COMPUTER SIMULATION OF THE ATOMIC BEHAVIOUR IN CONDENSED PHASES

*A. GIRO; **J.A. PADRO

Universitat Politècnica de Catalunya i Universitat de Barcelona

Molecular dynamics simulation method for the study of condensed phases of matter is described in this paper. Computer programs for the simulation of atomic motion have been developed. Time–saving techniques, like the "cellular method", have been incorporated in order to optimize the available computer resources. We have applied this method to the simulation of Argon near its melting point. Differences in the structure, thermodynamic properties and time correlation functions of solid and liquid phases are discussed.

Keywords: Computer simulation, molecular dynamics, statistical mechanics, condensed matter, structural–properties, thermodynamic properties, transport properties.

1. INTRODUCTION

The aim of the theory of molecular systems is to predict macroscopic properties on the basis of the interactions between the constituent particles. However, the prediction of the properties of a large ensemble of molecules interacting through pair potentials is an unsolved problem: the N–body problem. An alternative to analytical theories are computer experiments that generate representative statistical samples of the system from wich macroscopic and microscopic properties can be derived. Altough the theory used to generate simulations is much simpler than the statistical mechanical theories, the results can be far more accurate and less assumptions go into the derivation of the results.

Computer simulations are often used to test the reliability of analytical theories using simple potential models. But, when realistic potentials are considered, computer simulation can also play a role analogous to the experiment e.g., predicting the properties of real systems in situations where an experimental study demands very costly resources. On the other hand, computer simulation methods allow to consider ideal experiments with unreal particles, wich can be very interesting in order to understand the basis of the behaviour of matter. In the past computer simulations have been used to study simple systems but during the last years these methods have also been applied to complex systems e.g., mixtures [1] and solutions [2], ionic liquids [3] macromolecules [4] colloidal systems [5], surfaces [6], chemical reactions [7], liquid crystals [8], etc.

There are two principal simulation methods: Monte Carlo (MC) and Molecular Dynamics (MD). MC method generate a representative statistical equilibrium ensemble in wich each configuration occurs with its Boltzman probability, for a given temperature and volume. All static equilibrium properties can be obtained by computing that property for each configuration and averaging over the ensemble. MD method, on the other hand, reproduce the trajectories of all the particles in the system by solving the classical equations of motion. If the trajectories are sufficiently long it also contain a representative ensemble of equilibrium configurations, but, in addition, the trajectories will contain dynamical information. The computer effort for a comparable statistical accuracy is of the same order the magnitude for MD and MC. However the former permit to consider the dynamical properties, and we will concentrate on it in this paper. In Section 2, we describe the MD method and we show the main characteristics of our computer programs, wich have been used in the computer simulation of solid and liquid Ar (details are given in Section 3). Section 4 and 5 are devoted to define the properties usually obtained from MD simulations and to discuss their differences when solid and liquid phases are considered. Finally, the perspectives for our future researches based on the MD simulation method are outlined in Section 6.

2. DESCRIPTION OF MOLECULAR DYNAMICS METHOD

Molecular Dynamics (MD) allows the study of a great variety of properties of matter [19], [10], [11] by evaluating the adequate average over microscopic configurations. These configurations are obtained by integration of the classical equations of motion corresponding to a system of N particles interacting through a truncated two–body potential. In order to solve this system of $6N$ differential equations an important power of numeric calculus is required. It is so why the development of MD has followed the development of computer's capacity and speed.

The most obvious difficulty of the MD method is the fact that the size of the sample wich can be studied is extremely small ($N < 1000$). In order to minimize surface effects and to simulate more closely the properties of an infinite system, periodic boundary conditions [12] are imposed. The particles of interest lie in the central box and this basic unit is sorrounded on all sides by periodically repeating replicas of itself. We allow the walls of the central box to be completely permeable so that if a particle passes through a wall one of its images enters through the opposite wall.

Fig. 1 includes a flow–chart diagram of our MD program. This shows clearly that is easily turned due its composition with independents blocks. Differents possibilities are available: change of initial conditions, interatomics potentials, integration method of equation of motion,...
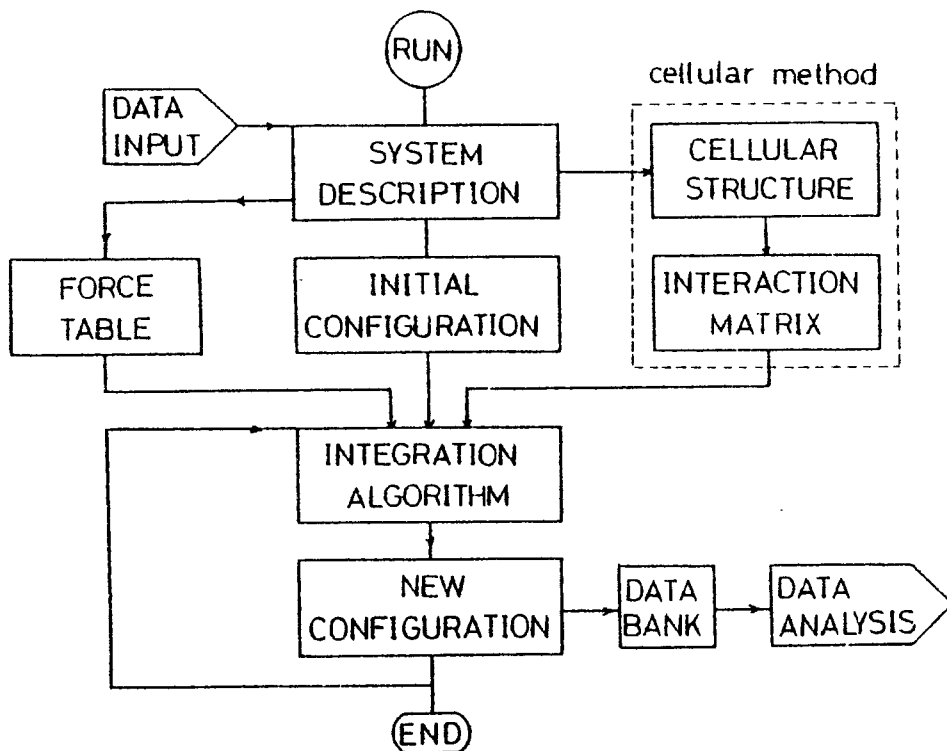

FIGURA 1. Molecular Dynamics flow chart

In order to calculate the evolution of a set of N molecules we start from an initial configuration $(\vec{r}_o, \vec{v}_o)$. Computer time–saving forces to select an initial configuration very near to equilibrium state. In this way, it is convenient to begin with a face centered cubic structure slightly distorted at random [13] and with a maxwelian velocity distribution. The condition $\sum_i \vec{v}_i = 0$ must be always imposed to prevent that the motion of the center of mass could disturb the calculus of certain time–functions as the mean square displacement.

Once the density and the potential's range are fixed we only must compute the interaction of each molecule with those that are within its interaction range. In order to shorten the computing time we have used the "cellular method" [14], [15]. To this purpose we divide the main cube in a net of cubic cells (fig. 2). The calculation begins by stablishing a table in wich each cell is associated with all those cells, images or not, located at smaller distance than the potential range r_f. For each time step a new table is constructed which associates to each cell the molecules included in it. The interaction among particles are then calculated computing only the distances between particles located in the same cell or in the neighboring ones, according the tables previously constructed.
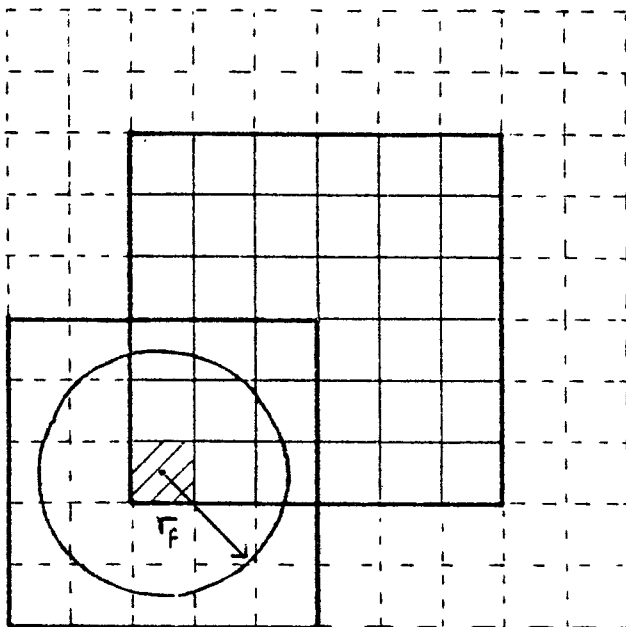

FIGURA 2. Cellular structure for a two–dimensional system

Once given the pairwise interaction potential, the particle position $\vec{r}_i(t)$ and the velocities $\vec{v}_i(t)$ $(i = 1, \ldots, N)$ at time t, the main problem is to find the corresponding values of the variables at time $t + \Delta t$. Several integration algorithms have been proposed to solve this problem [13]. In this work we use a simple predictor–corrector method such as that used by Rahman [10] in this simulation of liquid Argon. From $\vec{r}_i(t), \vec{v}_i(t)$ and $\vec{a}_i(t)$ an estimate of $\vec{r}_i(t + \Delta t)$ is given by:

$$(1) \qquad \vec{r}_i^I(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \vec{a}_i(t).\Delta t^2/2$$

From $\vec{r'}_i(t + \Delta t)$ we obtain a new interaction force and we can know $\vec{a}_i'(t + \Delta t)$. The corrected values of the positions and velocities at $t + \Delta t$ are then given by:

$$(2) \qquad \vec{v}_i(t + \Delta t) = \vec{v}_i(t) + (\vec{a}_i'(t + \Delta t) + \vec{a}_i(t)).\Delta t/2$$

$$(3) \qquad \vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + (\vec{a}_i'(t + \Delta t) + \vec{a}_i(t)).\Delta t^2/4.$$

3. APPLICATION: COMPUTER SIMULATION OF Ar

The Molecular Dynamics method described in the former section has been applied to simulate a system of 500 particles of *Ar* interacting through a pairwise Lennard–Jones potential.

$$(4) \qquad V(r) = 4\varepsilon((\sigma/r)^{12} - (\sigma/r)^6)$$

with $\sigma = 3.4 \mathring{A}$ and $\varepsilon = 1.653.10^{-21}J$. The intermolecular force $(F = -dV/dr)$ is cut at 7.65 $\mathring{A}$. In previous works [16], [17] it has been shown that this intermolecular potential allows a good reproduction of the Ar properties for both, liquid and solid phases.

Initially, we have assumed a face–centered cubic structure slightly distorted at random. In the first time–steps the velocity of molecules has been controlled by adjusting them when the root–mean–square velocity differs more than 3% from the desired value. After, the evolution is free and the system remains in

its equilibrium state for 1000 time–steps (one time–step $\Delta t = 10^{-14}s$). The temperatures and densities of the simulated systems are shown in Table 1.

TABLE 1: THERMODYNAMIC PROPERTIES

STATE	SOLID	LIQUID
$V(m^3.mol^{-1})$	2.44 10^{-5}	3.09 10^{-5}
$T(K)$	77.5	83
$P(bar)$	-10	-360
$U(KJ.mol^{-1}K^{-1}$	$-$ 6.36	$-$ 4.52
$Cv(J.mol^{-1}K^{-1}$	21	22
$D(m^2.s^{-1})$	0	2.5 10^{-9}

4. STRUCTURE AND THERMODYNAMIC PROPERTIES

An image of the microscopic structure of the system is provided by the radial distribution function,

(5) $$g(r) = n(r)/\rho_0 4\pi r.^2 \Delta r$$

where $n(r)$ is the number of atoms contained in a spherical shell of radii r and $r + \Delta r$ centered at a given molecule and ρ_0 is the mean density.

Radial distribution functions consist of a pronounced first peak located roughly on the pair potential minimum. In dense liquid systems the first peak is followed by a number of subsidiary oscillations damping out to unity beyond four or five atomic diameters (Figure 3). On the contrary, the solid phases show a long range structure, with maximums located at distances corresponding to a perfect face centered cubic structure.
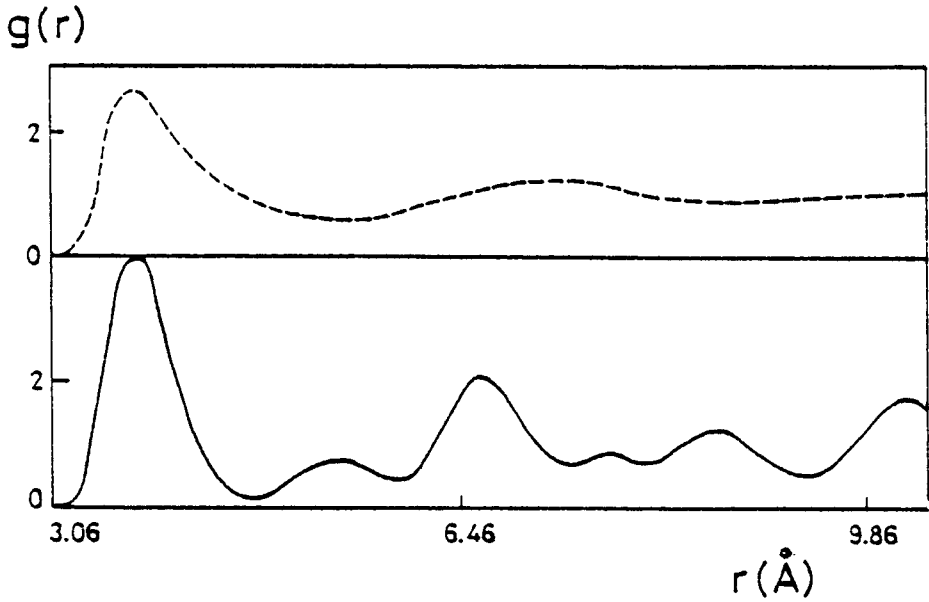
FIGURA 3. Radial distribution function.
The solid lines correspond to solid Ar.
The dashed line is for Ar liquid.

The Fourier transform of g(r) yields the structure factor $S(k)$, which is directly related to diffraction experiments:

$$(6) \qquad S(K) = 1 + \rho_0 \int_0^\infty [4\pi r^2 (g(r) - 1)(\sin kr)/kr] dr$$

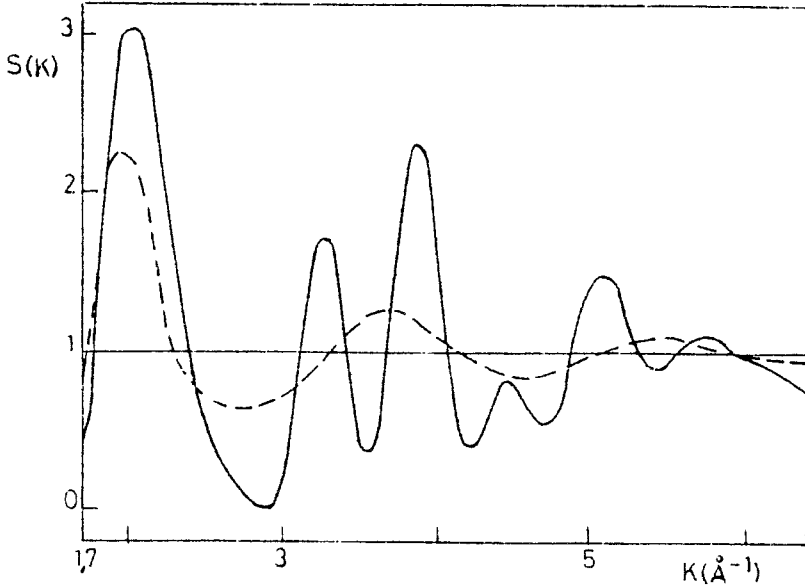Figure 4 shows the differences between the solid–like and the liquid–like $S(K)$.

71

FIGURA 4. Structure factor of Argon.
The solid lines correspond to solid Ar.
The dashed line is for Ar liquid.

From $g(r)$ functions, the pressure and internal energy can be obtained through the expressions [18]:

$$(7) \qquad P = \rho_0 KT - 2\pi\rho_0^2 \int_0^\infty g(r) \quad (dV/dr) r^3 \, dr$$

$$(8) \qquad U = 3KT/2 - 2\pi\rho_0 \int_0^\infty g(r) V(r) r^2 \, dr$$

The values obtained from our simulations are shown in Table I. The error introduced in the numerical integration of integral (7) is important, since its final value is smaller than some of the terms wich are included during the computation. In addition the two terms of (7) have the same order of magnitud in the systems near melting point and therefore the accuracy of the values obtained for P es quite small ($\sim \pm 20$ bar). The error associated with the computation of U is smaller and we estimate it to be about 1%. The heat capacity at constant volume may be calculated from the fluctuation on the root mean square velocity following the equation [19]

72

(9)
$$C_v = N_A K_B / (2/3 - N < (\Delta T)^2 > /T^2)$$

where $<>$ means a time average over the squares of the deviations of temperature from its mean value. N_A is the Avodrago's number, K_B the Boltzman's constant and N the number of particles.

5. TIME–CORRELATION FUNCTIONS

The dynamical evolution of particles isusually analysed through two time–correlation functions, the velocity autocorrelation function.

(10)
$$\psi(t) = < \sum_i \vec{v}_i(0), \vec{v}_i(t)) / N(v_i(0))^2 >$$

and the mean square displacement function,

(11)
$$< r^2(t) > = < (\sum_i |\vec{r}_i(t) - \vec{r}_i(0)|^2) / N >$$

where $<>$ means that the time average is taken with several time origines.

Velocity autocorrelation function basically gives correlation between directions of vector velocity and hence between succesive directions of motion. The backscattering (negative values of $\psi(t)$) indicates high probability of large–angle deflections [20] and can already be noticed in high density liquids near the triple point, where the behaviour of molecules is intermediate between that of a dilute gas and that of an anharmonic solid. Backscattering is obviously much stronger in solids and therefore their $\psi(t)$ reaches greater negative values (Figure 5).
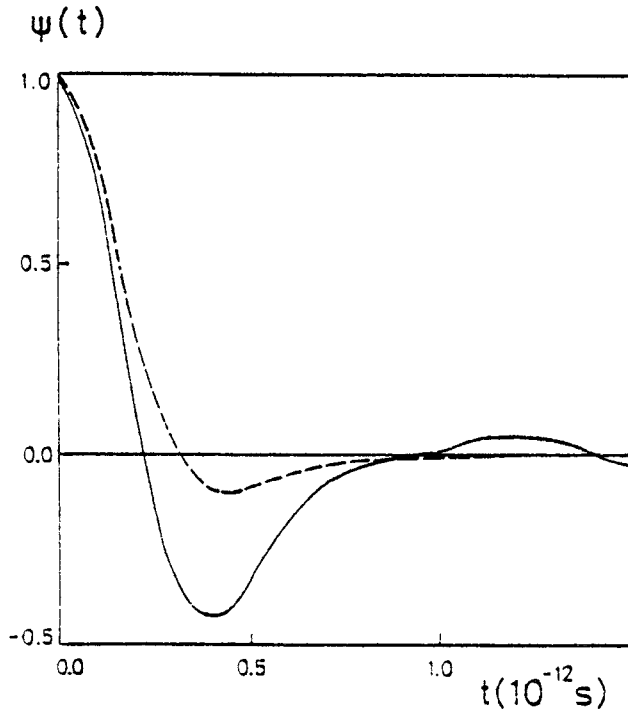
FIGURA 5. Velocity autocrrelation functions.
The solid lines correspond to solid Ar.
The dashed line is for Ar liquid.

It is logic that the mean square displacement of the molecules in a crystallyne solid fluctuates with time around a constant value (Figure 6). On the contrary in the liquid state a linear dependence or $< r^2(t) >$ with respect to time can be observed.
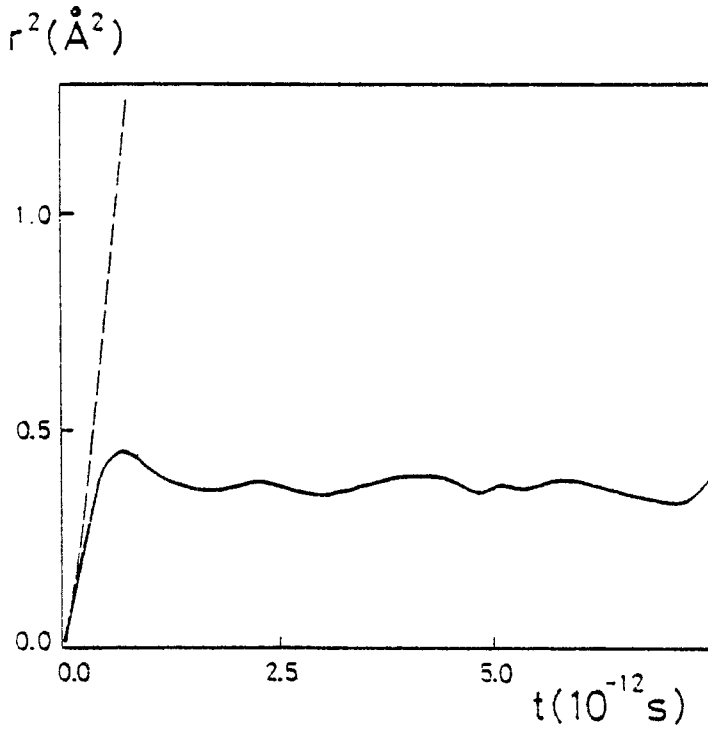
FIGURA 6. Mean Square displacements.
The solid lines correspond to solid Ar.
The dashed line is for Ar liquid.

The typical macroscopic property that usually is used to characterize the dynamical behaviour of atoms is the self–diffusion coefficient D. It can also be obtained from the Molecular Dynamics simulations following the expressions [20],

$$(12) \qquad D = K_B T/m \quad \int_0^\infty \psi(t)\,dt$$

$$(13) \qquad \lim_{t \to \infty} r^2(t) = 6Dt$$

Atomic motion in solid phases do not show, obviously, any diffusion component and we have not observed a significant value for D (see Table 1). The

value of D for the liquid has been obtained from the arithmetic mean of the values obtained from (12) and (13).

In Fig. 7 we plot some oscillatory movement of particles projected over a set of coordinate axes parallel to the sides of the cube containing the system during the solid simulations. The difference between these movements and harmonic oscillations of ideal solids at temperatures lower than the ones considered in this work is evident.
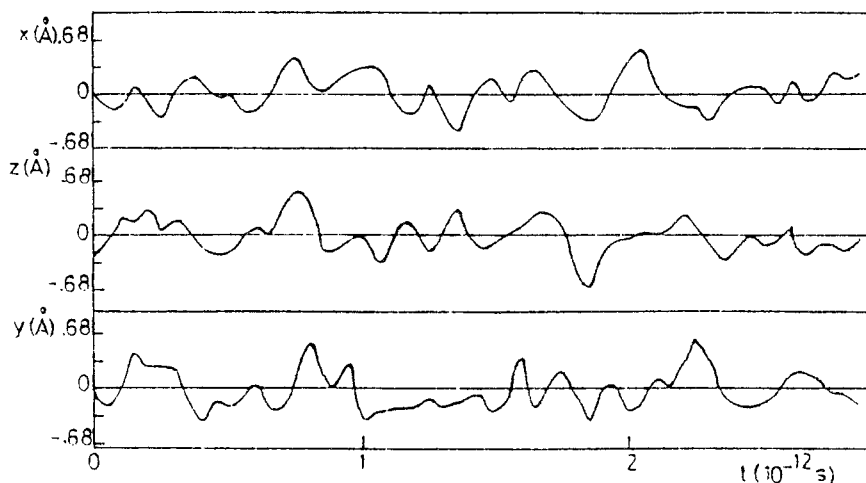

FIGURA 7. Oscillatory movement of a particle over X, Y, Z coordinate axes parallels to the sides of the cube in simulations of solid phase

6. PERSPECTIVES

It has been shown along this work that the MD simulation technique is a useful method for the analysis of the properties of matter from a microscopic point of view. Moreover, the information provided by these kind of studies is not only very helpful for the development of realistic physical models of the atomic behaviour but also may be a valuable aid for the interpretation of spectroscopic experiments [21].

We have extended the MD simulations discussed in this paper to the consideration of more complex systems. So, we have already analysed the properties of the isotopic liquid mixtures [22] and molten salts [23] (previously, it has

76

been incorporated in our MD programs the Ewald's method [24], which allows the consideration of the long–ranged Coulomb interactions). Further–more, the use of the Langevin's equation instead of the classical Newton's equation (Langevin dynamics method [25] , [26]), provides a time–saving method that is being now used in computer simualtions of the ionic evolutions in electrolyte solutions. We are planning to apply also this methodology to chemical reactions and macromolecules in solution. On the other hand, we think that the MD simulation method may be a useful tool for the study of the phase transitions and interfacial systems and we hope that our research will be soon extended towards these attractive subjects.

7. REFERENCES

[1] **Balcells, M.; Giró, A.; Padró J. A.** "Correlations in the Ar–Kr Liquid Mixture", Physica 135A, 414–425 (1986).

[2] **Heizinger, K.** "Computer Simulations of Aqueous Electrolyte Solutions", Physica 131B, 196–216(1985).

[3] **March, N. H.; Tosi, M. P.** "Coulomb Liquids". Academic Press. (1984).

[4] **Van Gunsteren, W. F.; Berendsen, H. J. C.; Rullmann, J. A. C.** "Stochastic Dynamics with Constraints. Brownian Dynamics of n–alkanes". Mol. Phys 44, 69–95 (1981)

[5] **Van Megen, W.; Snook, I** "Brownian–Dynamics Simulations of Concentrated Charge–stabilized Dispersions". J. Chem. Soc. Faraday Trans. 2, 80, 383–394 (1984).

[6] **Croxton, C. A.** "Statistichal Mechanics of the liquid Surface". (Chap. 10), John Wiley & Sons, (1980).

[7] **Bergsma, J. P.; Hynes, J. T.** "Dynamics of the A+BC Reaction in Solution", Chem. Phys. Letters 123, 394–398 (1986).

[8] **Akesson, T.; Jönsson, B.** "Brownian Dynamics Simulation of an Electric Double Layer. Applications to Lamellar Liquid Crystals". J. Phys. Chem 89, 2401–2405 (1985).

[9] **Alder, D. J.; Wainwright, T. E.** "Studies in Molecular Dynamics General Method". J. Chem. Phys. 31, 459–466, (1959).

[10] **Rahman, A.** "Correlations in the Motion of Atoms in Liquid Argon". Phys. Rev. A. 136. 405–411, (1964).

[11] **Verlet, L.** "Computer Experiments on Classical Fluids". Phys. Rev. A 165, 98–103, (1967).

[12] **Hansen, J. P.; MC Donald, I. R. M.** "Theory of Simple Liquids" (Chap. 3) Academic Press (1976).

[13] **Giró, A.; González, J. M.; Padró, J. A.; Torra, V.** "Molecular Dynamics: Analysis of Initial Conditions and Integration Methods". An. Fis. A, 77, 57–62 (1981).

[14] **Giró, A.; González J. M.; Torra, V.** "A time saving Method in Molecular Dynamics". An. Fis. 75, 154–158 (1979)

[15] **Giró, A.; González, J. M.; Padró, J, A.; Torra, V.** "The Structure of the Liquid Lead at 670 K through Molecular Dynamics". J. Chem. Phys. 73, 2970-2972, (1980)

[16] **Giró, A.; Padró, J. A.; Torra, V.** "Molecular Dynamics: Structure and Thermodinamic Properties of Liquid Argon". An. Fis. A, 78, 26–35, (1982).

[17] **Giró, A.; Padró, J. A.** "A Molecular Dynamics Study of Solid Argon Near its Melting Point: Structure, Thermodynamic Properties and Time–correlation Functions", An. Fis. B, 9–17 (1985).

[18] **McQuarrie, D. A.** "Statistical Mechanics" (Chap. 13), Harper & Row (1976).

[19] **Rahman, A.** "Molecular Dynamics Studies of Liquids" in "Interatomic Potentials and Simulation of Lattice Defects" (P. C. Gehlen, J. R. Beeler, R. I. Jafee, Eds.) 233–245, Plenum Press (1972).

[20] **Croxton, C.** "Introduction to Liquid State Physics" (Chap. 10) John Wiley & Sons, (1975).

[21] **Madden P. A.** "Simulation of Properties of Spectroscopic Interest". Proc. Internat. School Enrico Fermi. "Molecular–Dynmics Simulation of Statistical Mechanics Systems", Part V, 371–397, North–Holland (1986).

[22] **Padró, J.; Canales, M.; Sesé, G; Giró, A.** "Time–correlation functions in Isotopic Liquid Mixtures", Physica (to be published) (1988).

[23] **Tullás, J.** "Dinàmica Molecular de sistemes amb interacció coulombiana". Tesina. Facultat de Física. Universitat de Barcelona (1986).

[24] **Trullàs, J.; Giró, A.** "Computer Simulation of Ionic Systems". Proc. Int. AMSE Conference: "Modeling and Simulation" (Sorrento), 3, 4, 67–68 (1986).

[25] **Padró, J. A.; Guàrdia, E.; Giró, A.** "Langevin dynamics simulation of $L - J$ liquids. An analysis of solute concentration influence". Mol. Phys. 57, 4, 687–696 (1986).

[26] **Guàrdia, E.; Giró, A.; Padró, J. A.** "Nonaddittivity effects in generalized Langevin dynamics simulation of interacting particles". J. Chem. Phys. <u>84</u>, 4569–4573 (1986).