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SIMULATION AND MODELING IN COMPUTATIONAL CHEMISTRY: A MOLECULAR PORTFOLIO

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Abstract: This communication describes the scientific research work of the author at Centro de Química Estrutural, Instituto Superior Técnico, between 1996 and 2006, in the area of computational methods applied within the framework of statistical mechanics. The first simulation methods to be introduced are those based on Monte Carlo algorithms, namely the extended version of the Gibbs Ensemble Monte Carlo (GEMC) method. Several examples of the application of the method to the study of fluid phase equilibria in model systems are discussed. The rest of the communication is dedicated to Molecular Dynamics techniques and their application to the study of molecular systems. The case of ionic liquids, a class of compounds that attracted in recent years a lot of attention from the scientific and technological communities, is particularly addressed. The diversity of the molecular systems that were studied using computer simulations (and that can be described as the molecular portfolio of the author) is a measure of the growing importance of these methods at the forefront of scientific research

Key words: Computational Chemistry, Statistical Mechanics, Monte Carlo, Molecular Dynamics.

1. INTRODUCTION

This article describes the author's simulation and modeling work at Centro de Química Estrutural of Instituto Superior Técnico, IST, of Universidade Técnica de Lisboa, UTL, from 1996 to the beginning of 2006. The presentation of the different research topics follows approximately a

chronological order although the structure of the article is mostly based on the way those topics are interconnected to each other. In other words, this communication can be understood as a collection of abstracts of scientific papers (published or under preparation) describing in a logical way the scientific activity of the author in the area of computational chemistry and statistical mechanics of molecular systems. Each abstract is followed by a figure that tries to capture the issues under discussion.

2. GIBBS ENSEMBLE MONTE CARLO SIMULATIONS

The work in the area of simulation methods within the framework of statistical mechanics started in 1996 at Imperial College, London, during a post-doctoral fellowship under the supervision of Professor Dominic Tildesley.

The first computational method to be studied was the Gibbs Ensemble Monte Carlo (GEMC) algorithm, a method particularly suited to the study of phase equilibria [1]: The Gibbs ensemble simulation method was extended to multiphase equilibria by increasing the number of boxes that can be used concurrently in the simulation. Atoms were moved within each box and pairs of boxes were selected at random for the volume and particle exchange moves. The equivalence between the Gibbs ensemble with an arbitrary number of boxes and the corresponding canonical ensemble was established. Simulations of two-component, three-phase equilibria and three-component, four-phase and three-phase equilibria were demonstrated for simple model systems, and the model phase diagrams were determined.

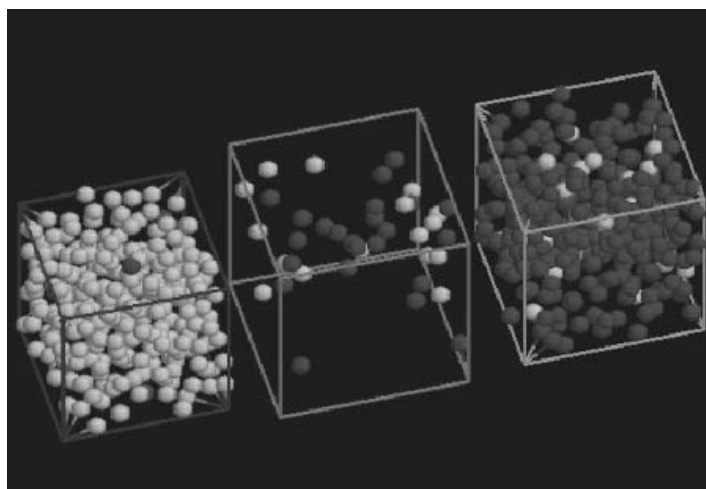


Figure 1. Equimolar mixture of 600 Lennard-Jones atoms in liquid-liquid-vapor equilibrium. Snapshot of a NVT-GEMC simulation with 106 steps.

The extended Gibbs Ensemble Monte Carlo method was then applied to the systematic study of phase diagrams and their relation with the parameters that govern the interactions between atoms. This is the field of the so-called Global Phase Diagrams and this line of research produced at this stage two papers [2,3] describing the “building-up of Phase Diagrams”.

In the first of those papers, a three-box version of the Gibbs ensemble Monte Carlo method was used to determine the phase diagram type of several binary mixtures of one-centre Lennard-Jones particles. The method was used to establish a direct link between the intermolecular potential modeling the interactions in a given system and its fluid phase diagram, without the knowledge of the corresponding equation of state governing its pVT behavior. As an example of the application of the method, closed-loop behavior in an isotropic system could be found using a set of Lennard-Jones parameters exhibiting a cross-interaction diameter with a negative deviation from the Lorentz-Berthelot combination rule.

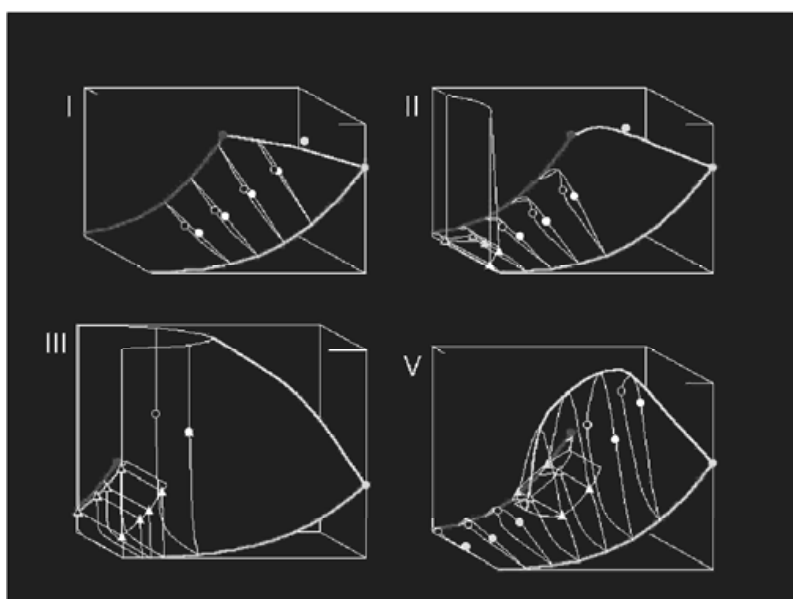


Figure 2. Four types of vapor-liquid equilibria (Scott & van Konynenburg classification) generated by the GEMC method.

The second article, published in *Pure and Applied Chemistry* [3], began with a bird's-eye view of the history of phase equilibrium diagrams for mixtures, their classification and interpretation. Running throughout the discussion are the fertile ideas of van der Waals. The Scott and van Konynenburg classification was revisited, and various types of phase diagrams were generated by computer simulation, using the Gibbs Ensemble Monte Carlo Method for one-centre 12-6 Lennard-Jones molecules. The work was hopefully made more attractive and appealing to students by a judicious choice of architectural and engineering equivalents.

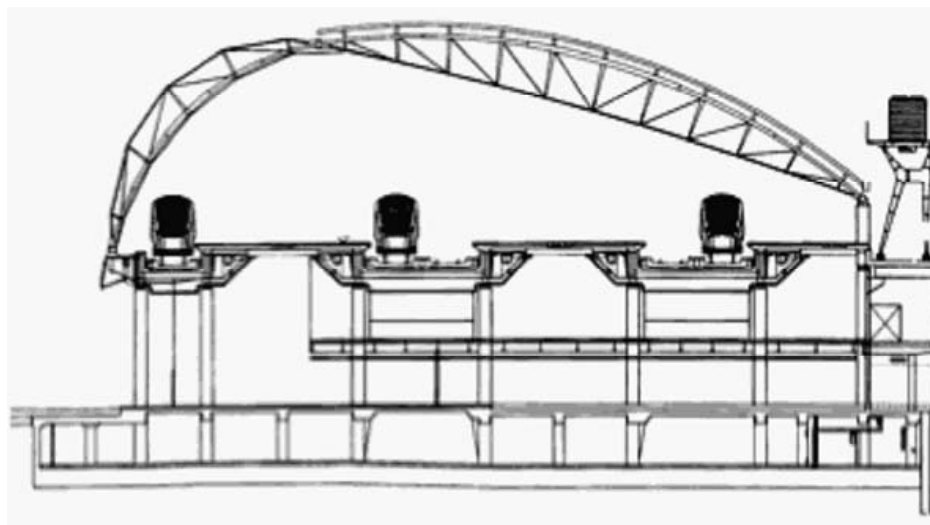


Figure 3. Cross-section of the international terminal at Waterloo Station, London, “exhibiting a positive azeotrope”. © Nicholas Grimshaw & Partners Ltd. (1993)

The implementation of the extended GEMC method produced other more recent and diversified studies, ranging from the possibility of phase separation under osmotic conditions [4], to the formation of nano-structures in isotropic systems [5], to the application of the extended GEMC concept to ternary systems [6].

In the first case the Gibbs Ensemble Monte Carlo method was used to simulate osmotic equilibria for Lennard-Jones mixtures. When simulations were performed with two independent boxes separated by a selective membrane (exchange algorithm), one containing solvent and the other a mixture of solute and solvent significantly negative osmotic pressures (Π) developed. Those simulations were extended to include a third box and the possibility of modeling three coexisting phases. The new simulations showed that the two phase equilibria with negative values of Π were metastable and that the system spontaneously separated into three phases: pure solvent, dilute solute plus solvent and dense solute plus solvent with a resulting osmotic pressure that was normally small and positive.

In the second study [5], several binary systems composed of one-centre Lennard-Jones particles with identical size and interaction parameters but different cross diameter parameters were simulated using the extended version of the Gibbs ensemble Monte Carlo method, in an attempt to predict the fluid phase behavior in such systems. No liquid–liquid phase separation was found in the mixtures but all cases studied exhibit a structured liquid phase in equilibrium with its vapor. The domain shapes and patterns observed both in three- and two-dimensional simulations (stripe and bubble phases) were interpreted within the framework of the phenomenology of modulated phases, also known as microphase separated fluids. The appearance of stripe patterns occurs when the cross-interaction diameter is

larger than particles diameter, while the opposite is true for the bubble phases.

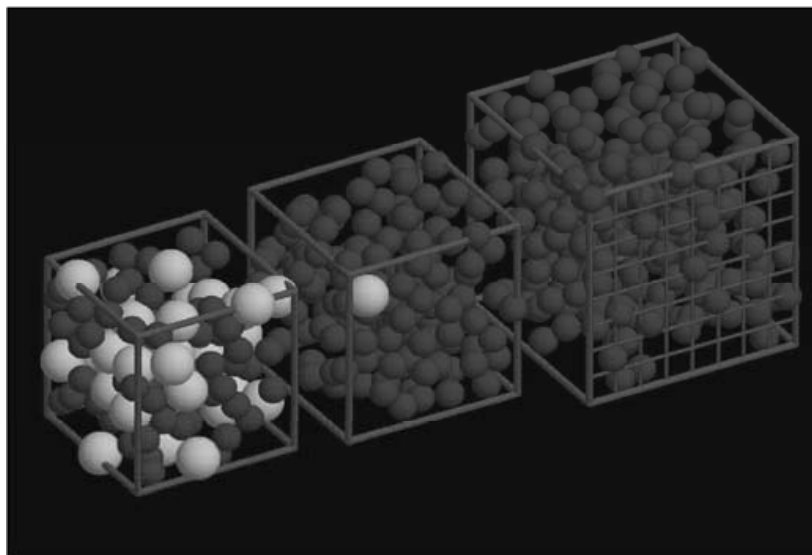


Figure 4. Osmotic equilibria in solutions of Lennard-Jones atoms.

The last article [6] discussed some of the issues related to the classification and representation of ternary diagrams and how these can be incorporated into the more general framework of global phase diagrams. It was shown that the representation of binary mixtures in the form of T - x diagrams constitutes an insightful and logical approach to the problem of a systematic classification of fluid phase behavior in terms of bifurcations (the yin and yang) and that the concept can be extended to the classification of ternary systems.

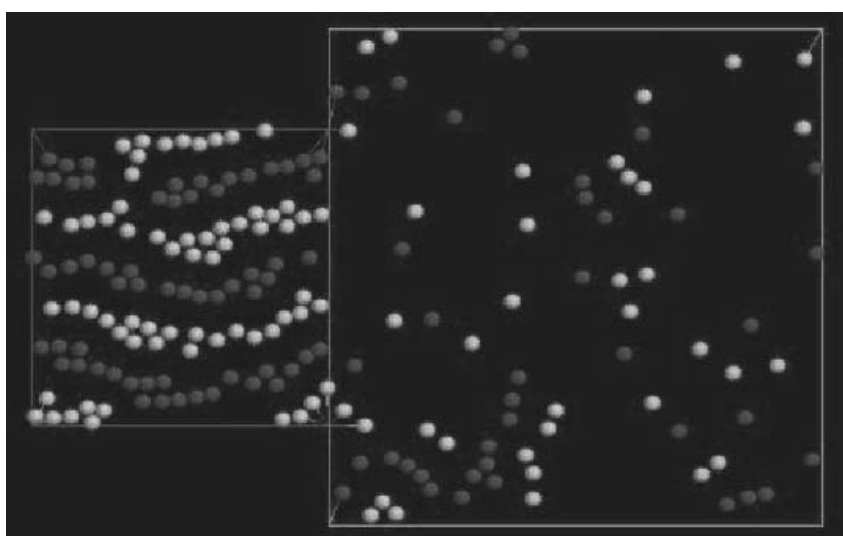


Figure 5. Microphase separation in a bidimensional simulation of a mixture of Lennard-Jones atoms using the GEMC method.

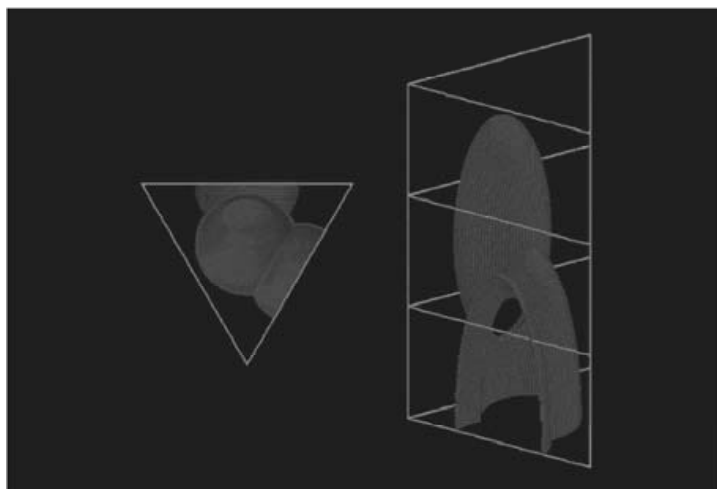


Figure 6. Application of the extended GEMC method to ternary systems: ternary diagram showing the boundaries of liquid-liquid immiscibility.

3. MOLECULAR DYNAMICS SIMULATIONS

The change from atomic to molecular – and from Monte Carlo to Molecular Dynamics methods - was a natural step that occurred more or less in the middle of the period corresponding to the different studies just presented (around 2000). Surprisingly it was old experimental work, from the time of the PhD. Thesis at IST/UTL, under the supervision of Professor Jorge Calado, that started this new line of research. From those times (and also from other more recent ones) remained the interest concerning the experimental study of isotope effects on the thermodynamic properties of pure substances and their mixtures. Unfortunately, the relation between Molecular Dynamics simulations and isotope effects is not a straightforward one: the former methods are based on classical equations of motion, which do not contain the quantum mechanical treatment necessary to interpret correctly the latter effects. Nevertheless, and without the need to use more complicated schemes involving the incorporation of quantum corrections into the computational methods, it was possible to use the statistical theory of isotope effects in condensed phase (a theoretical tool that includes the required quantum treatment) in combination with data obtained from Molecular Dynamics simulations. Another interesting turn of events was that most of the Molecular Dynamics work that was to follow was done in collaboration with Professor Agílio Pádua, presently at Blaise Pascal Université in Clermont Ferrand, France, but also a fellow PhD. student at IST/UTL.

The first problem to be studied in this way was the isotope effect on the solubility of methane in aqueous solution [7].

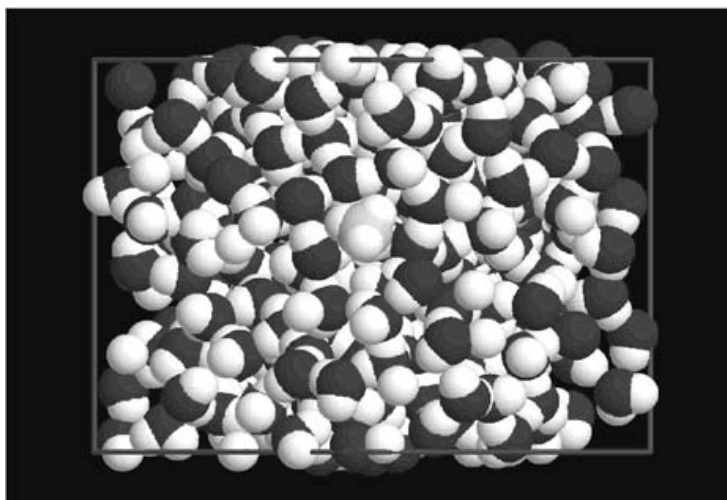


Figure 7. One methane molecule (center) surrounded by 511 water molecules. Molecular Dynamics simulation to obtain data on the solubility of isotopically substituted methane in water.

The isotope effect on the Henry's law coefficients of methane in aqueous solution (H/D and $^{12}\text{C}/^{13}\text{C}$ substitution) were interpreted using the statistical mechanical theory of condensed phase isotope effects. The missing spectroscopic data needed for the implementation of the theory were obtained either experimentally (infrared measurements), by computer simulation (Molecular Dynamics technique), or estimated using the Wilson's *GF* matrix method. The order of magnitude and sign of both solute isotope effects can be predicted by the theory. Even a crude estimation based on data from previous vapor pressure isotope effect studies of pure methane at low temperature can explain the inverse effect found for the solubility of deuterated methane in water.

Another similar problem (involving isotope effects) was also solved using a statistical mechanics theory solved by computational (numerical) methods [8].

Vapor pressure isotope effects (VPIEs) in monatomic systems (neon to xenon, either between pure isotopes or in their binary mixtures) were evaluated using an integral equation theory for a Lennard-Jones fluid with the Duh–Haymet–Handerson closure. The most relevant quantity obtained in this way is the average of the Laplacian of the potential energy of the system, also known as the mean force constant. The results correctly predict the different rare-gas VPIEs which span over several orders of magnitude. Using a simple two-parameter corresponding states principle, the method was capable of predicting VPIEs simply from the knowledge of isotopically independent Lennard-Jones parameters of each rare gas and the masses of its isotopes. Each type of VPIE (in pure isotopes or mixtures) map onto two reduced variable equations. The first variable represents a reduced form of the reduced partition function ratio (a measure of the VPIE between pure

isotopes) while the second is a reduced form of the liquid activity coefficient at infinite dilution (a measure of VPIEs in isotopic binary mixtures). Several issues related to the temperature and density dependence of the mean force constant are also addressed in this work.

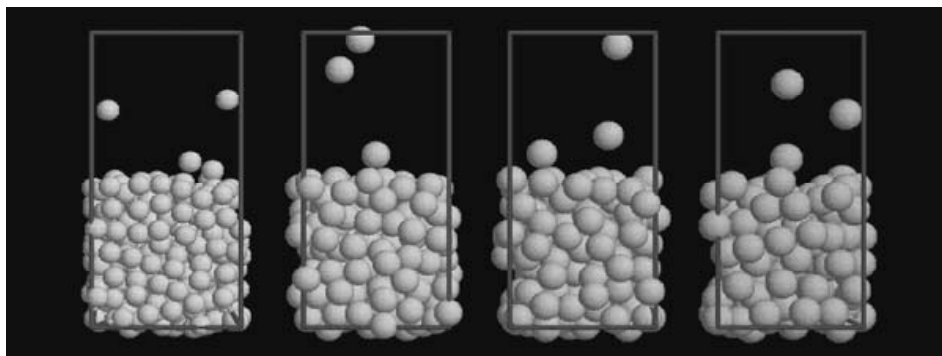


Figure 8. Schematic representation of the work involving the determination of the vapor pressure isotope effect in the rare gases (neon, argon, krypton and xenon) using integral equations theory.

After the study of isotope effects using Molecular Dynamics simulations as a means to obtain auxiliary data, the investigations using Molecular Dynamics as the central predictive or interpretative tool rapidly gained center-stage status on a wide variety of molecular systems: polycyclic aromatic compounds (heptacyclene isomers, [9]), organometallics (ferrocene and its derivatives, [10]), inorganic crystals (apatites, [11-13]), ramified oligomers and polymers of controlled generation (dendrimers, [14]) and “last but indeed not the least” low melting temperature salts (room temperature ionic liquids, [15-19]).

In the case of heptacyclene molecules, the energetics of the thermal dimerization of acenaphthylene to give *Z*- or *E*-heptacyclene was investigated. The standard molar enthalpy of the formation of monoclinic *Z*- and *E*-heptacyclene isomers at 298.15 K were determined by microcombustion calorimetry and the corresponding enthalpies of sublimation were also obtained by Knudsen effusion and Calvet-drop microcalorimetry methods. These results, in conjunction with the reported enthalpies of formation of solid and gaseous acenaphthylene, and the entropies of acenaphthylene and both heptacyclene isomers obtained by quantum mechanical calculations led to the conclusion that at 298.15 K the thermal dimerization of acenaphthylene is considerably exothermic and exergonic in the solid and gaseous states, suggesting that the non-observation of the reaction under these conditions is of kinetic nature. A full determination of the molecular and crystal structure of the *E* dimer by X-ray diffraction was also reported for the first time. Finally, molecular dynamics computer simulations on acenaphthylene and the heptacyclene solids were

carried out and the results discussed in light of the corresponding structural and enthalpy of formation data obtained experimentally.

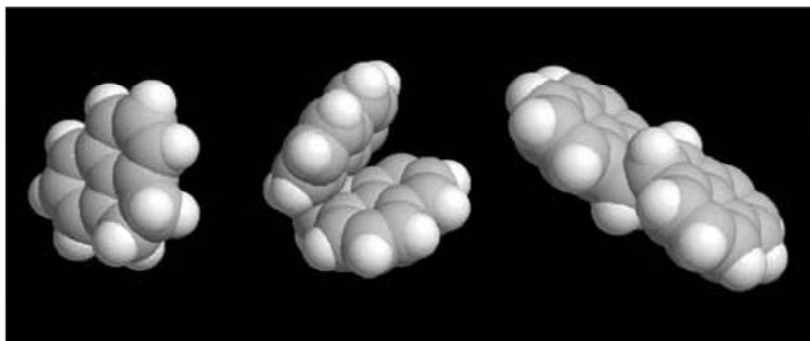


Figure 9 Acenaphthylene and the Z and E isomers of heptacyclene.

For metallocenes of the ferrocene family, a new force field for their molecular modeling was constructed [10]. The model was based on the OPLS-AA/AMBER framework. Ab initio calculations were performed to obtain several terms in the force field not yet defined in the literature. These included geometrical parameters, torsion energy profiles and distributions of atomic charges that blend smoothly with the OPLS-AA specification for alkyl chains. Validation was carried out by comparing simulated and experimental data for five different ferrocene-based complexes in the crystalline phase.

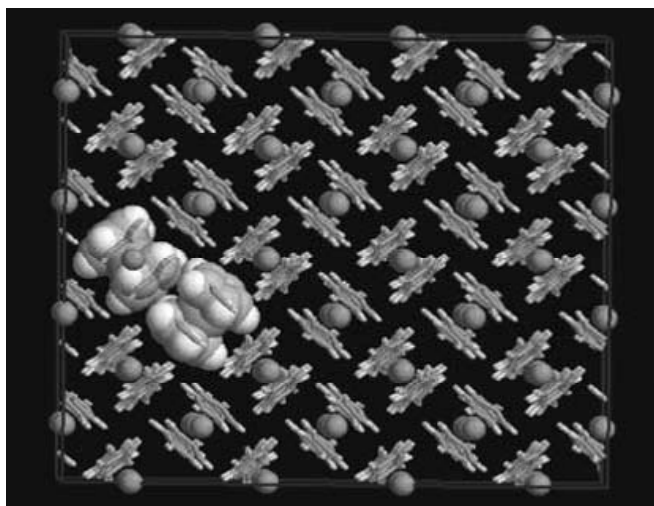


Figure 10. Snapshot of a Molecular Dynamics simulation of a ferrocene crystal.

The structural and thermodynamic properties of crystalline calcium apatites, $\text{Ca}_{10}(\text{PO}_4)_6(\text{X})_2$ ($\text{X} = \text{OH}, \text{F}, \text{Cl}, \text{Br}$), were investigated using an all-atom Born-Huggins-Mayer potential by a molecular dynamics technique [11,12]. The accuracy of the model at room temperature and atmospheric pressure was checked against crystal structural data, with maximum deviations of ca. 4% for the haloapatites and 8% for hydroxyapatite. The

standard molar lattice enthalpy of the crystalline apatites was calculated and compared with previously published experimental results, the agreement being better than 2%. The molar heat capacity at constant pressure, $C_{p,m}$, in the range 298-1298 K, was estimated from the plot of the molar enthalpy of the crystal as a function of temperature. High-pressure simulation runs, in the range 0.5-75 kbar, were performed in order to estimate the isothermal compressibility coefficient, κ_T , of those compounds. The deformation of the compressed solids is always elastically anisotropic, with BrAp exhibiting a markedly different behavior from those displayed by HOAp and ClAp. High-pressure p - V data were fitted to the Parsafar-Mason equation of state with an accuracy better than 1%.

Molecular dynamics simulations of molten hydroxyapatite were also performed, for the first time, in the range $2000\text{K} < T < 3000\text{K}$ and pressures up to 20 GPa [13]. The all-atom Born–Huggins–Mayer potential energy function employed had been previously used to study the thermodynamic properties of the solid compound (see above). High-temperature simulation runs were used to generate the pVT surface of the melt, from which properties like the isobaric thermal expansion coefficient, α_p and the isothermal compressibility, κ_T , could be evaluated. The heat capacity at room pressure, C_p , in the range 2000–3000 K, was estimated from the plot of the molar enthalpy of the melt as a function of temperature. The intermolecular atom–atom distribution functions, at several temperatures and pressures, were also investigated. A universal EoS proposed by Parsafar et al. was shown to give a good account of the MD data, the precision being better than 0.5%. Likewise, the Parsafar–Mason regularity which assumes a linear dependence of $(Z-1)V^2$ on ρ^2 , has been established for molten hydroxyapatite.

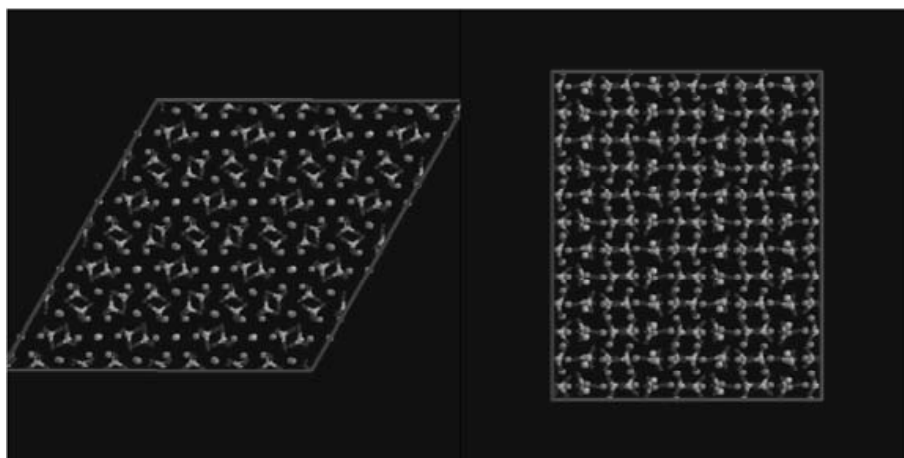


Figure 11. Two views of a chloro-apatite crystal showing the spatial arrangement of the chloride anions (isolated atoms) in hexagonal channels.

The structure and dynamics of poly(amido amide) (PAMAM) dendrimers have been of great interest both scientifically and industrially, but such important features as the distributions of atoms, channels, and strain inside these molecules remain unresolved. The work on this systems [14] involves systematic investigations of the atomistic structure of PAMAM dendrimers as a function of their generation. Structural properties such as the radius of gyration, shape tensor, asphericity, fractal dimension, monomer density distribution, solvent accessible surface area, molecular volume, and end group distribution functions, were evaluated from extensive molecular dynamics simulations.

In the case of ionic liquids, the first studies concentrated on the development of force-fields specially adapted to this class of compounds [15-18].

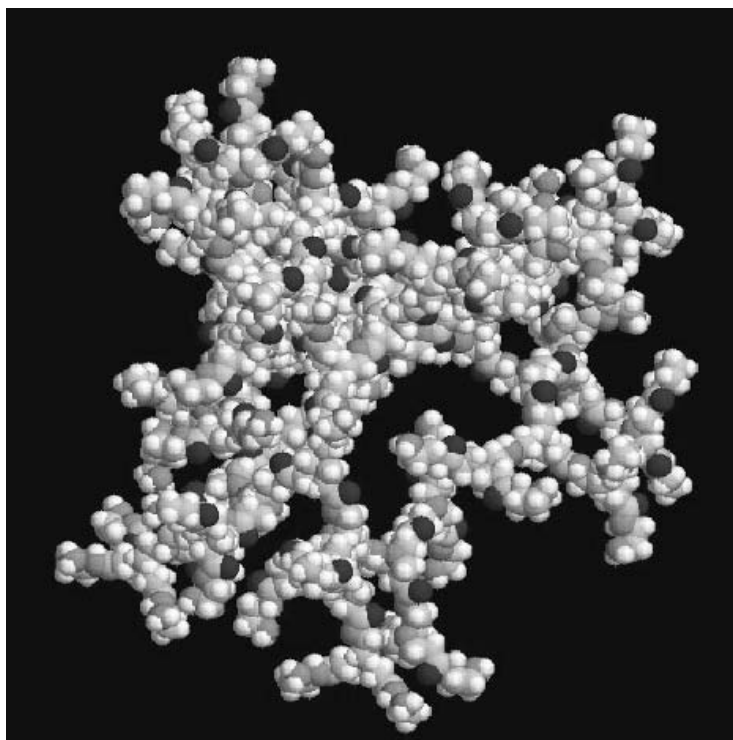


Figure 12. Fourth generation PAMAM dendrimer.

A new force field for the molecular modeling of ionic liquids of the dialkylimidazolium cation family was constructed [15,16]. The model is based on the OPLS-AA/AMBER framework. Ab initio calculations were performed to obtain several terms in the force field not yet defined in the literature. These include torsion energy profiles and distributions of atomic charges that blend smoothly with the OPLS-AA specification for alkyl chains. Validation was carried out by comparing simulated and experimental data on fourteen different salts, comprising three types of anion and five lengths of alkyl chain, in both the crystalline and liquid phases. The present

model can be regarded as a step toward a general force field for ionic liquids of the imidazolium cation family that was built in a systematic way, is easily integrated with OPLS-AA/AMBER, and is transferable between different combinations of cation-anion.

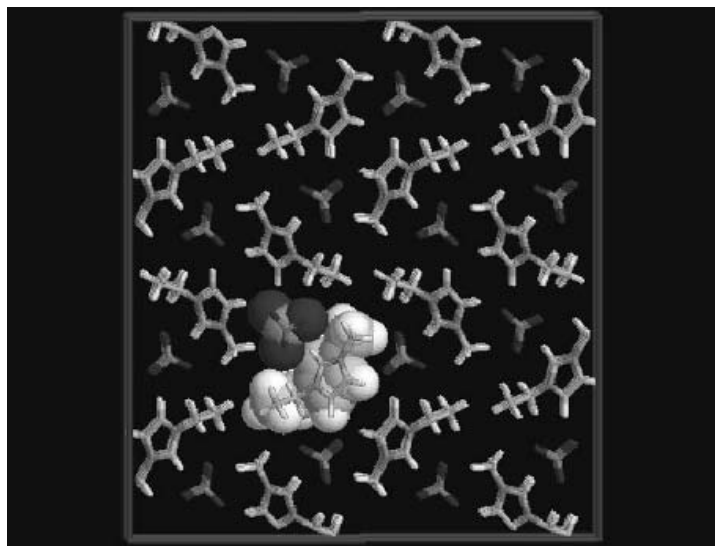


Figure 13. Initial configuration of a Molecular Dynamics simulation of a 1-ethyl-3-methylimidazolium nitrate ionic liquid below its melting temperature.

After the dialkylimidazolium cations, the force field development concentrated on two anions that started to be widely used in ionic liquids formulations [17]: a set of force field parameters was proposed for the molecular simulation of ionic liquids containing the anions trifluoromethylsulfate and bis(trifluoromethylsulfonyl)imide, also known as triflate and bistriflylimide, respectively. The new set can be combined with existing force fields for cations in order to simulate common room-temperature ionic liquids, such as those of the dialkylimidazolium family, and can be integrated with the OPLS-AA or similar force fields. Ab initio quantum chemical calculations were employed to obtain molecular geometry, torsional energy profiles, and partial charge distribution in the triflate and bistriflylimide anions. One of the torsions in bistriflylimide, corresponding to the dihedral angle S-N-S-C, has a complex energy profile which is precisely reproduced by the present parameter set. A new set of partial electrostatic charges is also proposed for the pyrrolidinium and tri- and tetra-alkylammonium cations. Again, these parameters can be combined with the OPLS-AA specification for amines in order to simulate alkylammonium salts. The force-field models were validated against crystal structures and liquid-state densities.

An article describing the force fields for other cations (monoalkylimidazolium, phosphonium and pyridinium) and anions (bromide, dicyanamide) is currently under preparation [18].

The second line of research concerning ionic liquids refers to the obtention of their structural properties using simulation data [19,20].

Nanometer-scale structuring in room-temperature ionic liquids was observed using molecular simulation [19]. The ionic liquids studied belong to the 1-alkyl-3-methylimidazolium family with hexafluorophosphate or with bis(trifluoro-methanesulfonyl)amide as the anions, respectively. They were represented, for the first time in a simulation study focusing on long-range structures, by an all-atom force field of the AMBER/OPLS_AA family containing parameters developed specifically for these compounds. For ionic liquids with alkyl side chains longer than or equal to four carbon atoms, aggregation of the alkyl chains in nonpolar domains was observed. These domains permeated a tridimensional network of ionic channels formed by anions and by the imidazolium rings of the cations. The nanostructures were visualized in a conspicuous way simply by color coding the two types of domains (in this work, we chose red (polar) and green (nonpolar)). As the length of the alkyl chain increases, the nonpolar domains became larger and more connected and caused swelling of the ionic network, in a manner analogous to systems exhibiting microphase separation. The consequences of these nanostructural features on the properties of the ionic liquids were analyzed.

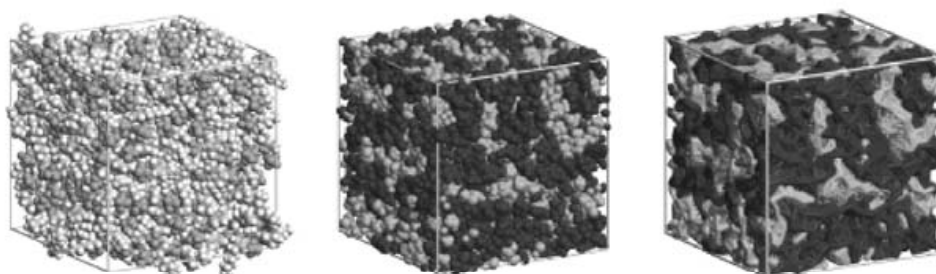


Figure 14. Nano structures in ionic liquids. The polar and non-polar domains are color-coded dark and light grey, respectively. In the last representation the bonds between atoms are shown in order to enhance the distinction between the two domains. .

In a second work, the dihedral distribution of the alkyl side chain of the imidazolium cations of ionic liquids was discussed by comparison of spectroscopical (Raman) and *ab initio* data with results obtained by molecular dynamics simulations [20]: a molecular force field for the computer simulation of ionic liquids was validated *a posteriori* by confrontation against Raman spectroscopic data, published after the force field had been formulated. Specifically, the terms in the force field describing the conformational aspects of dialkylimidazolium cations, that

were specifically developed for these compounds using high level ab initio calculations, were those affecting the distribution of conformers in simulated ionic liquids. Those distributions are compared with analyses of the liquid-phase Raman spectra, and the features of a series of dihedral torsions along the alkyl side chains in 1-alkyl-3-methylimidazolium cations in several ionic liquids were discussed.

4. CONCLUSION

The diversity of computer simulations presented in this paper (the portfolio) demonstrates on one hand the ease of implementing this kind of calculation for new systems and, on the other hand, the predictive and interpretative power of these methods to address issues that are not easy to study by purely experimental or theoretical techniques.

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