COMPUTER SIMULATION OF POLARIZABLE FLUIDS: A PARALLEL IMPLEMENTATION USING LINDA AND PVM

V.Di Martino, G. Ruocco, M. Sampoli
CASPUR, Univ. di Roma "La Sapienza"
Dipartimento di fisica, Universita' di L'Aquila
Dipartimento di Energetica, Universita' di Firenze

ABSTRACT

A parallel version of a molecular dynamic program has been implemented and tested on a cluster of alpha processors connected via gigaswitch.

A replicated data method has been used to evaluate the long range dipolar forces and many-body polarization effects. The proposed scheme is convenient for medium to large size sample. The actual code is able to perform molecular dynamic calculations over very large cell, exploiting the full memory capacity of the cluster. This is achieved partitioning the memory requested by the algorithms over the memory of the single processors. This approach is less expensive in terms of computational cost with respect to traditional vector supercomputers. Almost all the code (97%) has been parallelized using pvm and linda parallel message passing primitives.

The parallelization strategy will be discussed to evidentiate difficulties and adopted solutions during the porting of the code. A full report of speedup and results obtained on the alpha cluster will be presented. A comparison between fddi+gigaswitch comunication facility versus ethernet connection will be presented too.

Performance data will be reported as function of the number of water molecules involved in the computation (4k,13.5k,32k) and for different cut-off radii (0.8,1,1.2 nanometer).

As result of the analisys the trade-off between number of processes and speedup will be discussed.

Performances data comparison between linda and pvm program implementation will be reported.

Non optimal work condition of the cluster in non balanced processor load condition will be discussed also.

As final step code for both pvm and linda environment will be available at the CASPUR WWW server HTTP://itaca.caspur.it/parallel/cluster/pvm/ mdh2o and .../linda/mdh2o respectively. Access via gopher will be at gopher.caspur.it /parallel computing/cluster/pvm. Further evolution of the code will include an internal check pointing to dynamically allocate the load over non dedicated processors. The detail of the solutions adopted to solve the phisyc of the MD problem follow.

THEORY

In our scheme the system under investigation is constituted of "rigid molecules" having fixed sites with associated point charges and/or masses and/or Lennard-Jones (LJ) interaction centres. In addition, we mimic the dipole polarizabilty of the molecule by putting at the centre of mass (CM) a point polarizability that can be both non-isotropic and non-linear. In an assembly of such "molecules", the electrostatic interaction energy can be written as the sum of the charge-charge contributions (U_{qq}), which accounts for all the interactions between the point charges, plus an induction term (U_{ind}), describing all the effects due to the induced dipoles [1, 2]:

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

$$U_{qq} = \frac{1}{4\pi\epsilon_o}\frac{1}{2}\sum_{i,\mu}\sum_{j,\nu}\frac{q_\mu q_\nu}{r_{i\mu,j\nu}} \tag{2}$$

The induction energy can conveniently be split into the sum of the dipole-dipole interactions (U_{pp}), the charge-dipole interactions (U_{pq}), and the self interaction energy (U_s), i.e. the work done by the electric field to distort the electron clouds of a polarizable molecule, so to originate an induced dipole moment:

$$U_{ind} = U_{pp} + U_{pq} + U_s \tag{3}$$

with

$$U_{pp} = -\frac{1}{2}\sum_{i,j\neq i}\bar{p}_i\cdot\bar{E}_i^{(p)} \tag{4}$$

$$U_{pq} = -\sum_i \bar{p}_i\cdot\bar{E}_i^{(q)} \tag{5}$$

$$U_s = \sum_i\int_0^{\bar{p}_i}\bar{E}_i\cdot d\bar{p}_i \tag{6}$$

In these equation, $\bar{p}_i$ stands for the induced dipole of the i-th molecule and $\bar{E}_i$ for the local electric field seen at the CM; $\bar{E}_i$ is due to the sum of the field generated by the distribution of the point charges $\bar{E}_i^{(q)}$ plus the field generated by the induced dipoles $\bar{E}_i^{(p)}$:

$$\bar{E}_i = \bar{E}_i^{(q)} + \bar{E}_i^{(p)} \tag{7}$$

with

$$\bar{E}_i^{(q)} = \frac{1}{4\pi\epsilon_o} \sum_{j\neq i,\nu} q_\nu \frac{\bar{r}_{i,j\nu}}{r_{i,j\nu}^3} \tag{8}$$

$$\bar{E}_i^{(p)} = \sum_{j\neq i} T_{i,j} \cdot \bar{p}_j \tag{9}$$

In equation (9), $T_{i,j}$ is the usual static dipole propagator

$$T_{i,j} = \frac{1}{4\pi\epsilon_o} \frac{3\bar{r}_{ij}\bar{r}_{ij} - 1r_{ij}^2}{r_{ij}^5} \tag{10}$$

At each step of the MD run, we have to evaluate the induced dipoles $\bar{p}_i$ consitent with the values of $\bar{E}_i^{(q)}$ due to a given distributions of the point charges. A central point in dealing with molecular systems having coulombic dipolar interactions is the use of a consistent method for the treatment of these long range interactions. To begin with, the sums over j appearing in equations (4), (8)) are split into two sums: the first (say $\sum^<$) over the molecules the CM's of which are belonging to the 'cutting' sphere of radius R_c centred at $\bar{r}_i$ (i.e., for which $r_{ij} < R_c$), the second ($\sum^>$) over the remaining particles. The first sum takes into account all electrostatic interactions inside the sphere while the interactions in the second sum can be approximated by a dielectric continuum and estimated through the reaction field method [2, 3]. For example, the electric field due to point charges and that due to induced dipoles only (see eqs. (8) and (9)) are approximated by

$$\bar{E}_i^{(q)} = \frac{1}{4\pi\epsilon_o} \left[\sum_{j\neq i,\nu}^{<} q_\nu \frac{\bar{r}_{i,j\nu}}{r_{i,j\nu}^3} + \sum_{j,\nu}^{>} q_\nu \frac{\bar{r}_{i,j\nu}}{r_{i,j\nu}^3} \right] \tag{11}$$

$$= \frac{1}{4\pi\epsilon_o} \left[\sum_{j\neq i,\nu}^{<} q_\nu \frac{\bar{r}_{i,j\nu}}{r_{i,j\nu}^3} + f_\tau \sum_{j}^{<} \bar{m}_j \right]$$

$$= \frac{1}{4\pi\epsilon_o} \left[\sum_{j\neq i,\nu}^{<} q_\nu \bar{r}_{i,j\nu} \left(\frac{1}{r_{i,j\nu}^3} - f_\tau \right) + f_\tau \bar{m}_i \right]$$

and

$$\bar{E}_i^{(p)} = \sum_{j \neq i}^{<} T_{i,j} \cdot \bar{p}_j + \sum_{j}^{>} T_{i,j} \cdot \bar{p}_j \tag{12}$$
$$= \sum_{j \neq i}^{<} T_{i,j} \cdot \bar{p}_j + \frac{f_\tau}{4\pi\epsilon_o} \sum_{j}^{<} \bar{p}_j$$
$$= \sum_{j \neq i}^{<} \left(T_{i,j} + \frac{f_\tau}{4\pi\epsilon_o} 1 \right) \cdot \bar{p}_j + \frac{f_\tau}{4\pi\epsilon_o} \bar{p}_i$$

where $\bar{m}_j = \sum_\nu q_\nu \bar{r}_{j\nu}$ is the permanent dipole moment of the j-th molecule associated to its fixed charge distribution and f_τ is given by:

$$f_\tau = \frac{\epsilon_r - 1}{\epsilon_r + \frac{1}{2}} \frac{1}{R_{eq}^3} \tag{13}$$

In equation (13) R_{eq} is the equivalent radius of the cut-off sphere, as discussed later and ϵ_r is the estimated relative dielectric constant of our system. So far all the sums run over the particles inside the cutting sphere, but equations (11) and (12) yield reasonable estimates of the fields for an infinite sample.

A net cutting sphere implies impulsive forces when a particle crosses the border. This has been recognized [4] as a source of pumping in energy in MD simulations. This undesired effect can be avoided [4] by adopting a tapering function $\tau(R)$ that tapers the switch to reaction field approximation, i.e. between the terms evaluated directly through a sum of $\sum^<$ type and those estimated through the reaction field, which originate from sums of $\sum^>$ type.

Each potential energy term has to be differentiated with respect to the coordinates of the charges and CM's in order to obtain forces and torques. Great semplifications arise since all indirect derivative through $\bar{E}$ or $\bar{p}$ are vanishing.

The introduction of many-body interactions due to polarization leads to a significant increase of the number of quantities to evaluate each MD step. Therefore, it is important to utilize a simple and very efficient algorithm for the integration of the equations of motion and to use a MD time step as long as possible without affecting the conservation of the energy and momenta appreciably. For this aim the standard leap-frog algorithm have been employed for the translational motion, while a similar modified algorithm have been developed to solve the equations for the rotational motion in terms of quaternions $\{\bar{q}^N\}$ [5]. As a check of the whole procedure we present some results obtained in the case of liquid water at room conditions. We have considered $N = 500$ D_2O molecules enclosed in a cubic box with periodic boundary conditions and the MD simulations have been performed in a NVE (microcanonical) ensemble using the alpha cluster of the CASPUR. The density was $\rho = 1.11\ g/cm^3$ and the (mean) temperature was $T = 310\ K$. The values for the polarizability and hyperpolarizability tensors elements have been taken from recent *ab initio* calculation [6] of the isolate molecule.

References

[1] F.J. Vesely, *J.comput.Phys.* **24**, 361, (1977)

[2] C.F.J. Bottcher, "Theory of electric Polarization", Vol.1, 2nd edition (Elsevier, 1973).

[3] M.P. Allen and D.J. Tildesley, "Computer Simulation of Liquids.",Clarendon, Oxford (1987).

[4] D.J. Adams, E.M. Adams and G.J. Hills, *Mol.Phys.* **38**, 387, (1979).

[5] D.J. Evans, *Mol.Phys.* **34**, 317, (1977).

[6] G. Maroulis, *J.Chem.Phys.* **94**, 1182, (1991)