for. The classical method for calculating the electrostatic potential energy of a system of charges in a periodic cell is the Ewald sum [22]. However, the original expression and the computer code are rather involved. Adams and Dubey [42, 43] derived a modified expression for the Ewald sum in terms of an effective pair potential. This enables the calculations to be performed in a very simple and efficient way. The modified Ewald sum is straightforwardly introduced in a conventional program. The calculations are also carried out with

the minimum image approximation, now without truncation, but taking into account explicitly only the molecules or images within the simulation box.

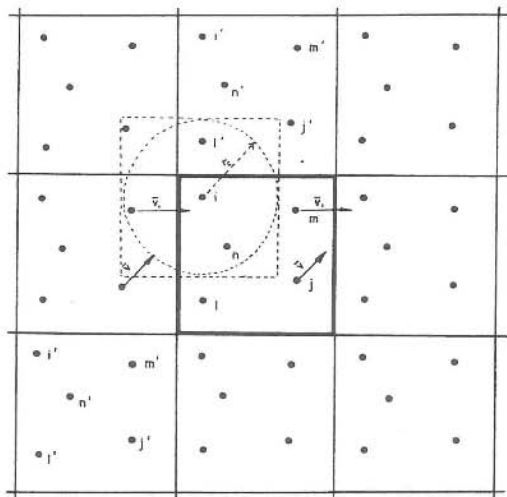


Fig. 3. Simulation box, its translation and boundary conditions in two dimensions. For clarity, only five particles are shown in each square.

The density is maintained by assuming that when a molecule leaves the simulation box through a wall, an image enters the opposite wall with the same velocity.

There are a variety of boundary conditions [44], but, apart from the cube, the most suitable shape seems to be the truncated octahedron.

7. Basic Computer Algorithms

The following steps are involved in a conventional MD program at (E, V, N) conditions:

- a) Assign initial positions $r_i(0)$ to the molecules in the simulation box. The positions of a lattice are generally chosen to initiate a calculation. Alternatively, the positions of a previous run can be taken.
- b) Assign initial velocities $v_i(0)$ to the molecules corresponding to a pre-defined temperature and a total momentum zero.
- c) Calculate the intermolecular potential energy $U(r^N)$.
- d) Derive the force acting on each molecule:

$$F_i = -\nabla_i U(r^N)$$

If necessary, the calculations of the potential energy and forces take into account boundary conditions.

- e) Integrate Newton's equations of motion for each of the N molecules, if necessary taking into account boundary conditions.

There are a variety of numerical algorithms to carry out the integration, but a very simple and stable one is the Verlet's algorithm which may be written [22] in the so-called leapfrog version:

$$v_i(t + \Delta t/2) = v_i(t - \Delta t/2) + F_i(t) \Delta t/m_i$$

$$r_i(t + \Delta t) = r_i(t) + v_i(t + \Delta t/2) \Delta t$$

$$v_i(t) = [v_i(t + \Delta t/2) + v_i(t - \Delta t/2)]/2$$

where Δt is the integration time-step. It must be less than the molecular relaxation times and is of the order $10^{-16} - 10^{-14}$ seconds depending on the type of molecules.

- f) Let the system evolve in time for the next n_e time-steps, an appropriate number to reach equilibrium.
- g) Let the system evolve in time for the next n_p time-steps, an appropriate number to obtain a good statistics.
- h) Calculate time averages of the properties over the n_p microstates.

The algorithm keeps the volume and number of molecules constant. Furthermore, once the initial positions and velocities are assigned, the initial total energy is defined. As the system evolves in time without external interferences, the total energy must also be a constant during the run. All the other properties will, however, fluctuate.

The extension of the algorithm to other ensembles involves the definition of the respective constraints and the modification of the motion equations in order to allow the coupling of the system to a heat bath, a pressure reservoir or a bath at constant chemical potential [13, 19, 22].

The above algorithm is only appropriate for the molecular centre of mass motion. For polyatomic molecules rotational and vibrational degrees of freedom must be considered. In many systems of importance namely hydrocarbon melts, polymers and lipid bilayers, internal rotation and vibration are important in determining equilibrium and dynamical properties.

The motion of rigid models, or models with internal rotations and torsions, may be treated classically in the limit referred to in paragraph 5. There are a variety of algorithms to describe rotation [22]. The inclusion of vibration directly in a simulation is not an easy matter. As we have seen, it is essentially a quantum phenomenon, which can not be approached, in general terms, using the classical equations of motion.

When quantum phenomena is involved, the classical methods have either to take into account quantum corrections [22] or to be complemented by special quantum simulation methods referred to in paragraph 5.

The conventional algorithm for the Monte Carlo method is similar and somewhat simpler. There are neither calculation of forces nor integration of motion equations (steps d) and e)). Also, for most of the MC methods there are no sampling of the momenta space. Thus, the assignment of molecular velocities (step b)) and their random alteration are absent. To generate a new configuration *just one* molecule of the model is taken and given a displacement in directions chosen at random. After the calculation of the potential energy the corresponding configuration is accepted or rejected with the probabilities referred to in paragraph 4. All the other steps in the algorithm are the same for MD and MC.

Finally, it should be emphasised that one conventional Monte Carlo step corresponds to the random displacement of just one molecule. Indeed, trying to move all the molecules simultaneously, at random, would result, for most of the situations, in a configuration with a very low probability. On the contrary, one Molecular Dynamics time-step corresponds to the simultaneous deterministic displacement of all the molecules in the model, since the molecular motions are oriented by the right forces acting on them. Thus, it is usual to measure a MC run in cycles; one cycle corresponds to having tried random displacements for each molecule in the sample.

8. Hybrid methods

The conventional MC method established by Metropolis et al. [23] is based in single-particle moves as we have referred to in the previous paragraph. It is possible, however, to introduce some of the character of Molecular Dynamics, which is intrinsically many-body, into a MC simulation [22]. This implies to move the particles, in some way, preferentially in the direction of the forces acting on them. Such a possibility could be important in order to increase the efficiency in guiding the system in its search for favourable configurations, particularly if collective motions are important in avoiding bottlenecks in phase-space.

Another kind of problem is concerned with time scales. Suppose, for instance, a set of heavy ions in a solvent such that the solvent molecules move much faster than the ions. This can be a serious problem in MD, for the short time-steps needed to follow the fast motions of the solvent and the very long runs needed to follow the slower motions of the heavy ions can make the simulation very expensive. Even if the motion of the solvent molecules is not very important they are present in large numbers and their explicit account could make the calculations prohibitive. The approach, in such a case, may be the omission of the solvent molecules and the representation of their effects

by a combination of random forces and frictional terms. The Newton's equations of motion for the heavy ions are then replaced by some kind of Langevin's equation [22].

9. Measurements

Molecular simulation conducts computer experiments on molecular models. The aim of the methods is to perform measurements of the properties of the models whose results are analysed and compared with the measurements performed on real systems available in the laboratory.

The total energy of the system is given by:

$$E = \left\langle \sum_{i=1}^N \frac{1}{2} m_i v_i^2 + U(\mathbf{r}^N) \right\rangle$$

where the brackets $\langle \rangle$ mean the ensemble or time averages.

If an effective pair potential [22] is used the potential energy is pairwise additive, simply given by:

$$U(\mathbf{r}^N) = \sum_{i<j} u(\mathbf{r}_{ij})$$

where $u(\mathbf{r}_{ij})$ is the effective pair potential and $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

If a Monte Carlo method without sampling of the momenta space is used, the kinetic energy of each microstate is not explicitly calculated and the average kinetic energy is given by $3/2 N kT$, according to the theorem of equipartition of energy.

The pressure of the system is given by the virial theorem [22]:

$$P = \left\langle \left(\frac{1}{3V} \right) \left(\sum_{i=1}^N \frac{p_i^2}{2m_i} + \sum_{i=1}^N \sum_{j>i}^N \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right) \right\rangle$$

where V is the volume and \mathbf{F}_{ij} is the force on molecule i due to molecule j .

Again, if a Monte Carlo method without sampling of the momenta space is used, NkT/V gives the average kinetic part of the pressure.

The temperature of the system is also given by the equipartition theorem [22]:

$$T = \frac{1}{3Nk} \left\langle \sum_{i=1}^N \frac{p_i^2}{2m_i} \right\rangle$$

Second order properties of the system, like the heat capacities, can be measured from the fluctuations of the microstate properties [22]. For example, the heat capacity at constant volume is given by:

$$C_v = \frac{3}{2}k + \frac{\langle U^2 \rangle - \langle U \rangle^2}{kT^2}$$

where U is the potential energy.

One structural property of the utmost importance is the radial distribution function (rdf). This function gives the local density of the system at a distance r of a molecule taken as origin. It reflects the space correlations between the molecules. Indeed, when $r \rightarrow \infty$, the radial distribution function must approach the bulk density of the system. The normalised radial distribution function is given by:

$$g(r) = \left\langle \frac{V \Delta n(r)}{N 4\pi r^2 \Delta r} \right\rangle$$

where $\Delta n(r)$ is the number of molecules in the spherical shell of volume $4\pi r^2 \Delta r$ at a distance r from the molecule taken as origin.

The radial distribution function is one of the properties very difficult to obtain from experiment. The experimental methods suitable to measure radial distribution functions are based on X-ray and neutron scattering. However, those measurements do not give the rdfs directly, but the structure factor, which has to be numerically Fourier transformed in order to get the rdfs. Also, by experiment, it is very difficult or even impossible to resolve the rdfs in different contributions. For example, the cation-anion, cation-cation and anion-anion contributions in molten electrolytes. No such difficulty exists if they are obtained by computer simulation. Fig. 4 shows rdfs for molten KCl obtained by MD and MC [45].

Dynamical properties, like the transport coefficients, can also be measured by molecular dynamics. For example, the self-diffusion coefficient can be obtained from the velocity auto-correlation function defined as:

$$Z(t) = \langle v_i(t) \cdot v_i(0) \rangle$$

where v_i is the velocity vector of molecule i . The average is taken over the time and the number of molecules.

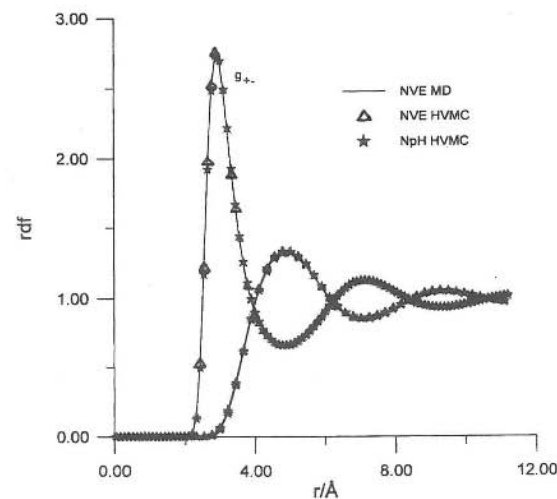


Fig. 4. The radial distribution functions g_{+-} , g_{++} , g_{--} for KCl at ~ 2870 K

The shape of $Z(t)$ and its Fourier transform (frequency spectrum) give information about the molecular mechanism of diffusion [46]. The self-diffusion coefficient is given by:

$$D = \frac{1}{3} \int_0^{\infty} Z(t) dt$$

The last equation expresses the fact that the self-diffusion coefficient is directly related to the fluctuations of the molecular velocities at the equilibrium state. It is a particular case of a general type of formula for the phenomenological transport coefficients, the so-called Green-Kubo formulae, based on Linear Response Theory [47]. It establishes a relation between the response of a system to an external generalised field and the fluctuations of the system in the equilibrium state. If the field is weakly coupled to the system, then the response of the system can be described in terms of time correlation functions of the system in equilibrium in the absence of the field.

The calculation of the electrical conductivity, for example, can be carried out through:

$$\sigma = \frac{1}{kTV} \int_0^{\infty} \langle I_x(t) \cdot I_x(0) \rangle dt$$

where I_x is the electric charge current due to a static electric field applied in the x direction and given by

$$I_x(t) = \sum_{i=1}^N q_i \cdot x_i(t)$$

Analogous expressions can be derived for the other transport coefficients [47].

In more general terms it is possible to perform MD with the system under external perturbations and to study directly the response of the system. The theory shows [44, 48] that the ratio of the response to the external field gives the transport coefficient of interest. Such methods are known as non-equilibrium molecular dynamics (NEMD) [48]. An important feature of NEMD is that it produce not merely the steady-state response of the system to an applied perturbation, but also the average time dependent response, so that it becomes possible to obtain the frequency-dependent transport coefficients. NEMD techniques are not restricted to use for the calculation of transport coefficients, but also can successfully be used to measure second order properties [44] as an alternative to the fluctuation method referred to above.

The auto-correlation function of a dynamical property $f(t)$ may be Fourier transformed to the correspondent frequency spectrum, as we have referred to for the velocity auto-correlation function. A general simplified expression is:

$$I(\omega) = \frac{1}{\pi} \int_0^{\infty} \langle f(t)f(0) \rangle \cos(\omega t) dt$$

For infra-red absorption and Raman band shapes, f corresponds to the dipole moment and polarizability tensor, respectively. The angular momentum auto-correlation function is simply related to the NMR spin relaxation time. Brillouin and Rayleigh light scattered spectra also Fourier transform to auto-correlation functions of dynamical properties. Therefore, additionally to thermal and transport properties, absorption and scattering properties may also be measured by computer simulation [6, 49].

All the properties referred to so far are *mechanical properties*. This means they can be expressed as averages of instantaneous properties of the microstates, which, in turn, are expressed in terms of the positions and velocities of the molecules. There is, however, another class of properties, based on the definition of entropy, such as Gibbs energy, Helmholtz energy and chemical potential, the so-called *statistical properties*, which can not be expressed in those terms. They are global properties of the deterministic trajectories in phase space (in the case of MD) or of the stochastic ensembles (in the case of MC). The direct calculation of the entropy fundamentally involves counting techniques, easily giving rise to *combinatorial explosion*, which is impossible to solve, even in computational terms, for the majority of molecular systems. There are some interesting proposals to approach the problem of the direct calculation of the entropy from the

trajectory of the system in phase-space [50]. Nevertheless, presently, we have mainly to rely on other techniques to measure statistical properties, namely the Widom's method [22] for the calculation of chemical potentials. In the context of the canonical ensemble, the excess chemical potential can be written as:

$$\mu_{\text{exc}} = -kT \ln \langle \exp(-u_{\text{test}} / kT) \rangle$$

where u_{test} is the potential energy change due to the randomly addition of a virtual particle to the system. This is the so-called *particle insertion method* easily implemented in a computer program [22]. Unfortunately, the method is not a general one. In fact, for high densities the probability of inserting a particle in the system is obviously very small and the resulting poor statistics prevents reliable results. Various techniques have been proposed to circumvent the problem, but even so, the basic problem persists at high densities. Recently, Rowley et al. [51] have proposed the so-called *osmotic method* for the direct determination of chemical potentials by MD. As the method does not involve particle insertion it allows the determination of chemical potentials at virtually all densities.

It is noteworthy that the problem of the measurement of statistical properties is only concerned with the excess contributions. The ideal contributions are analytically calculated. For example, the ideal part of the chemical potential is readily given by:

$$\mu_{\text{id}} = -kT \ln(\Lambda^3 \rho)$$

where Λ is de Broglie's thermal wave length and ρ the density of the system.

If the simulations are carried out in the grand-canonical ensemble, the chemical potential is one of the constraints. It turns out [22] that the Helmholtz free energy can be obtained directly from:

$$A / N = \mu - \langle p \rangle_{\mu VT} V / \langle N \rangle_{\mu VT}$$

and, using that equation, it is possible to calculate all the remaining statistical properties.

Another alternative is to perform the simulations in the grand-adiabatic ensemble [36], where the constraints are the Ray energy, R , the pressure and the chemical potential. The beauty of that kind of simulation is that the entropy can be calculated directly:

$$S = R / \langle T \rangle_{R p \mu}$$

If instead of absolute properties, the interest is in differences of energy, as the difference of Helmholtz energies, ΔA , between the reagents and products in a chemical reaction, it is shown [22, 40] that :

$$\Delta A = A_1 - A_0 = -kT \ln \langle \exp[-\Delta U(\mathbf{r}^N)/kT] \rangle_0$$

where the average is performed over the representative configurations of the initial state of the system. In order to obtain a convenient convergence, the potential energy difference between the initial and final states $\Delta U(\mathbf{r}^N)$ must be $< kT$ which is not observed in most reactions. To circumvent the problem, the calculation may be divided into a number of *windows* so that the total free energy difference is the sum over all windows [40]. To this end, a coupling parameter, λ , is introduced in a perturbation mixed energy expression linking the two limiting states:

$$U_\lambda(\mathbf{r}^N) = \lambda U_1 + (1 - \lambda) U_0$$

The coupling parameter is varied from 0 to 1 over a number of intermediate simulations, each with a different mixed potential energy.

Finally, differences of statistical properties between two states can be measured by setting up a reversible path (isochoric, isothermal or isobaric) connecting the states and carrying out a number of independent simulations over the path. At the end, an appropriate thermodynamic integration is performed over the state points [22]. For example, the difference in Helmholtz free energy between two states in a reversible isothermal process may be obtained by:

$$\Delta A / NkT = - \int_1^2 \left(\frac{pV}{NkT} \right) \frac{dV}{V}$$

10. Applications to Electrochemistry

The molecular simulation methods have successfully been applied to systems with interest for Electrochemistry since 1970. The MD and MC calculations of water by Rahman and Stillinger [52], of electrolyte solutions by Heinzinger and Vogel [53, 54], Card and Valleau [55], Rasaiah et al. [56], Turq et al. [57] and of molten electrolytes by Woodcock and Singer [58] and Lantelme et al. [59] are the pillars of the progress in this field.

Until now, very many applications have been accomplished, ranging from electrolyte solutions and molten electrolytes up to the electrical double layer, specific adsorption, nucleation, polymers, electrical conductivity, metal oxides, insulator-metal transitions, the positions of counterions in zeolites and molecule-metal potential surfaces. The interested readers on the theoretical and molecular simulation methods applied to Electrochemistry have good sources in a review paper by Barthel [60] and in the *Journal of Electroanalytical Chemistry*, **450** (1998), the late entirely dedicated to theoretical and computer simulation methods.

In this paper we shall only refer to two specific applications recently developed in Portugal. The first one comes from the Research Group of Professor Ferreira Gomes in Porto and is concerned with the problem of specific adsorption of halide ions on noble metals. The second application comes from our own Research Group in Lisboa and is concerned with phase transitions of ionic clusters, namely clusters of potassium chloride.

10.1 Specific adsorption of halide ions on noble metals

A phenomenological definition relates the term *specific adsorption* to three types of phenomenon [61]: the chemisorption of ions on an electrode at point of zero charge, the chemisorption of anions on a negatively charged electrode and the chemisorption of cations on a positively charged electrode. The two latter cases seem against the rules of electrostatics.

The experimental results on the specific adsorption of halide ions on noble metals show that the strongest adsorbed ion is iodide and the weakest is fluoride. Also, in the group of noble metals (copper, silver and gold) gold appears to be the most attractive for halide ions.

The calculations have involved, firstly, the analysis, by quantum mechanical methods, of the interactions between the present species: ion-ion, ion-metal, ion-water, water-water, water-metal and metal-metal. Secondly, based on those interactions, the Monte Carlo method has been used to study the system ion/solvent/electrode focusing on the specific adsorption of the ions on the electrode. The solvent contribution for the potential of mean force acting on the ion has been obtained for the different halide ions in contact with a Cu(100) electrode.

Several configurational details of the system have been worked out through density profiles, radial distribution functions and snapshots. A new potential for the description of the ion-metal interaction has been proposed. The free energy of adsorption of the ions obtained as a combination of that potential with the solvent mean force has been found to be close to the experimental estimates of this property for bromide and iodide. Also, the general tendency in the strength of the adsorption, experimentally verified to decrease from iodide to fluoride, has been reproduced, for the first time, by the results of the simulations, as it is shown in Fig.5.

This conclusion is especially important considering the fact that the pure ion-metal interactions, obtained from the quantum mechanical calculations, show an opposite trend. Although the model used in the simulations is relatively modest, regarding the total number of ions and solvent molecules in the model, the results are consistent and show the power of the method in order to clarify the problem of specific adsorption.

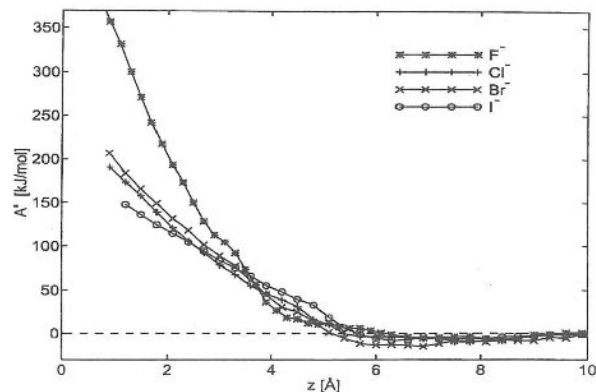


Fig. 5. The solvent mean force, A^s , on each of the four halide ions, as a function of the distance of the ions from the Cu(100) surface [61].

10.2. Phase transitions in ionic clusters

Clusters of atoms and molecules play an important role in the real world. Their structural and thermodynamic properties are of interest in many fields, for example, crystal growth, gas phase nucleation, structure of amorphous materials, catalysis and atmospheric chemistry.

Fernandes [62] carried out the first molecular dynamics simulations of ionic clusters in 1977. Phase transitions were not detected since the right range of temperatures was not probed. Amini et al. [63-65] studied, by molecular dynamics, the melting of alkali halide crystals with 512 ions, detecting melting and glass transitions, but no recrystallisation. Sakamoto [66] studied, by Monte Carlo, the behaviour of alkali halide clusters $(MX)_n$ with $n=4, 8$ and 18 using the Born-Mayer potential without dipole-dipole and dipole-quadrupole contributions. He detected a melting transition, but no information is given on recrystallisation or glassy states. The same kind of potential has been used in the extensive molecular dynamics simulations of KCl clusters carried out by Rose et al. [67-69]. They have detected melting and glassy states, but as far as freezing is concerned, they mention that the calculations, for the 64 ions cluster, revealed only a single case in which the cluster changed from its high potential energy liquid-like form back into its low potential solid-like form. In this instance, however, the return stay in solid-like form was relatively short and, moreover, once the cluster eventually transformed back into its liquid-like form it remained liquid-like for the duration of the simulation.

In order to settle down the problem, Fernandes and Neves [70] carried out extensive constant energy molecular dynamics simulations for KCl clusters with 8, 64, 216 and 512 ions

using the Born-Mayer-Huggins potential [58]. The results show that all the clusters exhibit first-order-like melting and freezing transitions with hysteresis regions. Fig. 6 displays the evolution of the configurational energy with temperature for a 64-ions cluster:

The behaviour of the 8-ions cluster is similar, but it shows a smaller hysteresis.

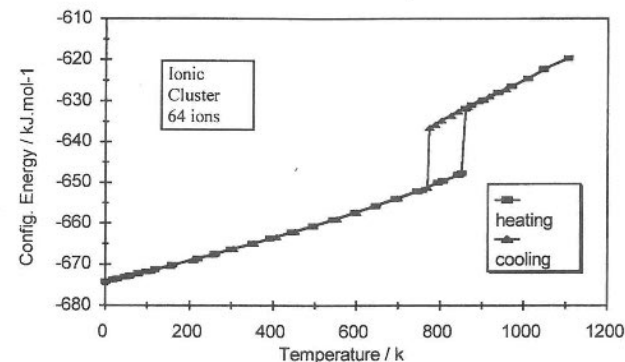


Fig. 6. Configurational energy versus temperature for a 64-ions cluster.

The curves were obtained by slow heating and cooling the cluster. The following snapshots show the structure of the cluster at different temperatures. It is evident that the cluster has recrystallised in its perfect original cubic lattice (see Fig.9)

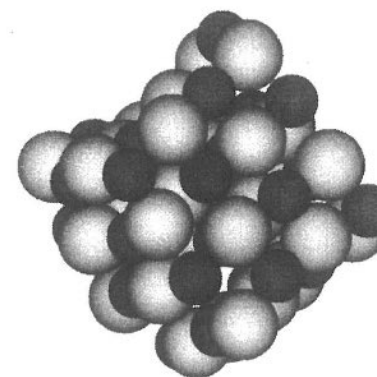


Fig. 7. Before melting, 851K (64 ions)

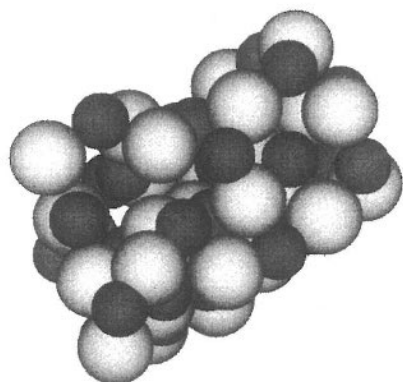


Fig. 8. After melting, 861K (64 ions)

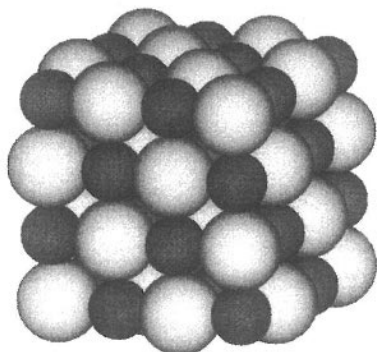


Fig. 9. After slow cooling, 2K (64 ions)

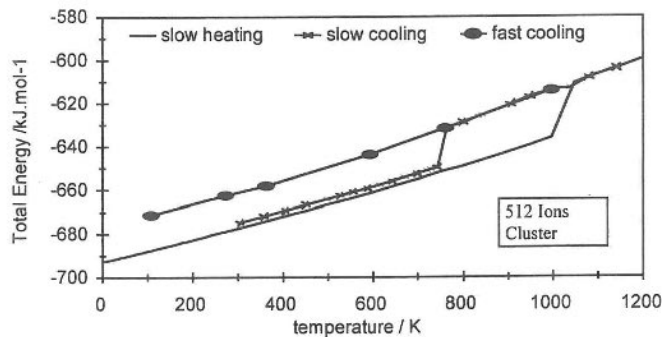


Fig. 10. Total energy versus temperature for a 512-ions cluster.

The clusters with 216 and 512 ions show a similar trend, although some differences must be noted.

Firstly, the respective hysteresis regions are greater than those presented by the 8 and 64-ions clusters as observed in Fig. 10.

Secondly, the slow cooling curve in the solid part does not coincide with the corresponding slow heating curve, being systematically ($\sim 4\text{kJ}$) higher in energy. This reflects an imperfect growth of the crystal as can be observed in Fig. 11, taken at the end of the slow cooling process ($\sim 100\text{K}$). The structure has, clearly, a surface energy higher than the perfect crystal:

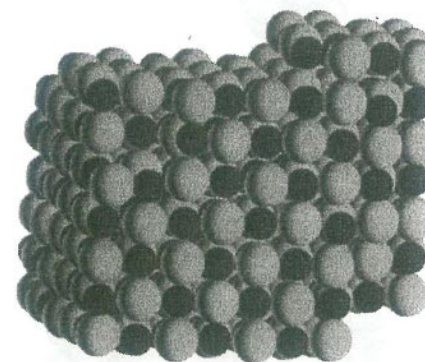


Fig. 11. After slow cooling, $\sim 100\text{K}$ (512 ions)

The melting points of the clusters were estimated by taking the arithmetic mean of the apparent melting and freezing temperatures. The following values were found: 696K (8 ions), 817K (64 ions), 890K (216 ions) and 906K (512 ions). As expected, the melting temperature increases with the cluster size and approaches the melting temperature of the bulk system ($\sim 1000\text{K}$).

The fast cooling curve in Fig. 10 was obtained by instantaneously cooling the liquid at 0.75, 0.5, 0.35, 0.25 and $0.1T_m$ where T_m is the estimated melting temperature. At about $0.3T_m$, a glass-like transition is detected by: a slight change in the slope of the enthalpy curve (note that in this case the enthalpy is equal to the total energy since the pressure is zero); a marked decrease in the mean square displacements of the ions; a thorough analysis of the radial density functions. This behaviour is similar to the ones reported for the bulk system [71, 72]. Fig. 12 shows the structure of the cluster at $0.1T_m$ ($\sim 100\text{K}$). In contrast with the snapshot in Fig. 11, taken at about the same temperature, but after slow cooling, the cluster does not show any crystal structure.

Finally, all the states, before and after the transitions, were stable for the duration of the simulation runs, based on 10^5 - 10^6 time steps.



Fig. 12. *After fast cooling, $\sim 100K$ ($0.1T_m$; 512 ions)*

Our findings encourage us to pursue the investigation with the following main objectives. Firstly, to produce computer animations that could show the details of the ionic dynamics through phase transitions. This part is mostly accomplished and can be appreciated at an Internet site [73]. Secondly, to increase the number of ions in the model in order to analyse surface effects, the influence of impurities in the structure and hysteresis regions, as well as, the effects of induction forces in the transitions points. This part of the research is still in progress. Fig.13 and 14 show snapshots of a 8000-ions cluster with an enclosed impurity:

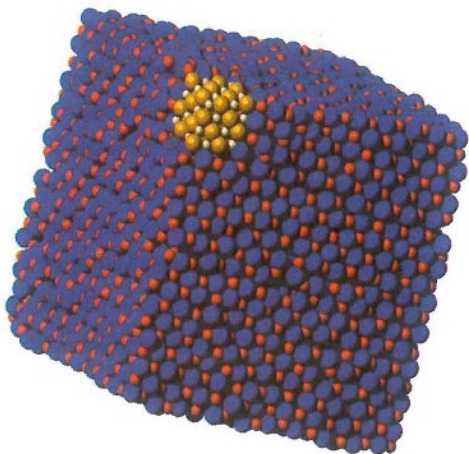


Fig. 13. *Before melting*

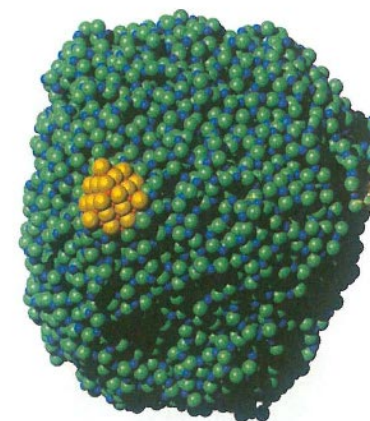


Fig. 14. *After melting*

Apart from the beauty of the snapshots, the preliminary numerical results suggest that the effect of the impurity is not relevant regarding the hysteresis regions. On the contrary, the number of ions and the existence of a surface seem to be of major importance.

11. Future developments

The present achievements and challenges of molecular simulation anticipate many fruitful developments in the years ahead.

Until recently, the total simulation times were limited by time-steps of $\sim 10^{-16}$ - 10^{-14} s used to take into account the fastest molecular motions. Additionally, the limitation in the number of particles in the models, and the effects of boundary conditions, have prevented the analysis of important space and time correlations as well as the influence of surfaces.

The spectacular increase in computer power and the establishment of new algorithms for massive parallel machines, in the present decade, will certainly lead to simulations extending over much longer time and space scales. This will be a crucial step forward regarding, for example, crystal growth, polymer rearrangements, liquid crystals and hydrodynamic phenomena.

The high complexity of most chemical systems can not be tackled, however, only by applying the brute force approach of increasing the length of the calculations. This is much so when the observable properties are independent of the fastest degrees of freedom. In such cases the use of more coarse-grained hamiltonians, where some interactions are not explicitly included, and some kind of Langevin dynamics will be an alternative.

The problems concerned with electrostatic forces, of utmost importance in Electrochemistry, will certainly receive much more attention, regarding the efficiency (or even the need) of the conventional Ewald sum for larger samples.

Another foreseeable direction is an increase in the application of hybrid quantum-classical methods. For example, the study of clusters embedded in a condensed solvent [6], so that the clusters are treated quantum mechanically while the solvent is treated classically.

The simulations of reactive and metallic systems by *ab initio* simulations, such as the Carr-Parrinello method referred to in paragraph 5., will certainly be extended. The method avoids the use of effective pair potential functions, although, it must be emphasised, they do not solve the time-dependent Schrödinger equation. Indeed, the motions of the nuclei are followed by classical molecular dynamics. Therefore, problems like the tunnelling of hydrogen atoms through the active sites of a polymer can not be properly assessed. Also, the method mainly produces trajectories on the electronic ground state. Thus, the generalisation of the molecular dynamics method in order to include the possibility of electronic transitions driven by nuclear motions will be an important achievement.

Although the quantum simulation methods are expected to have important developments in the next years, the classical simulation methods will continue to play a crucial role in Chemistry. They are able to sample phase space faster than the Carr-Parrinello method (~ 100 times). Therefore, for large systems and a meso-scale description they will be, as far as possible, the best alternative. Indeed, many chemical phenomena can be appropriately described and correlated in classical terms. Thus, the development of accurate force fields, including many-body forces, will continue as one of the main research aims of chemical-physics.

Finally, in the broader domain of Computational Chemistry, the next decades will see a major increase in the application of Artificial Intelligence methods [74], namely Neural Networks, Expert Systems and Genetic Algorithms. They try to reproduce intelligent reasoning using a computer. The concept of parallelism is implicit, like in the human brain, and they have two essential characteristics: intuitive jumps and capacity of learning from experiment. Additionally, they are well suited for using *Fuzzy Logic* [75], an area of increasing importance in Chemistry. Indeed, fuzzy logic is the science to approach complexity. The right connection between those methods and the computer simulation methods in Statistical Mechanics is yet to be seen, but important achievements in this field are certainly expected in the next years.

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