

# MODIFIED EWALD SUM AND N, V, T ENSEMBLE IN MOLECULAR DYNAMICS OF AN IONIC SYSTEM

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**ABSTRACT** — A molecular dynamics simulation of an ionic system has been done using a method recently suggested by Adams and Dubey for performing Ewald's summation. The damped force method of Hoover and Evans for simulation in the N, V, T ensemble has also been used. The results show that static and dynamic properties are in good agreement with experiment and N, V, E molecular dynamics simulation.

## 1 — INTRODUCTION

The molecular dynamics method (MD) [1] which enables the numerical solution of the Newton's equations for interacting many-body systems is now a well established approach in the study of classical fluids, and in particular, of ionic systems [2]. For these systems the truncation of the electrostatic energy contribution is not allowed and a crucial problem is to evaluate the electrostatic potential of a system of charges in a periodic cell. The classical method for calculating this potential was proposed by Ewald [3], but the expression obtained is rather complex, requiring two infinite summations, one in real space and the other in reciprocal lattice space. Nevertheless, it has been the method used so far, routinely, in molecular dynamics and Monte Carlo

simulations of ionic systems, although there exist other alternatives [4] used in the study of the One Component Plasma (OCP).

Recently, Adams and Dubey [5, 6] derived a modified expression for the Ewald's summation which enables the potential of a periodic system of charges to be obtained in a very simple and efficient way. In this approach, the electrostatic energy for a system of  $N$  interacting charges in a periodic cell is written in terms of an effective pair potential  $\psi_l(r)$  :

$$\phi^{\text{Coul}} = 1/2 \sum_i^N q_i^2 S + \sum_i^{N-1} q_i \sum_{j>i}^N q_j \psi_l(r_{ij}) \quad (1)$$

The term  $q_i^2 S$  is the energy due to the interaction between charge  $i$  and all its own periodic images. It is known as the self term and a neutral system it makes no contribution;  $r_{ij}$  is a nearest image vector and  $\psi_l(r)$  is expanded according to:

$$\psi_l(r) = 1/r + A_2 r^2 + \sum_{n=4,6,\dots}^l (A_n \text{KH}_n(r) + B_n \text{KHb}_n(r)) \quad (2)$$

where  $1/r$  is the interaction between the charges in the basic cell,  $A_2 r^2$  is the unique term which does not satisfy Laplace's equation; it is the solution of Poisson's equation and represents the contribution of the uniform neutralizing charge distribution that the Ewald summation puts around each charge. Finally the last terms is an expansion in Kubic Harmonics, which are polynomials of even order  $n \geq 4$ . For some values of  $n$  there are more than a single Kubic Harmonic. Adams and Dubey tabulated the Kubic Harmonics up to  $l = 20$  and the degeneracy occurs for  $n = 12, 16, 18$  and  $20$ , i. e.,  $B_n = 0$  except for these values of  $n$ .

The coefficients  $A_n, B_n$  for the expansion in Kubic Harmonics  $\text{KH}_n, \text{KHb}_n$  [7], for simple cubic (SC) and truncated octahedral (TO) boundary conditions, were optimized by Adams and Dubey for several approximations  $\psi_l$  [5, 6]. The optimization was made to give the best fit of  $\psi_l$  to the true Ewald  $\psi(r)$ . For molecular dynamics simulation  $\psi_l$  and its gradient are easily obtained since the Kubic Harmonics are simple known analytic functions.

In the present work we have employed SC periodic boundary conditions and  $\psi_l$  was expanded up to the tenth term. This choice

was determined by the results of the OCP study where  $\psi_{is}$  is a very good approximation [6].

Most of the simulations of ionic systems by molecular dynamics have been done using the N, V, E ensemble. This makes the comparison with Monte Carlo and experimental results rather difficult. Following the pioneering work of Woodcock [8] on isothermal molecular dynamics, other methods have been proposed to perform MD at constant mean temperature [9-13]. We have employed the damped force method of Hoover [11] and Evans [12] since it has been shown [9] that the method gives results identical to those of the N, Z, E ensemble.

The corresponding algorithm in the framework of the "leapfrog" form of the Verlet scheme has been given by Brown and Clarke [9]:

$$\mathbf{v}_i'(t) = \mathbf{v}_i(t - \Delta t/2) + \mathbf{F}_i(t) \Delta t/2m \quad (3)$$

$$\beta^2 = (3(N-1)K_B T_D) / \sum m_i v_i'^2(t) \quad (4)$$

$$\mathbf{v}_i(t + \Delta t/2) = \mathbf{v}_i(t - \Delta t/2) (2\beta - 1) + \mathbf{F}_i(t) \beta \Delta t/m \quad (5)$$

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t + \Delta t/2) \Delta t \quad (6)$$

$$\mathbf{v}_i(t) = [\mathbf{v}_i(t + \Delta t/2) + \mathbf{v}_i(t - \Delta t/2)]/2 \quad (7)$$

where  $\mathbf{v}_i'(t)$  is a projected velocity, i. e., a velocity in the absence of a damped force.  $T_D$  is the pre-defined temperature and  $K_B$  the Boltzmann constant. The damped force method reduces to simple scaling of the velocities and forces at each integration step.

## 2 - MODEL

Computations based on the above procedures have been carried out for molten NaCl at 1224.5 K and molar volume  $39.5 \text{ cm}^3 \text{ mol}^{-1}$  with 64 and 216 rigid ions in the basic MD cube. The same system was studied by Lantelme et al. [14], but they used the N, V, E ensemble and the classical Ewald's summation.

The pair potential was the Born-Mayer-Huggins potential with parameters for NaCl reported by Adams and MacDonald [15]:

$$\phi_{ij} = q_i q_j / r + B_{ij} \exp(-\alpha_{ij} r) - C_{ij} / r^6 - D_{ij} / r^8 \quad (8)$$

or

$$\phi_{ij} = \phi_{ij}^{\text{Coul}} + \phi_{ij}^{\text{Rep}} + \phi_{ij}^{\text{DD}} + \phi_{ij}^{\text{DQ}} \quad (9)$$

The simulation started from a face centred cubic lattice with randomly distributed velocities and the constraint of total zero momentum. The time step was  $0.8 \times 10^{-14}$  sec. Thermal equilibration was attained after 1400 time steps. For 64 ions 2000 time steps were generated for averages, while for 216 ions they were based on 5000 additional configurations (10 runs of 500 configurations). The calculations were done on a VAX 11/730 system using double precision arithmetic.

### 3 — RESULTS AND CONCLUSIONS

#### (a) *Thermodynamics*

Thermodynamical results are presented in the table I and compared with those of Lantelme et al. [14] and also with experiment. Comparison between the two molecular dynamics simulations shows a very good agreement. Identical Coulombic energies support the equivalence of both classical and modified Ewald summation methods. Furthermore, the results of a preliminary study with 64 particles (Table I) put into evidence a size independence of the method within the present approximation. The value of  $C_v$ , calculated by the usual canonical energy fluctuation formula [16] is in good agreement with the N, V, E and experimental results. The pressure, calculated from the virial expression, is about 1.3 kbar.

#### (b) *Structure*

The radial distribution functions are shown in the Fig. 1. For unlike ions ( $g_{+-}$ ) this function presents a first peak with

TABLE I — Thermodynamical data for NaCl

V (cm <sup>3</sup> /mol) = 39.5    T = 1224.5 K				
	N = 216	N = 216	N = 64	
	MD(N,V,E)[14]	MD(N,V,T)	MD(N,V,T)	Exp.
U (kJ/mol) (a)	- 680.2	- 682.7 ± 1.6	- 681.4 ± 1.8	- 692.7[17]
$\phi^{\text{Total}}$ (kJ/mol)	- 710.3	- 713.3 ± 1.6	- 712.0 ± 1.8	
$\phi^{\text{Coul}}$ (kJ/mol)	- 797.0	- 799.5	- 797.4	
$\phi^{\text{DD}}$ (kJ/mol)	- 14.2	- 15.5	- 14.7	
$\phi^{\text{DQ}}$ (kJ/mol)	- 2.1	- 2.1	- 2.1	
$\phi^{\text{Rep}}$ (kJ/mol)	103.0	103.8	102.2	
C <sub>v</sub> (J/Kmol)	56.9	53.1 ± 4		48.5[18]
P (kbar)		1.3 ± 0.8		
D <sub>+</sub> (10 <sup>-4</sup> cm <sup>2</sup> s <sup>-1</sup> )	1.08	1.02 (b) 1.22 (c)		1.31[19]
D <sub>-</sub> (10 <sup>-4</sup> cm <sup>2</sup> s <sup>-1</sup> )	0.988	0.94 (b) 0.90 (c)		0.959[19]

(a)  $U = E_k + \phi$  ;  $E_k$  is the kinetic energy.

(b) From the mean square displacement

$$D_\alpha = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{r}_\alpha(t) - \mathbf{r}_\alpha(0)|^2 \rangle ; \alpha = +, -$$

(c) From the velocity self-correlation function

$$D_\alpha = \lim_{t \rightarrow \infty} \int_0^t \langle \mathbf{v}_\alpha(t) \cdot \mathbf{v}_\alpha(0) \rangle (1-s/t) ds ; \alpha = +, -$$

height 3.6 at 2.64 Å and a second maximum with height 1.33 at 6.1 Å. The radial distribution functions for like ions ( $g_{--}$  and  $g_{++}$ ) are very similar as it is usual for the rigid ions model [2]. They present both a first maximum with values 1.76 and 1.66 at 4.0 Å and are identical after 5 Å, reflecting equivalent long range interactions for anions-anions and cations-cations.

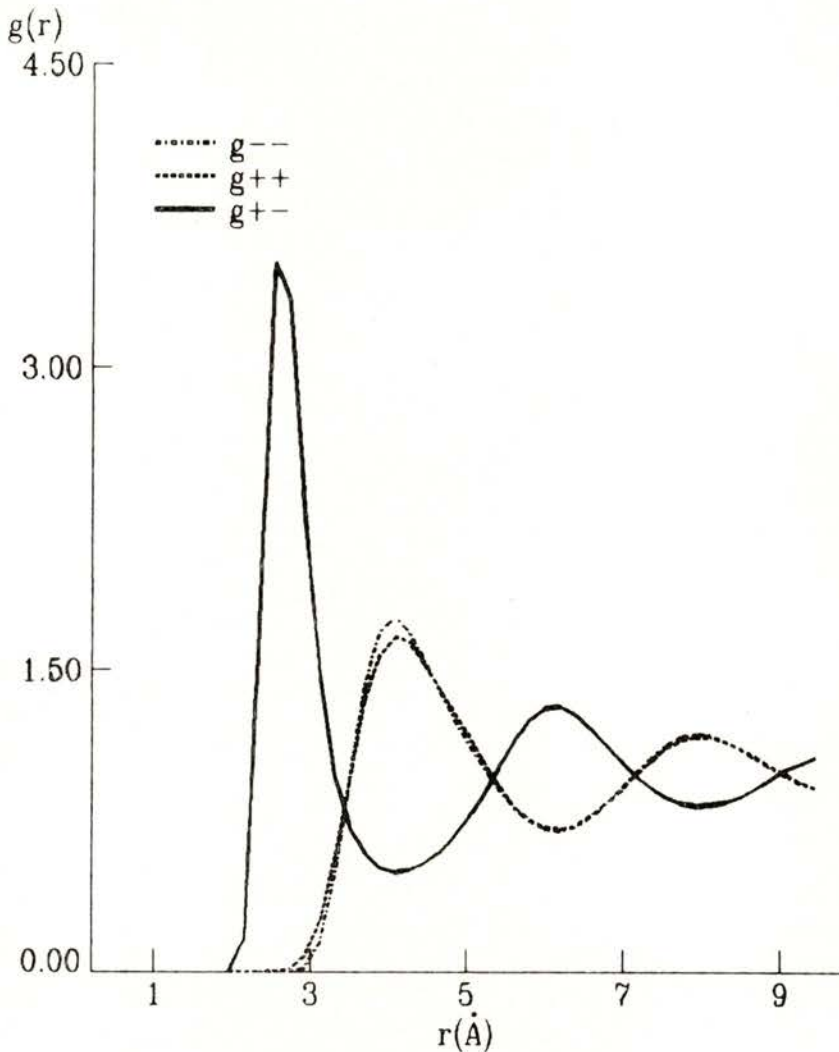


Fig. 1 — Radial distribution functions for NaCl at 1224.5 K

(c) *Time dependent-properties*

Results for the mean square displacement, velocity and force self-correlation functions are presented in the figures 2, 3 and 4. These quantities were evaluated during the simulation and each curve is the average of nine. The self-diffusion coefficient can be

evaluated either from the mean square displacement of the ions, or from the integration of the velocity self-correlation function. However, it is known [14] that in the simulation of a finite size system, during a limited time, the two methods may give different results. A difference of 19% was obtained in the present work as shown in the Table I.

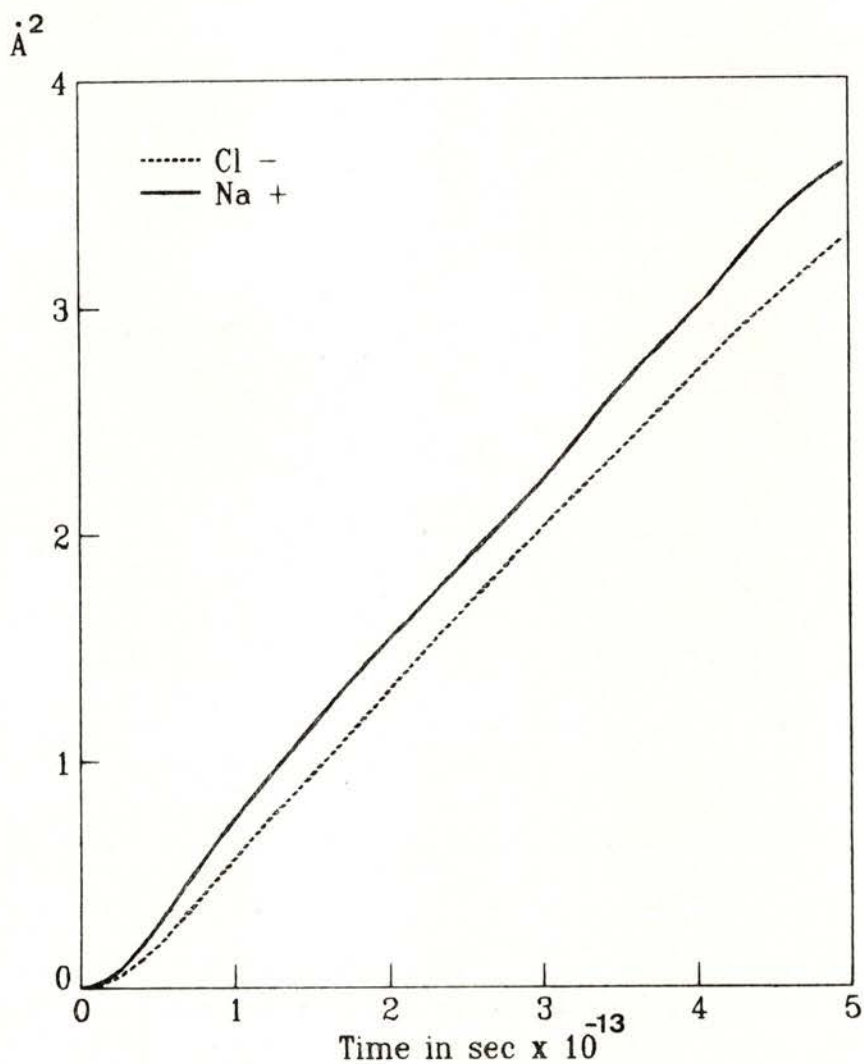


Fig. 2 — Mean square displacements of the ions in  $\text{\AA}^2$

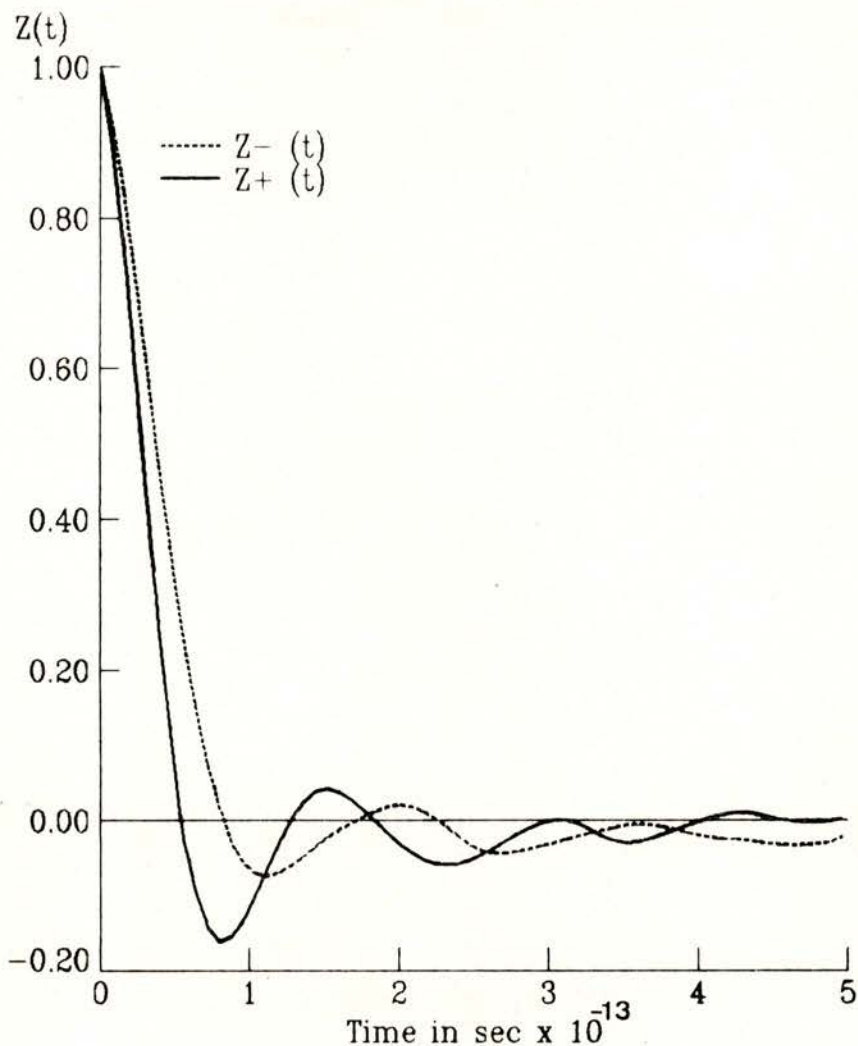


Fig. 3 — Velocity self-correlation functions for NaCl at 1224.5 K.  
 $z_{\alpha}(t) = \langle \mathbf{v}_{\alpha}(t) \cdot \mathbf{v}_{\alpha}(0) \rangle / \langle \mathbf{v}_{\alpha}(0) \cdot \mathbf{v}_{\alpha}(0) \rangle$ ;  $\alpha = +, -$

From this study it appears that the modified Ewald sum proposed by Adams and Dubey [5, 6] is a practical and efficient method to take into account long-range electrostatic interactions in the simulation of ionic systems. The agreement of our N, V, T



simulation with N, V, E molecular dynamics simulation shows the equivalence of these ensembles for finite size ionic systems.

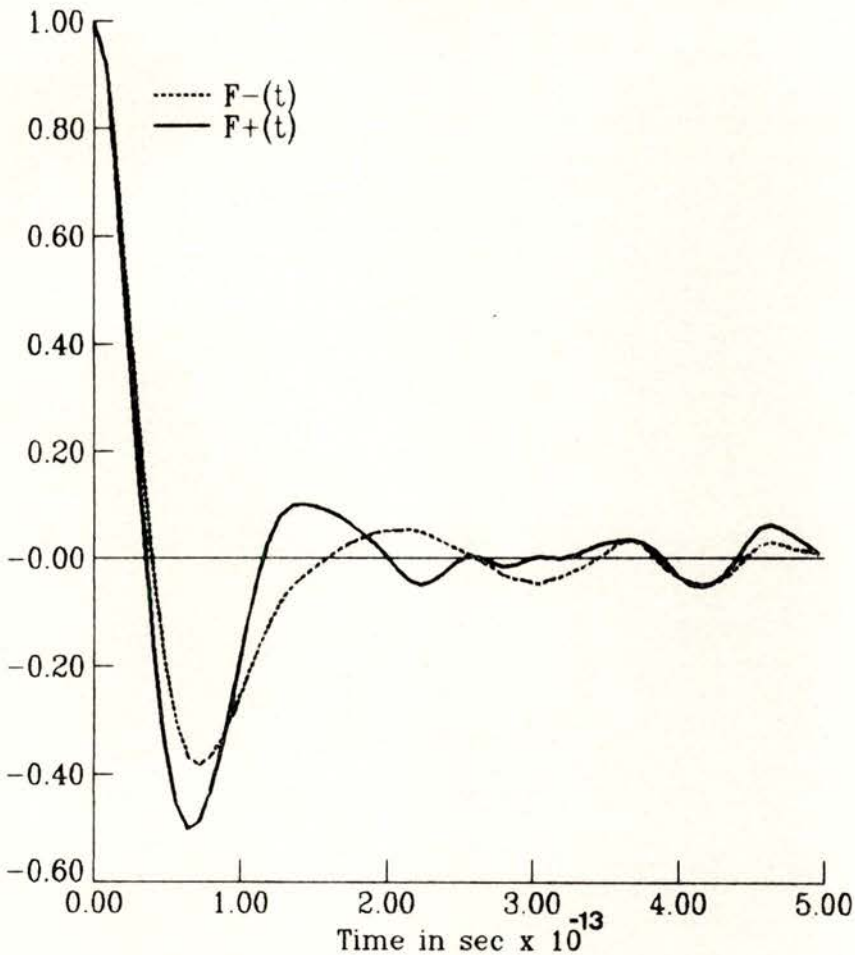


Fig. 4 — Force self-correlation functions for NaCl at 1224.5 K.

$$F_{\alpha}(t) = \langle \mathbf{a}_{\alpha}(t) \cdot \mathbf{a}_{\alpha}(0) \rangle / \langle \mathbf{a}_{\alpha}(0) \cdot \mathbf{a}_{\alpha}(0) \rangle$$

where  $\mathbf{a}_{\alpha}(t)$  is the acceleration of the ions;  $\alpha = +, -$

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