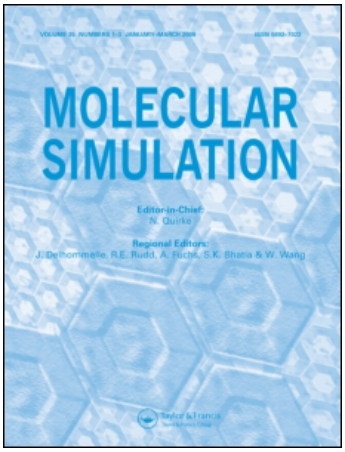

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Computer Simulation of Polarizarle Fluids: On the Determination of the Induced Dipoles

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COMPUTER SIMULATION OF POLARIZABLE FLUIDS: ON THE DETERMINATION OF THE INDUCED DIPOLES

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In a previous paper the reaction field method has been extended to include polarization effects [1]. This has been the basis for developing a consistent and fast scheme to be used in molecular dynamics simulations for dealing with long-range dipolar forces and many-body polarization effects. The iterative procedure has been found to be very convenient method to solve the electrostatic problem with a large number of induced dipoles and charge interactions. Here we analize the stability and the precision of the iterative solution in molecular dynamics runs, i.e. we study the capability of the algorithm to keep finite the errors on the evaluation of the induced dipoles during the run, as well as we evaluate the mean standard error themself as a function of the relevant free parameters of stable iterative procedures. The validity of the derived expressions has been tested numerically by performing molecular dynamics runs with a plausible polarizable model for water.

KEY WORDS: Molecular dynamics, polarizable fluids, induced dipoles, polarizable water.

INTRODUCTION

Induced polarization effects have long been recognized to play an important role [2] in the condensed phase of atoms or molecules with strong coulombic interactions. Many-body effects are difficult to be treated exactly, so, in the computer simulations of these liquids, the polarization contributions are taken into account only in an average way. For example, the permanent dipole moment of the molecule in all non-polarizable models for liquid water [2–6] is greater than the one of the isolated molecule (1.85 Debye). Indeed the charge distribution of these models gives rise to an effective dipole moment which is about 20 per cent higher (about 2.2 Debye). At least in this case, the assumption of pairwise additivity, i.e. that the potential energy can be expressed as a sum of pair interactions, seems to be a crude approximation [7] from quantum mechanical studies. Indeed about 10 per cent of the total intermolecular interaction energy in a water trimer is estimated to arise from three-body interactions and we expect that many-body effects contribute to a larger extent in the liquid. Therefore to

condense in an effective dipole moment all many body interactions due to electron cloud polarization does seem to be a very bad recipe, especially for studying fluid water at different densities. Indeed, an undesired consequence of the use of a partial charge distribution with an enhanced effective dipole moment is the strong dependence of the potential parameters on thermodynamic state, hence the potential model suitable for liquid water at standard conditions yields poor results when applied to calculate the virial coefficients [3, 8] or the structure factor of the vapour [9]. Similarly, far from standard conditions, different models give different results, as in the case of diffusion coefficient in stretched water [10] obtained from simulations using the ST2 [4] or TIP4P [6] models.

In recent years a great effort has been devoted to the development of more realistic potential models [11] suitable for reproducing fluid properties over a wide range of conditions [12]. For this purpose it is important to take into account the molecular polarizability, and special accelerating techniques for MD simulations have been studied to deal with induced dipoles [13, 14, 1].

To take into account polarization effects, two different method can be used: the first one is to solve the electrostatic problem; the second is to include the electronic degrees of freedom in the equations of motion. In the latter method, various approaches have been proposed. One one side, one can try to solve the Schrodinger equation for the electrons [15]. In this case, the approach is surely very accurate, but it is possible, at the present time, to handle only very small number of molecules. On the other side fictious masses and/or "springs" can be assigned to the electrons which undergo a classical (fast) dynamics [16, 17]. Here the number of molecules is not limited but, apart from the arbitrariness of the fictious masses, the computing time is greatly increased by the small time step needed to follow the fast electron dynamics.

As far as the methods of solving the electrostatic problem, a common point in all the adopted procedures is the calculation of the induced dipoles starting from the local electric field seen by a given molecule. The local electric field takes its origin from both the static and induced multipoles of all the molecules, so the calculation of the induced multipoles is a self consistent problem to be solved at each MD step. The solution of the resulting (linear) system of equation can be faced in two different ways: by standard direct methods, (e.g. by Gauss elimination) or by iterative methods. However, when the number of linear equations is so large ($3N$, N being the number of molecules), an iterative method is more attractive than a direct one [18].

In iterative methods, it is very important to choose a "good" starting point and to determine the minimum number of iterations which assures the stability of the procedure and the required precision in the induced multipoles. The aim of the present paper is to give a recipe for establishing the level of stability and the precision of the iterative method in the solution of the self-consistent electrostatic problem as a function of the initial guess and the number of iterations. The case of a polarizable water model at room temperature will be examined as a test system.

THEORETICAL BACKGROUND

In this section we briefly recall the basic equations describing the electrostatic problem in a fluid of polarizable molecules, as discussed in [1]. The system under investigation is

constituted of "rigid molecules" having fixed sites with associated point charges (or higher multipoles) and/or masses and/or non electrostatic interaction centres (Lennard-Jones or others). In addition a Buckingham like expansion is used to take into account the induced electric dipoles in presence of local electric field [19]. As a first term, an isotropic point polarizability is set at the molecular centre of mass (CM). The electrostatic interaction energy of this system can be written as the sum of the charge-charge contributions (U_{qq}), which account for all the interactions between the static multipoles, plus an induction term (U_{ind}), which describes the effects due to the induced dipoles [20,21]:

$$U_{el} = U_{qq} + U_{\text{ind}} \tag{1}$$

The induction energy can in turn be split into the sum of the induced dipole induced dipole interactions (U_{pp}), the static multipole induced dipole interactions (U_{pq}), and the self interaction energy (U_{self}), (i.e. the work done by the electric field to distort the electron clouds and create the induced dipole moment):

$$U_{\text{ind}} = U_{pp} + U_{pq} + U_{\text{self}} \tag{2}$$

with

$$U_{pp} = -\frac{1}{2}\sum_{j,j'\neq j} \bar{p}_j \cdot \mathbf{T}^{(2)}_{jj'} \cdot \bar{p}_{j'} \tag{3}$$

$$U_{pq} = -\sum_j \bar{p}_j \cdot \bar{E}^{(q)}_j \tag{4}$$

$$U_{\text{self}} = \sum_j \int_0^{\bar{p}_j} \bar{E}_j \cdot d\bar{p}_j \tag{5}$$

In these equation, $\bar{p}_j$ stands for the induced dipole of the j-th molecule and $\bar{E}_j$ for the local electric field seen at the CM; $\bar{E}_j$ is the sum of the field generated by the static multipoles $\bar{E}^{(q)}_j$ plus the field generated by the induced dipoles $\bar{E}^{(p)}_j$.

$$\bar{E}_j = \bar{E}^{(q)}_j + \bar{E}^{(p)}_j \tag{6}$$

with

$$\bar{E}^{(p)}_j = \sum_{j'\neq j} \mathbf{T}_{jj'} \cdot \bar{p}_{j'} \tag{7}$$

In the previous equations, $\mathbf{T}^{(2)}_{jj'}$ is the usual static dipole propagator

$$\mathbf{T}^{(2)}_{jj'} = \frac{1}{4\pi\varepsilon_o} \frac{3\bar{r}_{jj'}\bar{r}_{jj'} - \mathbf{1}r^2_{jj'}}{r^5_{jj'}} \tag{8}$$

At each step of the MD run, one has to evaluate the induced dipoles $\bar{p}_j$ consistent with the values of $\bar{E}_j^{(q)}$ due to a given distribution of the point multipoles. The induced dipoles arise from the distortion of the electron clouds, whose dynamics is much faster than the atomic dynamics followed by the MD integration step Δt. Therefore the evaluation of $\bar{p}_j$ can be performed in the adiabatic limit where $\bar{p}_j$ is related only to the local electric field seen by the molecular center of mass at the same time, i.e.

$$\bar{p}_j = \alpha \bar{E}_j \tag{9}$$

The values of $\bar{p}_j$ that satisfy simultaneously the set of Eqs. (6–9) are the solution of the electrostatic problem.

In order to simplify the notation, we can summarize the problem to be solved as follows

$$\bar{p}_n = \bar{A}_n + \mathbf{B}_n \cdot \bar{p}_n \tag{10}$$

where the index n refers to the n-th time-step. The molecular indices j, j' have been omitted and the vector $\bar{p}$ has $3N$ dimensions, N being the number of molecules in the system. The induced dipole moment $\bar{p}_n = \bar{p}(t_n)$ is the variable to be determined and

$$\begin{aligned} \bar{A}_n &= \bar{A}(t_n) = \alpha \bar{E}^{(q)}(t_n) \\ \mathbf{B}_n &= \bar{B}(t_n) = \alpha \mathbf{T}^{(2)}(t_n) \end{aligned} \tag{11}$$

are constant quantities at the n-th time step and they are dependent on the positions and orientations of the molecules of the sample.

The iterative solution of this problem is given by

$$\bar{p}_n^{(i)} = \bar{A}_n + \mathbf{B}_n \cdot \bar{p}_n^{(i-1)} \tag{12}$$

where i is the iteration counter. The iteration starts from an initial guess, say $\bar{p}_n^{(o)}$, and it is repeated a number of time, in order to get a good approximation to $\bar{p}_n$, the exact solution of Eq. (10). The physical problem is well-posed (in absence of ferroelectric behaviour), so the corresponding mathematical problem is convergent, $\bar{p}_n = \bar{p}_n^{(\infty)}$ at every MD time step and the symmetric matrix $\mathbf{B}_n$ has norm $\|\mathbf{B}_n\| < 1$ [18]. However in a computer simulation, it is convenient to keep the number of iteration as small as possible. Therefore it is of great importance to start the iteration with a good initial guess, rather close to the exact solution. For this purpose, the guess is calculated through a Newton backward extrapolation scheme from the estimated solutions $\bar{p}_n^{(\mathscr{C})}$ at the previous (equally spaced) time steps, i.e.

$$\bar{p}_n^{(o)} = \sum_{m=1}^{M} (-1)^{m+1} \binom{M}{m} \bar{p}_{n-m}^{(\mathscr{C})} \tag{13}$$

where $\mathscr{C}$ is the number of iteration used, M the number of time steps previously taken into account in the extrapolation formula and $\binom{M}{m}$ stands for the binomial coefficient.

As a consequence of the use of a finite number of iteration, the entire procedure may become unstable; the aim of this work is just the study of the stability and precision obtained by the procedure as a function of the parameters M and $\mathscr{C}$.

STABILITY

It is easy to show that the error on the variable $\bar{p}_n$ due to the truncation of the iteration procedure after $\mathscr{C}$ steps, i.e.

$$\Delta \bar{p}_n^{(\mathscr{C})} = \bar{p}_n^{(\mathscr{C})} - \bar{p}_n, \tag{14}$$

is a *linear* function of how far from the exact solution we start the iteration procedure

$$\Delta \bar{p}_n^{(\mathscr{C})} = \mathbf{\Lambda}_{\mathscr{C}} \cdot (\bar{p}_n^{(o)} - \bar{p}_n) = \mathbf{\Lambda}_{\mathscr{C}} \cdot \Delta \bar{p}_n^{(0)} \tag{15}$$

and that $\mathbf{\Lambda}_{\mathscr{C}} = [\mathbf{B}_n]^{\mathscr{C}}$.

Indeed, if we apply one iteration to $\bar{p}_n^{(\mathscr{C}-1)}$ we have from Eq. (12)

$$\bar{p}_n^{(\mathscr{C})} = \bar{A}_n + \mathbf{B}_n \cdot \bar{p}_n^{(\mathscr{C}-1)} \tag{16}$$

and subtracting $\bar{p}_n = \bar{A}_n + \mathbf{B}_n \cdot \bar{p}_n$, we have:

$$\Delta \bar{p}_n^{(\mathscr{C})} = \mathbf{B}_n \cdot \Delta \bar{p}_n^{(\mathscr{C}-1)} \tag{17}$$

Therefore we have:

$$\Delta \bar{p}_n^{(\mathscr{C})} = [\mathbf{B}_n]^2 \cdot \Delta \bar{p}_n^{(\mathscr{C}-2)} = \ldots = [\mathbf{B}_n]^{\mathscr{C}} \cdot \Delta \bar{p}_n^{(0)} \tag{18}$$

It is worth noting that the matrix $\mathbf{\Lambda}_{\mathscr{C}}$ does not depend on M but only on the number of iterations $\mathscr{C}$ and time step n. By inserting the expression of the initial guess $\bar{p}_n^{(0)}$, Eq. (13), in Eq. (15), we get

$$\Delta \bar{p}_n^{(\mathscr{C})} = \mathbf{\Lambda}_{\mathscr{C}} \cdot \left[\sum_{m=1}^{M} (-1)^{m+1} \binom{M}{m} \bar{p}_{n-m}^{(\mathscr{C})} - \bar{p}_n \right] \tag{19}$$

With some algebra, this equation can be rewritten in term of the truncation errors at the different steps

$$\Delta \bar{p}_n^{(\mathscr{C})} - \mathbf{\Lambda}_{\mathscr{C}} \cdot \sum_{m=1}^{M} (-1)^{m+1} \binom{M}{m} \Delta \bar{p}_{n-m}^{(\mathscr{C})} = \mathbf{\Lambda}_{\mathscr{C}} \cdot \sum_{m=0}^{M} (-1)^{m+1} \binom{M}{m} \bar{p}_{n-m}. \tag{20}$$

Let it be $\mathbf{G}$ the unitary matrix which diagonalizes $\mathbf{B}_n$ and $\mathbf{\Lambda}_{\mathscr{C}}$, so $\mathbf{D}_{\mathscr{C}} = \mathbf{G} \cdot \mathbf{\Lambda}_{\mathscr{C}} \cdot \mathbf{G}^{-1}$ is diagonal. If we denote with the letter $\bar{\mu}$ the $\mathbf{G}$ transform of the induced dipole $\bar{p}$ (i.e.

$\bar{\mu}_n = \mathbf{G}\cdot\bar{p}_n$ and so on), the Eq. (20) can be transformed in

$$\Delta\bar{\mu}_n^{(\mathscr{C})} - \mathbf{D}_{\mathscr{C}}\cdot\sum_{m=1}^{M}(-1)^{m+1}\binom{M}{m}\Delta\bar{\mu}_{n-m}^{(\mathscr{C})} = \mathbf{D}_{\mathscr{C}}\cdot\sum_{m=0}^{M}(-1)^{m+1}\binom{M}{m}\bar{\mu}_{n-m}. \tag{21}$$

In this way Eq. (20) is reduced to $3N$ independent equations for the components (the "error modes") of the vector $\Delta\mu_n^{(\mathscr{C})}$. Let us call $\lambda_{\mathscr{C}}(\alpha)$, with $\alpha = 1,\ldots,3N$, the diagonal elements of $\mathbf{D}_{\mathscr{C}}$, i.e. the eigenvalues of $\mathbf{\Lambda}_{\mathscr{C}}$, and $\Delta\mu_n^{(\mathscr{C})}(\alpha)$ the corresponding error modes, then the $3N$ scalar equations can be written as:

$$\Delta\mu_n^{(\mathscr{C})}(\alpha) - \lambda_{\mathscr{C}}(\alpha)\sum_{m=1}^{M}(-1)^{m+1}\binom{M}{m}\Delta\mu_{n-m}^{(\mathscr{C})}(\alpha)$$

$$= \lambda_{\mathscr{C}}(\alpha)\sum_{n=1}^{M}(-1)^{m+1}\binom{M}{m}\mu_{n-m}(\alpha) \tag{22}$$

The RHS term-let us call it $g_n(\alpha)$ in the following – can be considered as the non-homogeneous part of the (non linear) finite difference equation of order M where n is the independent variable. For the sake of brevity, later on we omit the mode index α and the number of iteration $\mathscr{C}$, so we rewrite the previous equation as:

$$\Delta\mu_n - \lambda\sum_{m=1}^{M}(-1)^{m+1}\binom{M}{m}\Delta\mu_{n-m} = g_n \tag{23}$$

For each eigenvalue λ, the sequence $\Delta\mu_n$, solution of the previous equation, can be divided as the sum of two term: a particular solution (which depend on the time variation of g_n and tell us that the "error mode" follows with some time delay the values of g_n) plus a solution of the homogeneous equation. For the study of the precision both the terms are effective, but for the study of the stability only the solution of the homogeneous equation,

$$\Delta\mu_n - \lambda\sum_{m=1}^{M}(-1)^{m+1}\binom{M}{m}\Delta\mu_{n-m} = 0, \tag{24}$$

is important since the particular solution is not divergent if g_n is not. Actually $\lambda = \lambda_{\mathscr{C}}(\alpha)$ depends on the time step n, but usually the dependence is very small if we limit to consider a small number of time steps (n of the order of a few tens at maximum and M an order of magnitude less). Indeed, the n-dependence of λ arise from the center of mass dynamics (via the **B** matrix) while the fast time dependence of μ_n, and therefore the behaviour of $\Delta\mu_n$, can be ascribed to the much faster orientational dynamics. Therefore in the previous equation we can safely consider λ as independent of n and look for a solution of the form:

$$\Delta\mu_n \propto y^n. \tag{25}$$

The resulting algebraic equation in y (for $y \neq 0$)

$$y^M - \lambda \sum_{m=1}^{M} (-1)^{m+1} \binom{M}{m} y^{M-m} = 0 \tag{26}$$

has M roots, let us say y_k with $k = 1, \ldots, M$. The homogeneous part of the solution for $\Delta \mu_n$ is given by

$$\Delta \mu_n^{(\text{hom})} = \sum_{k=1}^{M} c_k y_k^n \tag{27}$$

with c_k constant to be determined.

Therefore, in the approximation of considering the eigenvalues of the matrix $\Lambda_{\mathscr{C}}$ nearly independent of the time step n, we can conclude that: *in order to be the error not divergent as the time goes by* $(n \to \infty)$, *one needs that* $|y_k| < 1$ *for every* $k = 1, \ldots, M$ *and for every eigenvalues* $\lambda_{\mathscr{C}}(\alpha)$, $\alpha = 1, \ldots, 3N$.

Let us now find the y_k's. Eq. (26) can be rewritten as:

$$\left(\frac{y-1}{y}\right)^M = \frac{\lambda - 1}{\lambda} \tag{28}$$

Since the matrix $\Lambda_{\mathscr{C}} = [\mathbf{B}_n]^{\mathscr{C}}$, and $\|\mathbf{B}_n\| < 1$, all its eigenvalues $\lambda_{\mathscr{C}}(\alpha)$ have modulus less than one. Therefore if we define

$$\rho = \left|\frac{\lambda - 1}{\lambda}\right| \tag{29}$$

then Eq. (28) can be written as

$$\begin{aligned} &\left(\frac{y-1}{y}\right)^M = \rho \to \lambda < 0 \\ &\left(\frac{y-1}{y}\right)^M = \rho e^{i\pi} \to \lambda > 0 \end{aligned} \tag{30}$$

and its solutions are

$$y_k = \frac{1}{1 - \rho^{(1/M)} e^{i\phi_k(\lambda)}} \tag{31}$$

where

$$\phi_k(\lambda) = \frac{\xi(\lambda)}{M} + \frac{2\pi k}{M} \tag{32}$$

and

$$\xi(\lambda)=\begin{cases}\pi & \text{if } 0<\lambda<1\\ 0 & \text{if } -1<\lambda<0\end{cases} \tag{33}$$

Therefore the stability condition $|y_k|^2<1$ can be written as:

$$1+\rho^{(2/M)}-2\rho^{(1/M)}\cos(\phi_k(\lambda))>1 \tag{34}$$

or

$$\left|\frac{\lambda-1}{\lambda}\right|>2^M\cos(\phi_k(\lambda))^M \tag{35}$$

By analysing the two possibilities, $1>\lambda>0$ and $-1<\lambda<0$, from Eq. (35) one can conclude that the stability is ensured if all the eigenvalues of the matrix $\Lambda_{\mathscr{C}}$ satisfy the condition:

$$-\frac{1}{2^M-1}<\lambda<\frac{1}{1+2^M\cos(\pi/M)^M}. \tag{36}$$

Since the following relation holds for $M>1$

$$\frac{1}{2^M-1}\leq\frac{1}{1+2^M\cos(\pi/M)^M}, \tag{37}$$

we write the stability condition as

$$|\tilde{\lambda}|<\frac{1}{1+2^M\cos(\pi/M)^M}. \tag{38}$$

where $|\tilde{\lambda}|$ is the maximum modulus among all the $3N$ eigenvalues.

If we denote with $\tilde{b}$ the eigenvalue of $\mathbf{B}_n$ with the maximum modulus, the procedure will be not divergent if

$$|\tilde{b}^{\mathscr{C}}|=|\tilde{\lambda}|<\frac{1}{1+2^M\cos(\pi/M)^M} \tag{39}$$

This last relation can be rewritten as a condition for $\mathscr{C}$ with $|\tilde{b}|$ and M as parameters.

$$\mathscr{C}>\tilde{\mathscr{C}}(M,\tilde{b})=\frac{\ln(1+2^M\cos(\pi/M)^M)}{\ln(1/|\tilde{b}|)} \tag{40}$$

In Figure 1 are shown the curves $\mathscr{C}=\tilde{\mathscr{C}}(M,\tilde{b})$ for various values of $|\tilde{b}|$ ($|\tilde{b}|=0.15, 0.30, 0.45, 0.60, 0.75$). For a given value of $|\tilde{b}|$ the corresponding curve split the $(\mathscr{C}-M)$ plane

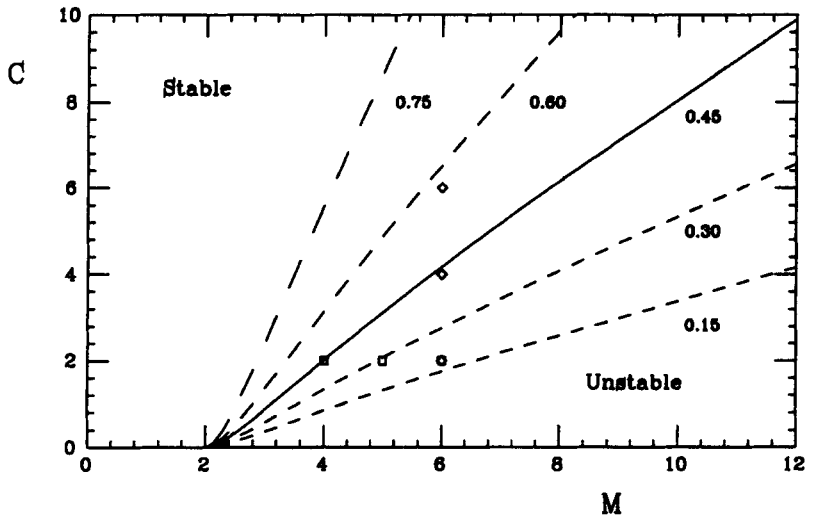

Figure 1 Stability boundaries on $(\mathscr{C}, M)$ plane, see Eq. (40), for different values of the parameter $\tilde{b}(\tilde{b} = 0.15, 0.30, 0.45, 0.60, 0.75)$. The plane is divided in a stable (upper left) and unstable (lower right) region. The solid curve ($\tilde{b} = 0.45$) has been evidentiated because this value is very close to proper one for heavy water at room condition, to which the numerical test refers. Tests have been performed on the points indicated with the squares ($\mathscr{C} = 2$, $M = 4, 5, 6$) and diamonds ($M = 6, \mathscr{C} = 2, 4, 6$).

in two regions. In the upper-left side the iterative algorithm for the calculation of the induced dipoles is predicted to be stable, while in the lower-right region it is unstable. The points indicated with squares and diamonds refer to particular $(\mathscr{C} - M)$ couples which are numerically investigated for testing Eq. (40), as discussed in the last section.

ACCURACY

When the stability condition, Eq. (40), is accomplished and the iterative procedure give rise to finite errors at all the time steps, we are interested in the accuracy of the resulting induced dipole, i.e. how far they are from the exact solution. For this purpose, let us define the mean instantaneous error, η_n,

$$\eta_n = [\Delta\bar{p}_n \cdot \Delta\bar{p}_n]^{1/2}, \tag{41}$$

its time average, η,

$$\eta = \sqrt{\frac{1}{\mathscr{N}} \sum_{n=1}^{\mathscr{N}} \eta_n^2} = \sqrt{\langle \eta_n^2 \rangle} \tag{42}$$

and the corresponding mean relative errors,

$$\varepsilon_n = \frac{\eta_n}{[\bar{p}_n \cdot \bar{p}_n]^{1/2}} \tag{43}$$

$$\varepsilon = \frac{\eta}{[\langle \bar{p}_n \cdot \bar{p}_n \rangle]^{1/2}}. \tag{44}$$

Of course these errors are functions of M and $\mathscr{C}$, as well as of the characteristics of the physical system we are studying through the matrix $\mathbf{B}_n$.

The unitarity of the **G** matrix implies that

$$\Delta\bar{p}_n\cdot\Delta\bar{p}_n=\Delta\bar{\mu}_n\cdot\Delta\bar{\mu}_n. \tag{45}$$

and from Eq. (15) we have

$$\Delta\bar{\mu}_n=\mathbf{D}\cdot(\bar{\mu}_n^{(0)}-\bar{\mu}_n); \tag{46}$$

then by inserting the previous expression for $\Delta\bar{\mu}_n$ in Eq. (45) we get

$$\Delta\bar{p}_n\cdot\Delta\bar{p}_n=\sum_{\alpha}\lambda^2(\alpha)|\mu_n^{(0)}(\alpha)-\mu_n(\alpha)|^2. \tag{47}$$

To estimate an upper bound of η_n, all the eigenvalues $\lambda(\alpha)$ are substituted with the maximum eigenvalue $\tilde{\lambda}$,

$$\Delta\bar{p}_n\cdot\Delta\bar{p}_n\le\tilde{\lambda}^2\sum_{\alpha}|\mu_n^{(0)}(\alpha)-\mu_n(\alpha)|^2=\tilde{\lambda}^2|\bar{p}_n-\bar{p}_n^{(0)}|^2. \tag{48}$$

By using the expression of the initial guess, Eq. (13),

$$\begin{aligned}\Delta\bar{p}_n\cdot\Delta\bar{p}_n&\le\tilde{\lambda}^2\left|\bar{p}_n-\sum_{m=1}^{M}(-1)^{m+1}\binom{M}{m}\bar{p}_{n-m}^{(\mathscr{C})}\right|^2\\&\simeq\tilde{\lambda}^2\left|\bar{p}_n-\sum_{m=1}^{M}(-1)^{m+1}\binom{M}{m}\bar{p}_{n-m}\right|^2\\&=\tilde{\lambda}^2\left|\sum_{m=0}^{M}(-1)^{m+1}\binom{M}{m}\bar{p}_{n-m}\right|^2\end{aligned} \tag{49}$$

then

$$\begin{aligned}\eta^2&\le\tilde{\lambda}^2\left\langle\left|\sum_{m=0}^{M}(-1)^{m+1}\binom{M}{m}\bar{p}_{n-m}\right|^2\right\rangle\\&=\tilde{\lambda}^2\sum_{m,m'=0}^{M}(-1)^{m+m'}\binom{M}{m}\binom{M}{m'}\langle\bar{p}_{n-m}\cdot\bar{p}_{n-m'}\rangle.\end{aligned} \tag{50}$$

If we introduce the normalized time autocorrelation function of the exact induced dipole moments, $\bar{p}_n$:

$$C_{pp}(m)=\frac{\langle\bar{p}_n\cdot\bar{p}_{n-m}\rangle}{\langle|\bar{p}_n|^2\rangle} \tag{51}$$

then, since $\tilde{\lambda} = \tilde{b}^{\mathscr{C}}$, Eq. (50) can be rewritten as

$$\varepsilon^2 \leq \tilde{b}^{2\mathscr{C}} \sum_{m,m'=0}^{M} (-1)^{m+m'} \binom{M}{m} \binom{M}{m'} C_{pp}(m-m') \tag{52}$$

We need to study the sum in Eq. (52) to get information on the accuracy. The classical autocorrelation $C_{pp}(t)$ is an even function of time and can be developed in an even Mac Laurin power series,

$$C_{pp}(t) = \sum_k \frac{t^{2k}}{(2k)!} \left[\frac{d^{2k}}{dt^{2k}} C_{pp}(t) \right]_{t=0} = \sum_k (-1)^k \frac{t^{2k}}{(2k)!} \Omega_{2k} \tag{53}$$

where Ω_k is the k-th spectral moment of $\tilde{C}_{pp}(\omega)$, the Fourier transform of $C_{pp}(t)$. If we substitute the previous expression in terms of Δt units, i.e.

$$C_{pp}(m-m') = \sum_k (-1)^k \frac{\Delta t^{2k}}{(2k)!} \Omega_{2k} (m-m')^{2k}, \tag{54}$$

in Eq. (52) we obtain:

$$\varepsilon^2 \leq \tilde{b}^{2\mathscr{C}} \sum_k \frac{\Delta t^{2k}}{(2k)!} \Omega_{2k} \sigma_M(2k) \tag{55}$$

where the quantity $\sigma_M(k)$ is defined as

$$\sigma_M(k) = \sum_{m,m'=0}^{M} (-1)^{m+m'} \binom{M}{m} \binom{M}{m'} (m-m')^k \tag{56}$$

In the appendix it is shown that $\sigma_M(k) = 0$ for $k < 2M$, while at the lowest order in $\Delta t (k = 2M)$ it results $\sigma_M(2M) = (-1)^M (2M)!$. Finally we have:

$$\varepsilon^2 \leq \tilde{b}^{2\mathscr{C}} \Omega_{2M} \Delta t^{2M} + \mathcal{O}(\Delta t^{2M+2}) \tag{57}$$

It is worth to note that the mean realtive error is maximized by a quantity which is proportional to the M-th power of the time step and to the $2\mathscr{C}$ of maximum eigenvalue of the **B** matrix, as well as to the $2M$-th spectral moment of the induced dipole autocorrelation function.

In order to clarify the meaning of Eq. (57), let us suppose that the time evolution of $\bar{p}(t)$ was controlled by a well-defined frequency, say ω_o, then

$$\varepsilon \leq \tilde{b}^{\mathscr{C}} (\omega_o \Delta t)^M \tag{58}$$

expresses ε as a function of some characteristics of the fluid under investigation ($\tilde{b}$ and ω_o) as well as of the parameters of the MD run (Δt, $M e \mathscr{C}$). On the other hand, if

the correlation function $C_{pp}(t)$ was pure exponential in time,

$$C_{pp}(t) = e^{-(|t|/\tau)} \tag{59}$$

then we would get

$$C_{pp}(m-m') = e^{-(\Delta t/\tau)|m-m'|} = \sum_k \frac{(-1)^k}{k!}\left(\frac{\Delta t}{\tau}\right)^k |m-m'|^k \tag{60}$$

with even as well odd power terms in Δt. As a consequence in the expression for $C_{pp}(m-m')$ as function of $\sigma_M(k)$, also terms like $\sigma'_M(k)$ would appear:

$$\sigma'_M(k) = \sum_{m,m'=0}^{M} (-1)^{m+m'} \binom{M}{m}\binom{M}{m'} |m-m'|^k \tag{61}$$

which are non vanishing for odd k value, and in particular for $k = 1$. The dominant term in Δt in the expression of ε results to be

$$\varepsilon \simeq \tilde{b}^{\mathscr{C}} \sqrt{\frac{\Delta t}{\tau}}. \tag{62}$$

It is worth to note that the Eq. (62) is independent of M: the "absence" of memory in a pure exponential autocorrelation function makes useless a predictive scheme for the initial guess $\bar{p}_n^{(o)}$.

WORKING POINT DETERMINATION

Equation (40) states a condition to be satisfied from the couple of free parameters $\mathscr{C}$ and M to ensure the stability of the iterative solutions to the electrostatic problem (when the initial guess, $\bar{p}_n^{(o)}$, is evaluated via the extrapolation scheme given by Eq. (13)). On the other hand, the accuracy in the evaluation of the induced dipole moments is related to Eq. (58) and depends on the same two free parameters and MD time step. The characteristics of the system enter in Eq. (40) through $\tilde{b}$, the maximum eigenvalue of the matrix **B**, and in Eq. (58) through $\tilde{b}$ and ω_o, the typical frequency of the induced dipole autocorrelation function.

When we want to use the proposed procedure in MD runs of a specific system, the time step Δt is determined by other conditions related to the fastest dynamics but not strictly connected to the electrostatic problem. Then the choice of $\mathscr{C}$ and M will be optimized when the required accuracy is obtained with the minimum cost of CPU time. Since the CPU time for iterative procedures is proportional to the number $\mathscr{C}$ of iteration, $\mathscr{C}$ has to be as little as possible. On the contrary M does not enter appreciably in the determination of the CPU time, but large values of M would require large values of $\mathscr{C}$ in agreement with the stability Eq. (40).

The previous considerations indicate that the most convenient working point in the $(\mathscr{C}, M)$ plane is close to the intersection of the two curves, see Eqs. (40) and (58).

$$\varepsilon = \tilde{b}^{\mathscr{C}}(\omega_o \Delta t)^M \tag{63}$$

$$1 = \tilde{b}^{\mathscr{C}}(1 + 2^M \cos^M(\pi/M)) \tag{64}$$

and lies in the stability region (see Fig. 2).

Of course in order to apply this analysis to a real system, estimates of the quantities $\tilde{b}$ and ω_o are required. An estimate of ω_o can be drawn easily from experimental data (e.g. from the dielectric relaxation or infrared absorption) and it does not deserve more discussion. On the contrary the quantity $\tilde{b}$ is not usually known. In the next section we will discuss how we can estimate it by determining the eigenvalue spectrum of **B**.

DETERMINATION OF THE EIGENVALUES $b(\alpha)$

We will face the calculation in two distinct way. From one side we will diagonalize the **B** matrix build up with the output of the MD run. This "experimental" way supplies "exact" eigenvalues for a particular thermodynamic state, but it does not give us information on the peculiarities of the dynamic system which are determining the eigenvalue spectrum. The second "a priori" way will make use of the center of mass pair correlation function $g(r)$, a primary feature of the system, to estimate the eigenvalue

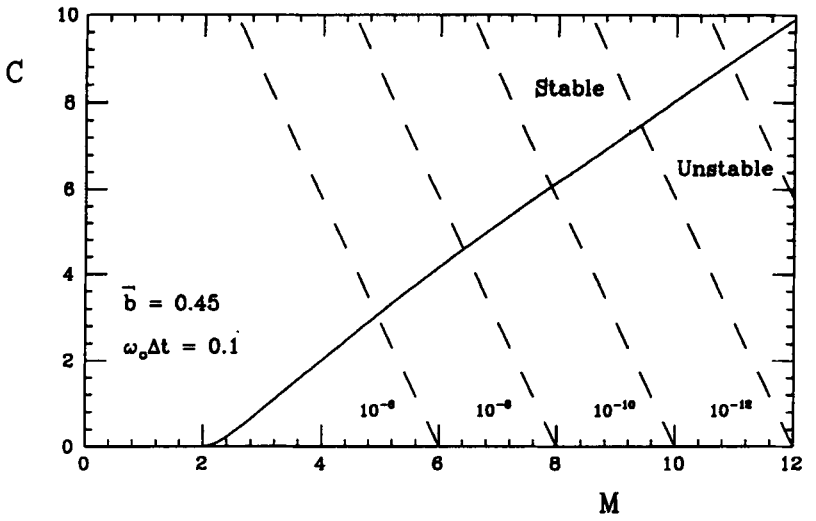

Figure 2 Separation of stable and unstable regions for $\tilde{b} = 0.45$ (full line). Broken lines are the iso-precision loci for different ε values ($\varepsilon = 10^{-6} \cdots 10^{-4}$) in the particular case of $\tilde{b} = 0.45$ and $\omega_o \Delta t = 0.1$. For a given precision the best working point is that with the lowest (integer) $\mathscr{C}$ in the stability region and in the upper right side of the iso-precision curve.

spectrum. The reliability of this last method is validated by comparison with the direct evaluation of the eigenvalues from MD runs.

As an example, we will use the MD runs performed with 500 TIP4P [6] heavy water molecules at normal room condition ($T = 310\,\mathrm{K}$ and $\rho = 1.11\,\mathrm{gcm}^{-3}$). About 200 configurations are stored every 0.3 ps (200 steps). From each configuration we calculate the center of mass $g(r)$ and the **B** matrix to be diagonalized.

Estimate of $\tilde{b}$ in the Limit of Total s correlation

In the case the elements of a given matrix **B** verify the following relations:

$$\begin{aligned} B_{\mu\nu} &\propto 1 - \delta_{\mu\nu} \\ \sum_{\mu\nu} B_{\mu\nu} &= 0 \\ \sum_{\mu\nu} B_{\mu\nu}^2 &= 3N\sigma^2 \end{aligned} \tag{65}$$

and the elements off-diagonal are random gaussian variables then following Wigner [22] the distribution of the eigenvalues of **B** is symmetric with respect to zero, is semicircular and the modulus of the maximum eigenvalues is equal to 2σ.

In the present case, with $\mathbf{B} = \alpha\mathbf{T}^{(2)}$, the previous relation can be written as

$$\begin{aligned} \alpha[\mathbf{T}_{jj'}^{(2)}]_{\beta\gamma} &\propto 1 - \delta_{jj'}\delta_{\beta\gamma} \\ \alpha\sum_{j}\sum_{j'}\sum_{\beta\gamma}[\mathbf{T}_{jj'}^{(2)}]_{\beta\gamma} &= 0 \\ \alpha\sum_{j}\sum_{j'}\sum_{\beta\gamma}[\mathbf{T}_{jj'}^{(2)}]_{\beta\gamma}^2 &= 3N\sigma^2 \end{aligned} \tag{66}$$

These first three relations are verified: the first one indicate that there are no self polarization of a molecule, the second one depend on the isotropy of the system and the third one is a definition of σ. Of course the condition on the randomness of the off-diagonal elements is not accomplished, because of the correlation between different molecules. However we will see in the next subsection that this will not introduce a large uncertainty in the evaluation of the maximum eigenvalue.

Let us then suppose that:

$$|\tilde{b}| = 2\sigma \tag{67}$$

where σ is explicity defined in Eq. (66), e.g.

$$\sigma^2 = \frac{1}{3N}\,\alpha^2 \sum_{ij}\frac{1}{|r_{ij}|^6}\sum_{\beta\gamma}\left[\frac{3r_{\beta,jj'}r_{\gamma,jj'} - |r_{jj'}|^2\delta_{\beta\gamma}}{|r_{jj'}|^2}\right]^2 \tag{68}$$

In an isotropic system, on average,

$$\sum_{\beta\gamma}\left[\frac{3r_{\beta,jj'}r_{\gamma,jj'}-|r_{jj'}|^2\delta_{\beta\gamma}}{|r_{jj'}|^2}\right]^2=6 \tag{69}$$

then

$$\sigma^2=\frac{2}{N}\alpha^2\sum_{ij}\frac{1}{|r_{ij}|^6}=8\pi\alpha^2\rho\int dr g(r)\frac{1}{r^4} \tag{70}$$

For sake of simplicity we define an dimensionless quantity χ as:

$$\chi^2=\frac{8\pi}{\rho}\int dr g(r)\frac{1}{r^4} \tag{71}$$

then

$$|\tilde{b}|=2\chi\alpha\rho \tag{72}$$

In the case of heavy water at room condition we get $\chi=4.6$ by numerical integration of Eq. (71) with the $g(r)$ obtained from the MD output. Therefore, by using $\alpha=1.44A^3$ and $\rho=3.34\cdot10^{-2}A^{-3}$, we obtain $|\tilde{b}|=0.44$.

Diagonalization of **B**

From a direct diagonalization of 200 replica of the **B** matrix, we obtain the eigenvalues distribution shown in Figure 3.

As can be seen the distribution is far from to be symmetric and semicircular, because of the correlations between the molecular centers which make loose the the Wigner hypothesis on the randomness of the out diagonal elements of the **B** matrix. However the extreme eigenvalues, $b_{\min}\approx-0.5$ and $b_{\max}\approx0.38$, are not too far from ±0.44 which have been estimated through the Wigner hypothesis.

We can conclude that the value of the parameter $\tilde{b}$ derived from the center of mass pair correlation function, see Eqs. (71) and (72), is a reasonable estimate of the real one.

NUMERICAL TEST AND CONCLUSION

In this section we report the numerical results obtained from a computer simulation of polarizable heavy water as a check for the validity of the previously reported prediction for the stability and for the precision achieved in the calculation of the induced dipoles in the framework of an iterative algorithm for the solution of the self consistent electrostatic problem.

All the details of the MD algorithm and adopted interaction potential have been reported in Ref. [1]. Here we want mention only that the parameters of the potential

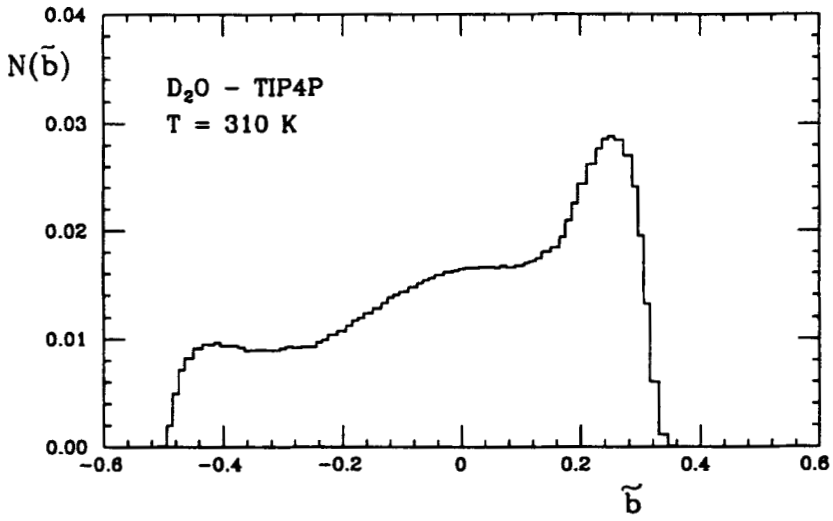

Figure 3 Distribution of the eigenvalues of the **B** matrix, for TIP4P heavy water at room condition, obtained by direct diagonalization of 200 statistically independent configurations. The maximum absolute eigenvalue results to be $|\tilde{b}| \simeq 0.5$.

are not optimized for real water. All the results shown hereafter refer to a sample of 500 heavy "water" molecules at $T = 310\,\mathrm{K}$ and $\rho = 1.11\,\mathrm{gcm}^{-3}$, with a timestep $\Delta t = 1\,\mathrm{fs}$.

In Figure 4 we have reported the mean relative error ε, see Eq. (44), as a function of $\mathscr{C}$ for various values of $M(M = 0, \ldots, 6)$. The diamonds represent the values of

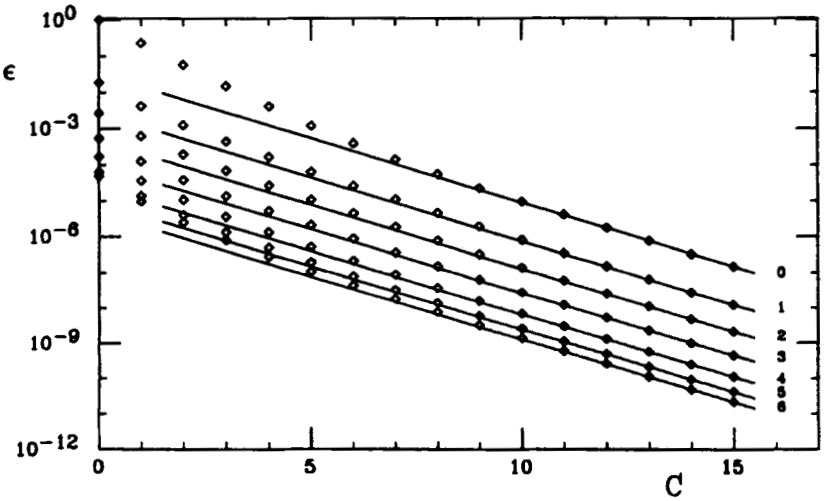

Figure 4 Computed relative mean errors, from MD simulation of a polarizable model of heavy water, in logarithmic scale ($\diamond$) as a function of $\mathscr{C}$ for different values of $M(M = 0, \ldots, 6)$. The full lines are the best fits, performed on the points with $\mathscr{C} > 10$, to $\log(\varepsilon) = \text{conts} + a(M)\mathscr{C}$. $a(M)$ results to be independent of M and equal to $-.35$.

ε averaged over 100 timestep. Th "exact" induced dipoles have been assumed to be $\bar{p}_n = \bar{p}_n^{(\mathscr{C}=20)}$. The full line reported in Figure 4 are the best fits obtained with a linear behaviour of $\log(\varepsilon)$ vs. $\mathscr{C}$ for each independent value of M. The following consideration hold:

- Following Eq. (57) $\log(\varepsilon) = \log(\Omega_{2M}) + \mathscr{C}\log(|\tilde{b}|)$. This $\log(\varepsilon)$ vs. $\mathscr{C}$ relation is verified, at least for high $\mathscr{C}$ values, as shown if Figure 4.
- The $|\tilde{b}|$ value calculated from the shape of the full lines is $|\tilde{b}| = 0.45$, in good agreement with the values estimated in the previous section.
- As predicted from Eq. (57) the slope of the full lines is independent of M, only the constant term $\log(\Omega_{2M})$ is dependent on M.
- On going from Eq. (57), to Eq. (63) we supposed that $\Omega_{2M} = (\omega_0 \Delta t)^M$, and therefore that $\log(\varepsilon) = M\log(\omega_0\Delta t) + \mathscr{C}\log(|\tilde{b}|)$. This result is not verified from the present calculation. Indeed the spacing between the different full line, belonging to different M values, are not constant and tend to vanish for high M indicating that: i) $\Omega_{2M} = (\omega_0\Delta t)^M$ is a poor approximation and ii) for high M the precision of the algorithm become independent of M, which is what we expect in the case of a fast memory decay.

In Figures 5a and 5b have reported the time evolution of ε_n, the instantaneous mean relative error on the induced dipoles for different couples of the parameters $(\mathscr{C}, M)$. The points corresponding to the couples reported on Figure 5a ($\mathscr{C} = 2, M = 4, 5, 6$) are indicated as squares in Figure 1. From Eq. (64) and Figure 1 we expect to be in a stable region for $M = 4$ and in an unstable region for $M = 5$ and 6. These behaviours are

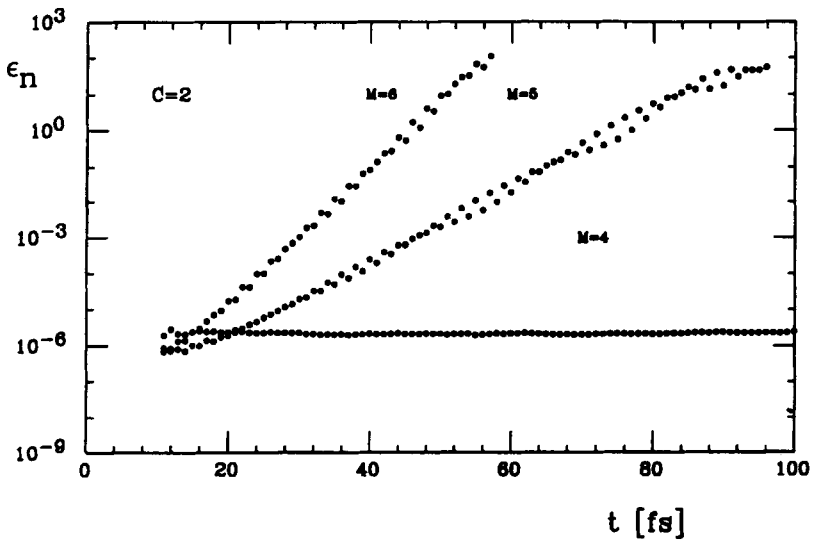

Figure 5a Time evolution of ε_n for three $\mathscr{C}$ and M values, namely $\mathscr{C} = 2$ and $M = 4, 5, 6$. Only $M = 4$ results to be stable, as predicted by Eq. (40). In the cases $M = 5$ or $M = 6$ the unstability is so large that after a few tens of time steps the calculated induced dipoles differ from the real ones by more than 100%.

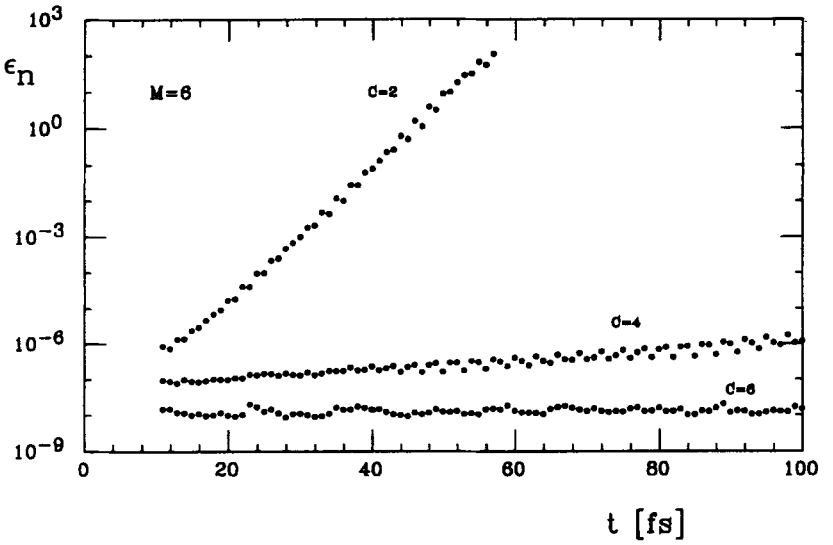

Figure 5b The same as for Figure 5a in the cases $M = 6$, $\mathscr{C} = 2, 4, 6$. Unstability is expected for $\mathscr{C} = 2$ and $\mathscr{C} = 4$.

confirmed by Figure 5a; the ε_n remain finite for $M = 2$ while it is growing in time for $M = 5, 6$.

A similar situation is found for the points in the $(\mathscr{C}, M)$ plane reported in Figure 5b, diamonds in Figure 1, i.e. $M = 6$, $\mathscr{C} = 2, 4, 6$. The algorithm is stable for $\mathscr{C} = 6$ while unstable for $\mathscr{C} = 2$ and 4. Moreover one can also notes that the rate of growth of $\log(\varepsilon_n)$ increases with the distance of the (C, M) point from stability region. Indeed the divergence at $\mathscr{C} = 6$, $M = 6$ is much higher than that for $\mathscr{C} = 4$, $M = 6$, the latter point being nearer to the stability region than the former one.

In conclusion we have shown that two simple equations, Eqs. (63) and (64), can be used to determine the best choice of the parameters to be used in MD simulation of polarizable fluids. These equations require only an estimate of some characteristics of the system under investigation. We have also shown a way to estimate these characteristics.

APPENDIX

We want to study the property of the sum

$$\sigma_M(k) = \sum_{m,m'=0}^{M} (-1)^{m+m'} \binom{M}{m} \binom{M}{m'} (m - m')^k \tag{73}$$

for all k-values such that $k \leq 2M$. First of all let us to define the function $f_M(x)$:

$$f_M(x) = \sum_{m,m'=0}^{M} (-1)^{m+m'} \binom{M}{m} \binom{M}{m'} e^{-x(m-m')}$$

$$= \sum_{m}^{M} (-1)^m \binom{M}{m} e^{-xm} \sum_{m'=0}^{M} (-1)^{m'} \binom{M}{m'} e^{xm'}$$

$$= (1-e^{-x})^M (1-e^{x})^M = 2^M (1-ch(x))^M \tag{74}$$

In the $x \to 0$ limit,

$$f_M(x)|_{x\to 0} \simeq (-1)^M x^{2M} + \mathcal{O}(x^{2M+2})$$

therefore for $k \leq 2M$

$$\lim_{x\to 0} \frac{d^k f_M(x)}{dx^k} = \begin{cases} (-1)^M (2M)! & \text{if } k = 2M \\ 0 & \text{otherwise} \end{cases} \tag{75}$$

On the other side we see that, if we expand the exponential appearing in the first row of Eq. (74) the function $f_M(x)$ can be written in term of $\sigma_M(k)$:

$$f_M(x) = \sum_{m,m'=0}^{M} (-1)^{m+m'} \binom{M}{m}\binom{M}{m'} \sum_{n} \frac{(-1)^n}{n!} x^n (m-m')^n$$

$$= \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} x^n \sum_{m,m'=0}^{M} (-1)^{m+m'} \binom{M}{m}\binom{M}{m'} (m-m')^n$$

$$= \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} x^n \sigma_M(n). \tag{76}$$

By exploiting the derivatives of both sides of Eq. (76) we find that $\sigma_M(k) = 0$ for $k \leq 2M$, being the first non zero value $\sigma_M(2M) = (-1)^M (2M)!$.

References

[1] G. Ruocco and M. Sampoli, "Computer simulation of polarizable fluids: A consistent and fast way for dealing with polarizability and hyperpolarizability", *Molecular Physics*, **82**, 875 (1994).

[2] H. J. C. Berendsen, J. Grigera and T. P. J. Stratsma, "The missing term in the effective pair potential", *J. Phys. Chem.*, **91**, 6269 (1987).

[3] O. Matsuoka, F. Clementi and M. Y. Yoshimine, "CI study of the water dimer potential surface", *J. Chem. Phys.*, **64**, 1351 (1976).

[4] F. H. Stillinger and A. Rahman, "Improved simulation of liquid water by molecular dynamics", *J. Chem. Phys.*, **60**, 1545 (1974).

[5] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren and H. J. Hermans, "Intermolecular Forces", edited by B. Pullman (Reidel, Dordrecht, Holland (1981)), p. 331.

[6] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey and M. L. Klein, "Comparison of simple potential functions for simulating liquid water", *J. Chem. Phys.*, **79**, 926 (1983).

[7] K. Hermansson, "Many-body effects in tetrahedral water cluster", *J. Chem. Phys.*, **89**, 2149 (1988).

[8] A. De Santis and A. Gregori, "Quantum correction to induced light scattering and the second virial coefficient of water and hydrogen sulphide", *Chem. Phys. Lett.*, **160**, 55 (1989).

[9] A. Fontana, P. Postorino, M. A. Ricci and A. K. Soper, "Radial distribution function in heavy water stream", in "Hydrogen bond network", M. C. Bellisent-Funnel and J. C., Dore, Eds. NATO-ASI Series C435.

[10] F. Sciortino, A. Geiger and H. E. Stariley, "Effect of defect on molecular mobility in liquid water", *Nature* **354**, 218 (1991); F. Sciortino, A. Geiger and H. E. Stanley, "Network defect and molecular mobility in liquid water", *J. Chem. Phys.*, **96**, 3857 (1992); G. Ruocco, M. Sampoli, A. Torini and R. Vallauri, "Molecular dynamics result for stretched water", *J. Chem. Phys.* **99**, 8095 (1993).
[11] A. Wallqvist and G. Kalstrom, "A new non-empirical force field for computer simulations", *Chemica Scripta* **29A**, 131 (1989); A. Wallqvist, P. Ahlstrom and G. Karestrom, "A new intermolecular energy calculation scheme: Application to potential surface and liquid properties of water", *J. Chem. Phys.*, **94**, 1649 (1990).
[12] U. Buontempo, P. Postorino, M. A. Ricci and A. K. Soper, "Neutron diffraction study of water at high temperature", *Europhys. Lett.*, **19**, 385 (1992).
[13] P. Ahlstrom, A. Wallqvist, S. Engstrom and B. Jonsson, "A molecular dynamics study of polarizable water", *Mol. Phys.*, **68**, 563 (1989).
[14] "Modern Techniques in Computational Chemistry", MOTECC-89, E. Clementi Ed., Escom, Leiden (NL) 1989.
[15] R. Car and M. Parrinello, "Unified approach for molecular dynamics and density-functional theory', *Phys. Rev. Lett.*, **55**, 2471 (1985).
[16] M. Sprik and M. Klein, "A polarizable model for water using distributed charge sites", *J. Chem. Phys.*, **89**, 7556 (1988); M. Sprik, "Hydrogen bonding and the static dielectric constant in liquid water", *J. Chem. Phys.*, **95**, 6762 (1991).
[17] M. Wilson and P. Madden, "Polarization effect in ionic systems from first principles", *J. Phys.*, Condensed Matter **5**, 2687 (1993).
[18] C. Fröberg, "Numerical Mathematics", Bonjamin/Cummings Inc. (1985).
[19] A. D. Buckingham, "Permanent and induced molecular moments and long range intermolecular forces", *Adv. Chem. Phys.*, **12**, 107 (1967).
[20] F. J. Vesely, "*N*-Particles dynamics of polarizable Stockmayer-type molecules", *J. Comput. Phys.*, **24**, 361 (1977).
[21] C. F. J. Bottcher, "Theory of electric polarization", **1**, 2nd edition (Elsevier, 1973).
[22] A. Crisanti, G. Paladin and A. Vulpiani, "Products of Random Matrices", Solid State Science 104, Springer-Verlag (1993).