Computer Modeling of Matter

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Peter Lykos, EDITOR

Illinois Institute of Technology

Based on a symposium

sponsored by the ACS

Division of Computers

in Chemistry at the 175th

Meeting of the American

Chemical Society, Anaheim,

California, March 14, 1978.

ACS SYMPOSIUM SERIES **86**

American Chemical
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FOREWORD

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PREFACE

The ever increasing power of computers and the continuing decrease in their cost enable the chemist to construct increasingly sophisticated mathematical models of bulk matter—both at equilibrium and changing in time—from a molecular perspective.

Thanks to the pioneering work of Bernie Alder and others who developed the method of molecular dynamics and to the Monte Carlo method of Metropolis used for equilibrium data, as the size and speed of computers increased it became feasible for Aneesur Rahman and Frank Stillinger (*J. Chem. Phys.* (1971) 55, 3336) to apply the method of molecular dynamics to the most important and complex bulk matter of all—liquid water. That seminal paper sparked a great interest in modeling on the part of chemists. The important discovery that a mathematical model whereby one averages the individual properties of a few hundred interacting molecules suffices to assess the bulk properties of many important systems suggests that chemists now can build more effective bridges between atomic and molecular physics on the one hand and surface chemistry and chemical thermodynamics and kinetics on the other.

In the recent "Science Update: Physical Chemistry" in *Chemical and Engineering News* ((1978) June 5, p 20–21), the impact of the computer primarily as an aid to modeling was highlighted as the most pervasive and important factor influencing physical chemistry today. In that article Mitch Waldrop wrote, "So important have the big computers become that number crunching and theoretical chemistry often seem synonymous. The applications can be divided into three broad areas: quantum chemistry, chemical dynamics, and statistical mechanics. If computers were big enough, those three would form a logical sequence for the complete ab initio calculation of the properties of bulk matter."

The number and range of computer-based models of bulk matter has increased rapidly. An important international conference (with proceedings), "Computational Physics of Liquids and Solids" held April, 1975, at Queen's College in Oxford, involved 34 papers that displayed a broad range of chemical phenomena being studied in this manner. Just a year and a half later the Faraday Division of the Chemical Society, London, held a two-day symposium on "Newer Aspects of Molecular Relaxation Processes" at the Royal Institution, London. The so-called 'experimental technique of examining motions in a computer-generated

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liquid' was considered together with experimental methods, with theoretical models of relaxation processes, and with the hydrodynamics of rotation in fluids.

Two books have appeared which, while not presenting a unified view of the field nor a critical assessment of the literature, do provide the interested scientist with an entree to the use of computer simulation of liquids ("Theory of Simple Liquids," J. P. Hansen, I. R. McDonald, Academic, 1976; "Atomic Dynamics in Liquids," N. H. March, M. P. Tosi, Halsted (Wiley), 1977). The impact on statistical mechanics as a discipline is reflected in the two-volume work, "Statistical Mechanics," B. J. Berne, Ed., Part A, Equilibrium Techniques, and Part B, Time-Dependent Processes, Plenum, 1977. Indeed, in his Nobel prize address, I. Prigogine made several references to the use of computer simulations as an aid to development of his Nobel prize winning work on the macroscopic and microscopic aspects of the second law of thermodynamics (*Science* (1978) **201**, 777–785).

Enough experience has been gained through the design and testing of such models that chemists interested in gaining insight into particular chemical systems are beginning to apply the models in a rather sophisticated manner. For example, William Jorgensen, a theoretical organic chemist interested in solvation effects in organic chemistry, has begun by looking at liquid hydrogen fluoride in a paper to be published in December, 1978, *J. Am. Chem. Soc.* Indeed theorists are organizing and presenting their theories with careful attention to how they might be applied using a computer (for example, *see* "Simulation of polymer dynamics 1. General theory and 2. Relaxation rates and dynamic viscosity," M. Fixman, *J. Chem. Phys.* (1978) **69**, p 1527, 1538).

The call for contributions to this symposium has resulted in an interesting collection of eighteen chapters which provide the reader with a variety of touchstones ranging from the first chapter, a straight-forward application by K. Heinzinger of the Rahman–Stillinger method to an aqueous solution of sodium chloride, to the last chapter, an overview from microphysics to macrochemistry via discrete simulations including chemical kinetics.

The other chapters include examination of an algorithm assessing the importance of three-body interactions and of algorithms reducing machine requirements with regard to size of store and speed.

Most of the work done to date has been based on classical mechanics. The chapter by M. H. Kalos brings home the fact that one needs to examine the validity of such models from within the framework of quantum mechanics. The interesting phenomenon of collective modes of motion is exemplified by M. L. Klein's chapter on collective modes in

solids. The liquid–vapor interface is addressed in two chapters, one by Rao and Berne and the other by Thompson and Gubbins.

Sundheim's chapter on high field conductivity emphasizes that the modeler is free to impose whatever simulated physical conditions he pleases and, in fact, can achieve in his computer experiment conditions which would be extremely difficult, if not impossible, to achieve in the laboratory.

Finally, the Chester, Gann, Gallagher, and Grimison chapter demonstrates that the computer mystique is being displaced by a hard-headed appraisal by chemists of what computer enhancements are possible with existing technology. Through the addition of a peripheral device (designed to do floating-point arithmetic very rapidly) to the campus large-scale data-processing machine, it was possible to improve the cost effectiveness of the total system about eightyfold when used for computer simulation of matter.

The growing sophistication of matter modeling as a result of advances in computer size, speed, and cost effectiveness may well have as its greatest impact, however, the enhancement of communication among those interested in any particular physical system.

Illinois Institute of Technology   PETER LYKOS
Chicago, Illinois
October 13, 1978

Molecular Dynamics Simulations of Liquids with Ionic Interactions

K. HEINZINGER, W. O. RIEDE, L. SCHAEFER, and GY. I. SZÁSZ

Max-Planck-Institut fuer Chemie (Otto Hahn-Institut), Mainz, Germany

Molecular dynamics (MD) simulations of liquids with ionic
interaction have so far been performed for molten salts and
aqueous electrolyte solutions. The characteristic problem for
this kind of simulation are the far ranging Coulombic forces.
The first preliminary MD calculations for molten salts have
been reported by Woodcock in 1971 (1). The large amount of work
published in the meantime has been reviewed by Sangster and Dixon
(2). In the case of aqueous electrolyte solutions only prelimi-
nary results for various alkali halide solutions have been pub-
lished so far (3).
The more advanced state of the art for the molten salts
leads to a concentration of the effort on the improvement of the
algorithm for the integration of the equation of motion necessary
to calculate dynamical properties with still higher accuracy. One
example where very high accuracy is needed is the calculation of
the isotope effect on the diffusion coefficients. In the section
on molten salts below one way to improve the algorithm is dis-
cussed and the progress is checked on the mass dependence of the
diffusion coefficients in a KCl melt.
Results with a certain degree of reliability from MD simu-
lations of aqueous solutions reported up to now are restricted
to structural properties of such solutions. In the section on
aqueous solutions below very preliminary velocity autocorrelation
functions are calculated from an improved simulation of a 0.55
molal NaCl solution. The problem connected with the stability of
the system and the different cut-off parameters for ion-ion, ion-
water and water-water interactions are discussed. Necessary steps
in order to achieve quantitative results for various dynamical
properties of aqueous electrolyte solutions are considered.

Molten Salts

The Hamilton differential equation system can be solved

numerically for a N particle system with a simple "leap-frog"
algorithm as used by Verlet (4) or by a predictor-corrector al-
gorithm. The most important criterion for the choice of the al-
gorithm is the numerical stability. The final decision follows
from necessary accuracy with which for example the energy is pre-
served, which in turn is determined by the desired accuracy of
the transport properties, say self diffusion coefficient. In the
simulated system of molten KCl it has been investigated how the
total energy, the total momentum, and the velocity autocorrelation
functions varies with different algorithms.

The MD calculation for the KCl-system was carried out at the
melting point (1043K). The basic cube contains $N=2\cdot108$ particles
and the cube length S is than calculated to be 20.6A. For the
pair potential the Born-Mayer-Huggins potential

$$\varphi(r) = \pm\ er^{-1} + bexp(-Br) + Cr^{-6} + Dr^{-8} \tag{1}$$

is used with the parameters given by Tosi and Fumi (5), listed
in Table I.

Table I

Parameters for the Born-Mayer-Huggins Potential

	b	B	C	D
	10^{-12}erg	A^{-1}	10^{-12}erg A^6	10^{-12}erg A^8
$K^+ - K^+$	1991.67768	2.967	− 24.3	− 24.0
$K^+ - Cl^-$	1224.32459	2.967	− 48.0	− 73.0
$Cl^- - Cl^-$	4107.95500	2.967	− 145.5	− 250.0

Three different algorithms were investigated. In the first version
(I) the Coulombic energies and forces were evaluated with the use
of the erfc part of the Ewald method (6) only. In the other two
versions (II and III) the full Ewald method was employed. In all
versions the separation parameter η, the number of nearest neigh-
bours n_η , and the maximum value of the reciprocal lattice vec-
tors h_1(not occuring in version I) were chosen to be:

$$\eta = 0.175, \quad n_\eta = 6, \quad h_1 = 8.$$

The algorithm which was used in version I is a so called "leap-
frog" algorithm:

$$\underline{r}_i(n+1) = \underline{r}_i(n-1) + 2\Delta t\ \underline{v}_i(n-1) + (\Delta t^2/m_i)\ \underline{F}_i(n) \tag{2}$$

$$\underline{v}_i(n) = \underline{v}_i(n-1) + \left[\underline{v}_i(n-1) - \underline{v}_i(n-2) \right]$$
$$+ (\Delta t^2/m_i) \left[\underline{F}_i(n) - \underline{F}_i(n-1) \right] \tag{3}$$

Here $\underline{r}_i(n)$, $\underline{v}_i(n)$, and $\underline{F}_i(n)$ are the position, velocity and force of particle i at time $t = n\Delta t$ respectively and m_i are the masses of the ions. The time step length was chosen to be $0.5 \cdot 10^{-14}$ sec. The behavior of the total energy for version I is shown in Figure 1 where $(\Delta E/E) = 6 \cdot 10^{-3}$.

A change from the "leap-frog" algorithm to a predictor-corrector algorithm has been made in version II. For the position vectors one can write:

$$\underline{r}_i^p(n+1) = \underline{r}_i^c(n-1) + 2\,\Delta t\,\underline{v}_i(n-1)$$
$$+ (\Delta t^2/m_i) \left[\underline{F}_i(n) + \underline{F}_i(n-1) \right] \tag{4}$$

$$\underline{r}_i^c(n+1) = \underline{r}_i^c(n-1) + 2\,\Delta t\,\underline{v}_i(n-1)$$
$$+ (\Delta t^2/4m_i) \left[\underline{F}_i(n+1) + 4\underline{F}_i(n) + 3\underline{F}_i(n-1) \right] \tag{5}$$

Here the indices p and c indicate predicted and corrected values respectively. The formula for the velocities has been changed slightly compared to the formula (3):

$$\underline{v}_i(n) = \underline{v}_i(n-1) + (\Delta t/2m_i) \left[\underline{F}_i(n) + \underline{F}_i(n-1) \right] \tag{6}$$

With this version II, two simulations with different time steps were carried out starting from the same configuration ($0.5\ 10^{-14}$s and $0.25\ 10^{-14}$s) over a time interval of 1.2 ps. The total energies for both runs are shown in Figure 1 . The value $(\Delta E/E)_{0.5}$ has decreased compared to the one of version I by one order of magnitude. Moreover $\Delta E/E$ decreased further by a factor 0.5 when the time step was shortened to $0.25 \cdot 10^{-14}$s.

In version III the positions and velocities have been treated with the same predictor-corrector algorithm. This means that $\dot{\underline{F}}_i(t)$, the derivative of the forces with respect to time, appears in the formula for the velocities.

$$\underline{r}_i^p(n+1) = \underline{r}_i^c(n-1) + 2\,\Delta t\,\underline{v}_i^c(n-1)$$
$$+ (2\Delta t^2/3m_i) \left[2\underline{F}_i(n) + \underline{F}_i(n-1) \right] \tag{7}$$
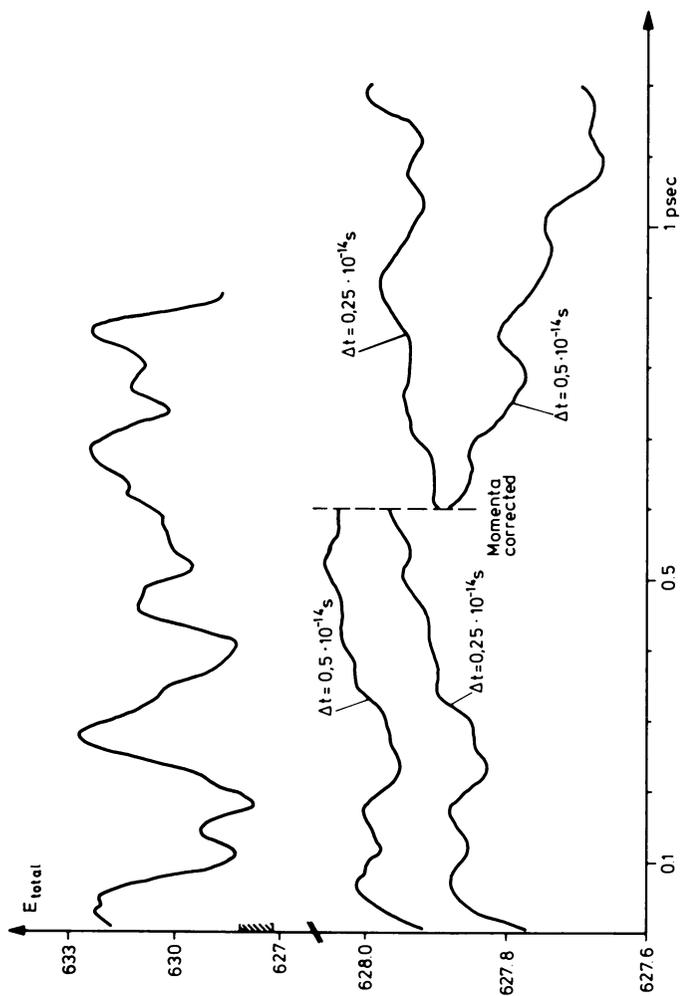
Figure 1. Total energy of version I (upper curve) in units of 10³ J/mol and of version II (lower curve) with a energy scale enlarged by a factor of 4¾. The length marked by (⊔⊔⊔⊔) in the upper scale corresponds to the interval of the lower scale. The time scale starts after an equilibration run over 7.2 psec from a roughly equilibrated starting configuration.

$$\underline{r}_i^c(n+1) = \underline{r}_i^c(n-1) + 2 \Delta t \ \underline{v}_i^c(n-1)$$

$$+ (\Delta t^2/6m_i) \left[\underline{F}_i(n+1) + 6\underline{F}_i(n) + 5\underline{F}_i(n-1) \right]$$

$$+ (\Delta t^3/24m_i) \left[3\underline{\dot{F}}_i(n-1) - 2\underline{\dot{F}}_i(n) - \underline{\dot{F}}_i(n+1) \right] \qquad (8)$$

and for the velocities:

$$\underline{v}_i^p(n) = \underline{v}_i^c(n-2) + 2 \Delta t/m_i \ \underline{F}_i(n-2)$$

$$+ (2\Delta t^2/3m_i) \left[2\underline{\dot{F}}_i(n-1) + \underline{\dot{F}}_i(n-2) \right] \qquad (9)$$

$$\underline{v}_i^c(n) = \underline{v}_i^c(n-1) + (\Delta t/2m_i) \left[\underline{F}_i(n) + \underline{F}_i(n-1) \right]$$

$$+ (\Delta t^2/12m_i) \left[\underline{\dot{F}}_i(n-1) - \underline{\dot{F}}_i(n) \right] \qquad (10)$$

It has to be emphasized that there is a basic difference between the algorithms of version II and III. In version II the velocities were not handled in the same way as the positions by a predictor-corrector algorithm. This is less time consuming per time step and might be sufficient for a given accuracy in the total energy for example.

The values of $(\Delta E/E)_{0.5}$ of Version III decreased by two orders of magnitude compared to version I. When the time step was shortened by half, $(\Delta E/E)_{0.25}$ decreased one order of magnitude more. Finally $\Delta E/E$ decreased by three orders of magnitudes compared with $\Delta E/E$ of version I. An compilation of all $\Delta E/E$ is given in Tab.II according to the different versions and time steps.

Table II

Values of $\Delta E/E$ according to the different versions

version	I	II		III	
$\Delta t \cdot 10^{-14}$ s	0.5	0.5	0.25	0.5	0.25
$\Delta E/E$	$6 \ 10^{-3}$	$6 \ 10^{-4}$	$3 \ 10^{-4}$	$3 \ 10^{-5}$	$2 \ 10^{-6}$

The fluctuation of the kinetic energy is about ±2500 J/mol corresponding to a fluctuation of temperature of about ± 100K. Compared with the total energy it follows $(\Delta E_{kin}/E)_{0.25} = 4 \cdot 10^{-3}$. This shows that the fluctuations of the kinetic energy are three orders of magnitude larger than the fluctuations of the total energy and hence the fluctuations of the kinetic energy are almost compensated by the corresponding fluctuations of the potential energy.

In order to keep the computing time small for each time step, care has been taken to calculate the right hand side (r.h.s) of the differential equation system only once per time step. This

means that the predicted values r_i^p should not be too different from the corrected values r_i^c. With version III

$$|r_i^p - r_i^c| < \varepsilon \tag{11}$$

for each component (x,y,z), each time step, and all particles i where $\varepsilon = 10^{-6}A$. Moreover for about 70% of the particles $\varepsilon = 10^{-7}A$ could have been chosen. From eq. (7) and (8) follows

$$\left| F_i(n) - F_i(n+1) - \left[F_i(n+1) - F_i(n) \right] \right.$$
$$\left. -(\Delta t/4)\left[3\dot{F}_i(n-1) - 2\dot{F}(n) - \dot{F}_i(n+1) \right] \right| < 6\varepsilon m_i/\Delta t^2 \tag{12}$$

This inequality can be estimated if one replaces the differentiation by the corresponding ratio of the differences which yields:

$$\left| \Delta F_i(n) - \Delta F_i(n-1) \right| < 4\varepsilon m_i/\Delta t^2 \tag{13}$$

with $F_i(n) - F_i(n-1) = \Delta F_i(n)$. Eq.(13) shows that the change of the force change within the given time step determines the ratio $\varepsilon/\Delta t^2$ for constant mass.

The desired accuracy of the particle positions requires an adequate time step Δt and determines the accuracy of the forces. Eq.(13) would be meaningless if the errors of the forces were as large as the changes of the force change, because the correction added to the predicted value of r_i would be of the order of the errors of the forces. However, ε has to be small enough because one wants to calculate the forces with the predicted values of r_i only.

An analogous equation to eq.(11) is given for the velocities with an ε' which is different from ε.

$$\left| v_i^p - v_i^c \right| < \varepsilon' \tag{14}$$

For ε' a value of 20 cm/s has been found which corresponds to a maximum change in the positions of $5 \cdot 10^{-6}A$.

This shows that the positions of the particles will be slightly changed by taking the corrected velocities rather than the predicted values in eq.(8). Moreover ε' corresponds to a maximal temperature difference ΔT which can be estimated by

$$\Delta T < (\bar{m}/3k)\varepsilon' \left[\varepsilon' + 2 \, (3kT/\bar{m})^{1/2} \right] \tag{15}$$

Here $\bar{m}$ is the average mass, k Boltzmann's constant, and T the temperature at the melting point. The value of the r.h.s. of eq. (15) is 0.5 K which is 5 $^o/oo$ of the temperature fluctuations of about ± 100 K. This means that the temperature fluctuations are mainly determined by the change of the velocities in time rather than by the corrections of the velocities.

The absolute value of the total momentum $|\underline{P}|$ of the system is shown in Figure 2 . It decreased by almost one order of magnitude between version I and II. Almost no change occured in $|\underline{P}|$ comparing version II with III. Therefore only $|\underline{P}|$ of version III has been plotted in Figure 2 . However, a decrease by a factor of 4 showed up when the time step was reduced. Additionally, $|\underline{P}|$ was reduced by a factor of about 3 when the initial configuration also included the differentiation of the forces. This total momentum curve is marked with a capital A in Figure 2 . A more precise analysis of the total momentum make it reasonable to assume

$$\underline{P} = \int_0^t \underline{F}(t') \, dt'. \tag{16}$$

Hence the total force $\underline{F}(t)$ does not vanish completely for each time step, the total momentum is the sum of the deviations of the total force from zero, rather than the total momentum of the system in a physical sense. $|\underline{P}|$ was brought to zero for the equilibrated initial configuration. The extrema of the total momentum components in Figure 3 correspond to the zeros of the total force components at the same time points. Moreover the forces of all particles have been separated into the different parts of the pair potentials, eq.(1), and have been summed up separately,

$$\underline{F} = \sum_1^N \underline{F}_i = \sum_1^N \underline{F}_i^c + \sum_1^N \underline{F}_i^{ex} + \sum_1^N \underline{F}_i^{(6)} + \sum_1^N \underline{F}_i^{(8)}. \tag{17}$$

Here the indices c, ex, 6, and 8 indicate to which part of the pair potential the forces belong. The calculation has shown that all terms of eq.(17) except the coulomb term are smaller than $3 \cdot 10^4$ dyn/mol for each component while the coulomb term is seven orders of magnitude larger, $3 \cdot 10^{11}$ dyn/mol. Consequently, the deviation of the total force from zero is determined by the sum of coulombic forces.

The velocity autocorrelation functions and from them the self diffusion coefficients have been calculated from all versions for the normal masses as well as for the mass of the anion reduced by 26%. They are shown together in Figure 4 . The velocity autocorrelation functions in version I do not behave qualitatively correct. If the anion mass decreases, the first zero of the anion correlation function should shift to smaller time, while the zero of the unchanged cation correlation function should slightly shift to larger time. The qualitatively correct behaviour of the velocity autocorrelation functions results from version II and III.

The behaviour of the total energy, kinetic energy, the instantaneous value of $P^+(t) = (2E_{kin} - \psi)/3V_m$, and the velocity autocorrelation functions of the system have been investigated with a change of the cut-off radius in the interaction which belongs to the pair potential part $1/r^6$. Here is the virial of the system calculated by

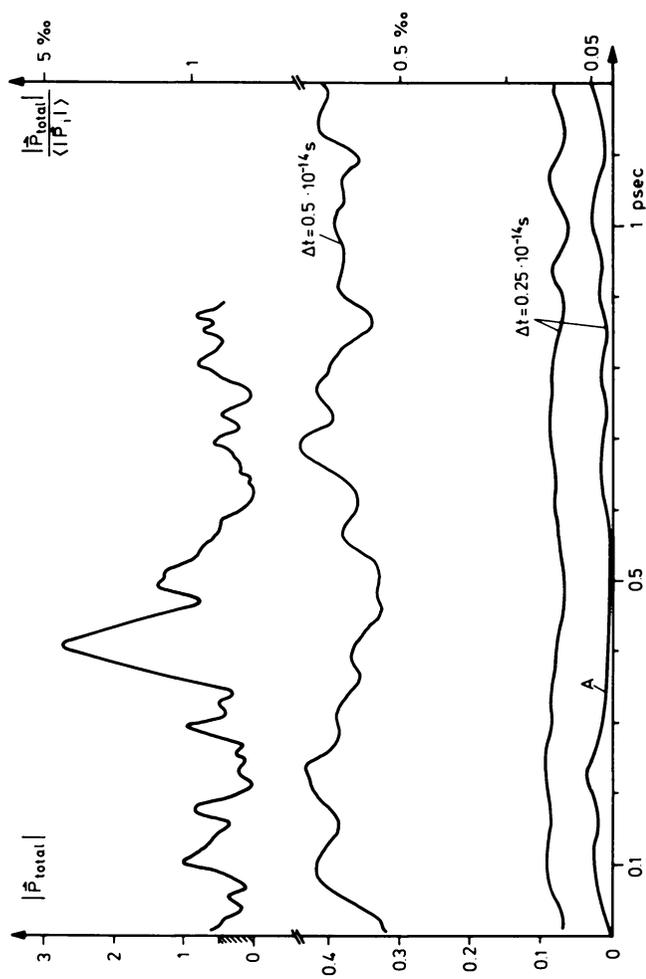$$\psi = - \sum_{i,j}^N r_{ij} F(r_{ij}) \tag{18}$$

Figure 2. Absolute total momentum in units of 10^4 cm g/sec mol on the left-hand scale, while the right-hand side relatively gives the absolute momentum to the averaged momentum per particle. The upper curve for version I, the lower curves for version III, with a scale enlarged by a factor of $4^{3}/_{4}$.
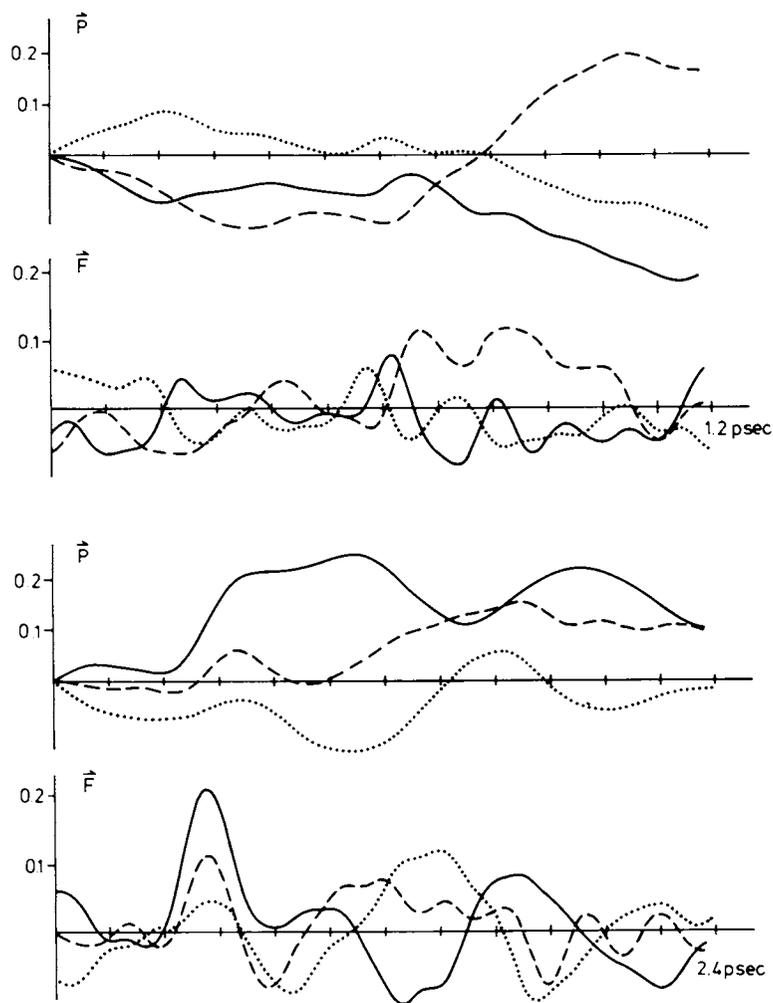
Figure 3.   Total momentum **P** in units of 10^4 cm g/sec mol, total force **F** in units of 10^{12} dyn/mol for the x,y,z components (solid, dashed, and dotted line, respectively)
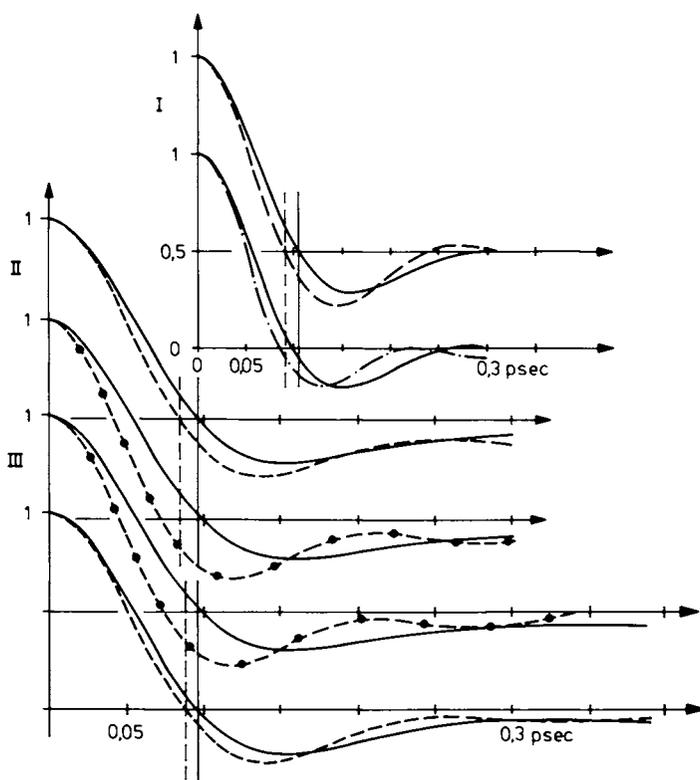
*Figure 4.   Velocity autocorrelation functions from version I, II, and III for $^{39}K^{+}$
(——), $^{35}Cl^{-}$ (— — —), ^{31}Cl (— · —), $^{27}Cl^{-}$ (—•— — —•—). Vertical lines allow zeros of
the correlation functions to be compared.*

No cut-off radii have been changed for the other interactions. In calculation (I) all 215 particles in the environment cube (the cube with edge of length S and particle i at its center) of particle i have been taken into account for the calculation of the force acting on particle i and the energy. In a second run (II), which was started from the same configuration, all the particles have been taken into account within the sphere which circumscribes the environment cube of particle i. The total energy decreased as expected by about 0.02%) and stayed constant within $(\Delta E/E)_{0.25} = 1.6 \cdot 10^{-6}$ over the whole run of 1440 time steps. As no iteration happened in either of the calculations I and II, eq.(13) still holds especially for the beginning of the runs. This result shows that the deviations have been of the order of the allowed uncertainties of the forces.

The kinetic energy and $P^+(t)$ differ more and more from each other as a function of time as is shown in Figure 5 . However, no qualitative changes of the kinetic energy nor of the quantity $P^+(t)$ have occured. Although the changes which have taken place in the forces $F_i^{(6)}$ are very small compared to the forces F_i themselves, a significant change appeared in the kinetic energy. Thus a small uncertainty in the forces at each time step which is not purely random or is not cancelled by summation, might produce a trend for example in the kinetic energy. Furthermore a slightly different starting configuration causes a quantitatively but not qualitatively different kinetic energy. This fact allows the choise of the starting velocity vector (3N-dimensional) independently of the time sequence of calculation of these vectors with regard to the averaging procedure for the autocorrelation functions. This is discussed in ref.([7]) in more detail. However, the cut-off radius does influence the velocity autocorrelation functions as shown in Figure 6 and the corresponding time integrations which lead to the diffusion coefficient as shown in Figure 7 . The differences between the velocity autocorrelation functions of runs I and II are larger than the root-mean-square error of the mean for part C (see curve I C and II C in Figure 6 . It is obvious that this error could lead to an underestimation of the errors for the velocity autocorrelation functions, as is discussed in more detail in ref. ([8]). Moreover, when comparing the velocity autocorrelation functions from Figure 6 with the ones from Figure 4 for the lighter anion mass, it seems to be necessary to have a higher accuracy for larger times (say round about 0.5 psec), at least as high as in version III, in order to get a significant difference in the self diffusion coefficients.

In order to reduce these errors, it seems to be better to increase the number of particles per cube rather than to increase the number of time steps. A larger number of particles brings about another improvement besides a better statistics. The necessity of introducing periodic boundary conditions (discussed in detail in many places, e.g.([1],[2],[8],[12])) has some influence on the