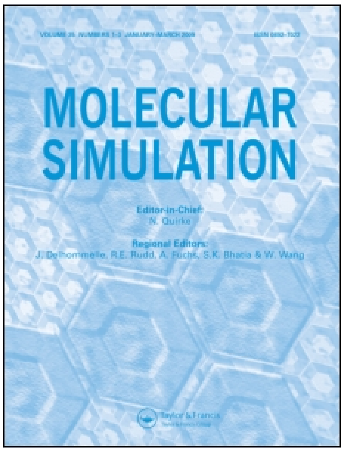

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MONTE CARLO IMPLEMENTATION ON THE CONNECTION MACHINE 2; WATER IN GRAPHITE PORES

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The implementation of Monte Carlo (Canonical and Grand Canonical Ensembles) codes on the Single Instruction Multi Data parallel supercomputer Connection Machine 2 are discussed and demonstrated. The program was developed for the simulation of water behavior in slit graphite pores in CM FORTRAN. A one dimensional data layout is the most suitable for MC realization on the CM-2. The code performance is compared with the performance of sequential and parallel codes on other computers. Preliminary results of the simulations are reported.

KEY WORDS: Connection Machine 2, algorithm, Grand Canonical Monte Carlo Simulation, water adsorption, graphite pore

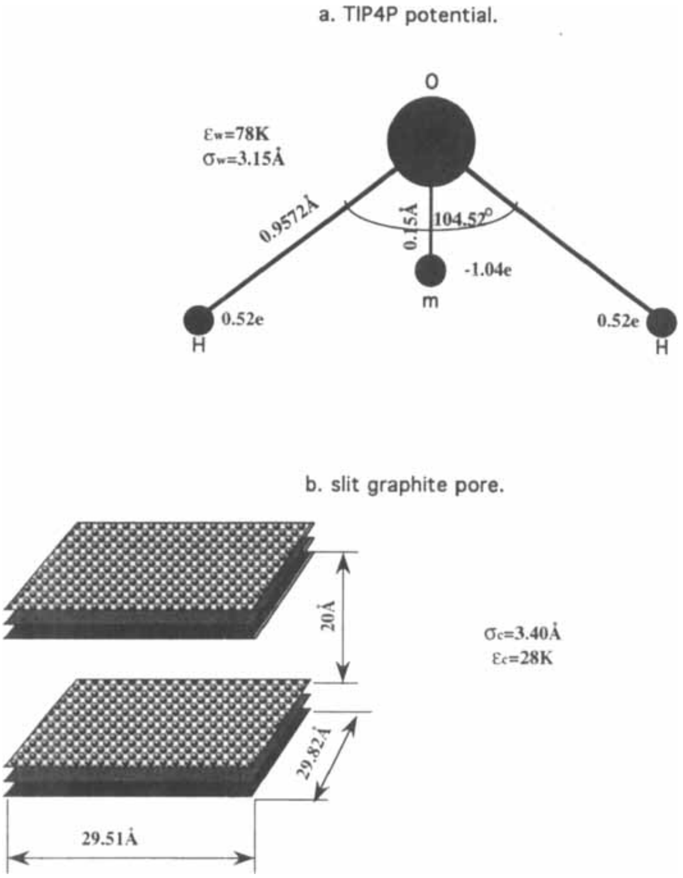
1 INTRODUCTION

The behavior of water adsorbed on the surface of graphitic and activated carbons is important in a variety of industrial purification and separation processes, where such carbons are commonly used, and also in investigations of carbonaceous rocks and oil and gas reservoirs. One would like to understand the role of temperature and pressure, the nature of the carbon surface, pore sizes, shapes and connectivity, etc. on the behavior of the adsorbed water. Questions of interest include: how is the adsorption and structure affected by the number and type of active surface groups, and what are the influence of the variables on diffusion rates, phase transitions, and so on, of the adsorbed water? Direct experimental study is difficult because of the complex morphology of the carbon. Molecular simulations [1] offer a particularly valuable method for investigating these phenomena in a systematic way.

The complex nature of the intermolecular forces for water and for its interaction with the active carbon surface make the simulation very slow on sequential computers. We have therefore undertaken these simulations on a parallel CM-2 supercomputer.

2 SIMULATION TECHNIQUES

In our work we use Canonical and Grand Canonical Monte Carlo methods (CMC and GCMC, respectively) [1, 2, 3, 4, 5, 6] to investigate water adsorption in carbon


a. TIP4P potential.

b. slit graphite pore.

Figure 1 Models used in simulation.

pores. In this work we used (Figure 1) the TIP4P [7] potential for water, so the water-water interaction energy may be represented in the form:

$$V_{i,j} = \sum_{i_a} \sum_{j_b} \frac{q_{i_a} q_{j_b} e^2}{r_{i_a,j_b}} + 4\epsilon_w \left[\left(\frac{\sigma_w}{r_{i,j}} \right)^{12} - \left(\frac{\sigma_w}{r_{i,j}} \right)^6 \right] \tag{1}$$

The first term in this equation represents the long range electrostatic interaction between the charged centers a, b of water molecules i and j; the second term is the short-range Lennard-Jones interaction. For the interaction between water molecules and carbon atoms the Lennard-Jones potential was used with the Lorentz-Berthelot combining rules:

$$\Phi_{wc} = 4\epsilon_{wc} \left[\left(\frac{\sigma_{wc}}{r} \right)^{12} - \left(\frac{\sigma_{wc}}{r} \right)^6 \right] \tag{2}$$

where $\sigma_{wc} = (\sigma_w + \sigma_c)/2$ is the water-carbon Lennard-Jones molecule size parameter and $\epsilon_{wc} = \sqrt{\epsilon_w \epsilon_c}$ is the corresponding Lennard-Jones energy parameter. The carbon atoms in each pore wall were arranged in three layers with the graphite structure (Figure 1). The total number of carbon atoms in each wall was taken to be 1008. The structural and potential parameters for carbon were taken from Steele [8], and the total interaction energy between a water molecule and the wall was obtained by summing eqn. (2) over all carbon atoms.

The CMC algorithm consists of the following steps. The number of molecules N, volume V, and temperature T are specified. In the first step the randomly chosen molecule is shifted an arbitrary distance. The molecule is then rotated through a random angle. The change in the internal energy of the system is calculated. The new configuration is adopted with the probability min $(1, e^{-\frac{\Delta E}{kT}})$, where ΔE is the difference of energy between the new and old configurations. The block-scheme of CMC is represented in Figure 2. The GCMC method represents more realistic conditions then CMC, since it allows fluctuations of the number of molecules during

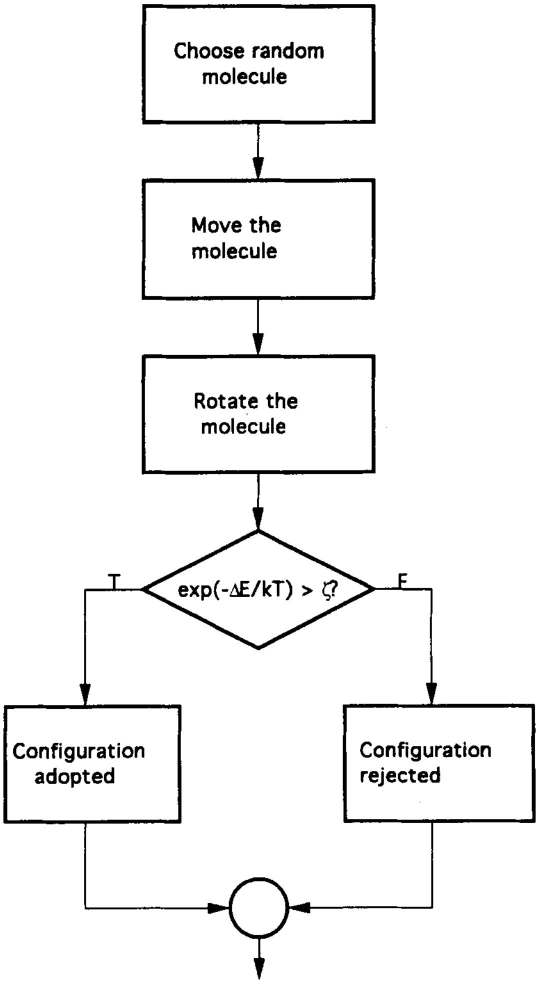


Figure 2 Block scheme of canonical Monte Carlo algorithm.

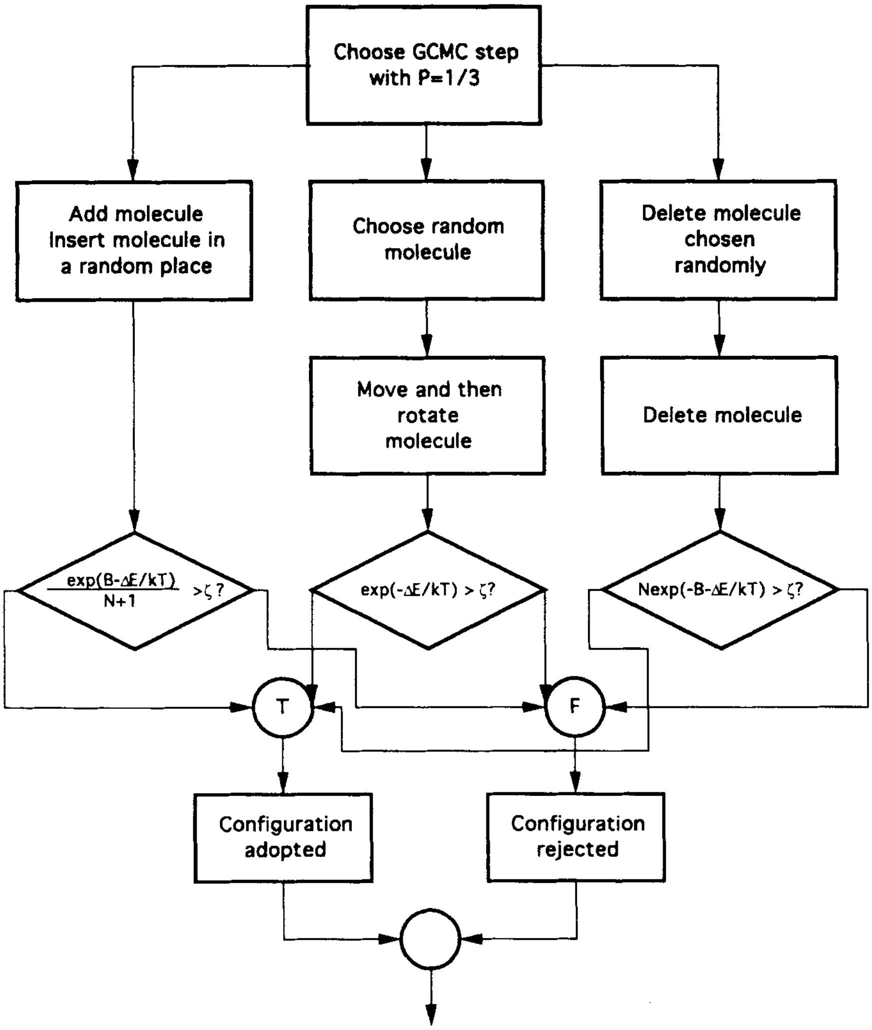


Figure 3 Block scheme of the Grand Canonical Monte Carlo algorithm.

the simulation. In this method the chemical potential, μ, (in place of N) is specified at the start of the simulation, together with V and T. To perform the fluctuation of molecule numbers two extra steps are added to the scheme. The first is the addition of molecules, and the second is their deletion. The probability to insert a molecule is $\min\left(1, \frac{1}{N+1} e^{B-\frac{\Delta E}{kT}}\right)$, and to delete a molecule it is $\min(1, Ne^{-B-\frac{\Delta k}{kT}})$, where $B = \mu_c + kT \ln V$ is an external parameter and N is the number of molecules in the initial configuration [2]. The block scheme of the GCMC algorithm is represented in Figure 3.

For bulk liquid simulations it is necessary to provide periodic boundary conditions, *i.e.* the simulation cell is replicated throughout space to form an infinite lattice. Any molecule *i* can interact only with the molecules lying within the cell image with center on molecule *i*. The interaction between molecules is truncated at a distance equal to half of the simulation box size. There are two ways to minimize errors due to this truncation. The first is based on the Ewald summation, but it can only be easily used for bulk systems. To investigate interface properties for general geometries there is only one way to solve this problem - to use as many water molecules as possible. Our calculations suggest that $N = 512$ water molecules can represent the equilibrium properties of bulk water (internal energy, heat capacity, etc.) adequately. The elementary cell for the graphite walls must be chosen so as to be consistent with the periodic boundary conditions. Our choice of elementary cell is shown in Figure 4. The carbon surface assembled from such cells has periodicity in the *Y* and *X* directions.

Due to the relatively long-lived hydrogen bonds in water, long runs, typically $10 - 50 \times 10^6$ configurations, are needed in GCMC simulations to obtain satisfactory estimates of the thermodynamic properties. Since the intermolecular potentials

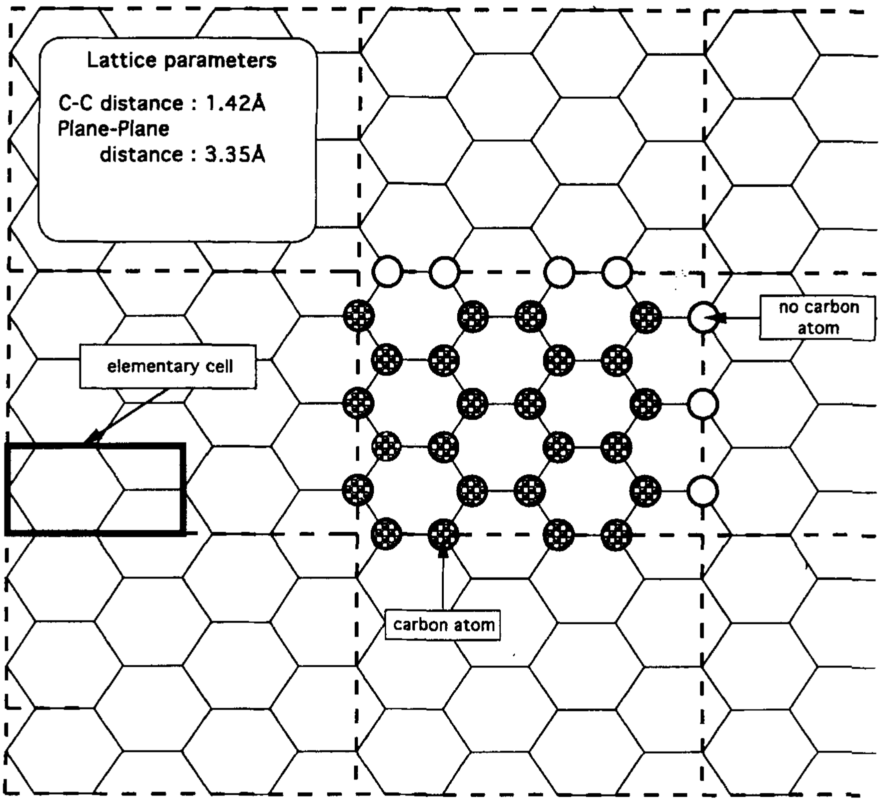


Figure 4 Graphite structure arrangement with periodic boundary conditions.

are strongly orientation-dependant, such runs are very time consuming on serial computers.

3 CM-2 AND MONTE CARLO CODE DEVELOPMENT

The CM-2 is a SIMD (single instruction multi data) supercomputer. Parallel computing associates one processor with each data element. The CM-2 consists of a front-end computer, which performs the sequential part of the executing code, and the parallel processing unit. A CM-2 parallel processing unit may contain from 8K to 64K one-bit data processors. Each data processor has its own memory and arithmetic-logic unit (ALU) that can operate on variable-length operands. Each processor has the same amount of memory, from 8 Kbytes to 32 Kbytes. Thus, the total amount of memory can reach 2 gigabytes. It's important to note that the data for the parallel units and the data for the front-end computer are stored separately, and the exchange of data between these two parts of the CM-2 is still very expensive.

The CM-2 can operate in Paris and slicewise modes. In the Paris mode the set of nodes is used for single bit operations. In the slicewise mode the CM may be represented as a set of 32 bit nodes with common memory. Thus, in this case the 8K parallel unit may be represented as a set of 256 processors. To provide very fast calculations with floating point data the CM is equipped with a floating point accelerator. This hardware can increase the computational rate of floating-point calculations by more than a factor of 20.

The communication between nodes in the parallel unit can still occupy a lot of time. To improve this situation the CM-2 is equipped with software and hardware (NEWS (North-East-West-South) Grid) which allows data to be sent from one node to another very quickly even if they are not nearest neighbors.

To develop the Monte Carlo code we used CM FORTRAN. The main advantage of CM FORTRAN is that it allows us to treat the array, or part of the array, as a single entity. A specific feature of this language is the FORALL statement, which facilitates working with parts of the arrays; a large number of fast intrinsic functions operate with the array objects (see Figure 6).

The software of the CM-2 can work with arrays larger than the physical number of nodes. In this case several values of the same array are located in the memory of the same node. The ratio of number of virtual processors to the number of physical ones is called the Virtual Processor Ratio (VP). If $VP > 1$ the CM-2 operates slowly, because it has to do the same operation VP times.

The CM-2 can operate very slowly if there are arrays with different shapes in the program. This occurs due to the very expensive internode communications reorganization needed to arrange operations on the arrays with different shapes.

There have been several successful attempts to develop Molecular Dynamics (MD) code on the Connection Machine [9, 10, 11, 12]. A common feature of the MD and MC methods is that the greatest part of the computational time (up to 98%) is due to the intermolecular potential computations in each step. Thus, the major goal in these applications has been to make these computations as fast as possible. In the programs described in [10, 11] the one dimensional data layout was used. This means that all molecular coordinates occupied independent processors. During the force calculations all coordinates are copied into the dummy array with the same layout as the original one. Then, using the intrinsic function CSHIFT, the dummy array was circularly shifted along the original one N times (N is the number of molecules in the system). During each iteration N forces were calculated in parallel. In this algorithm the computational time was proportional to N instead of $N(N-1)/2$ as in sequential codes.

A more sophisticated 'Square Algorithm' (SA) was developed in [10]. This method used the two dimensional molecular coordinates arrangement, in which the molecular positions were represented as a square symmetrical matrix R. The force calculation takes place in one step, as subtraction of R from the transpose matrix R^T. The SA appears to be only twice as fast as the linear one. This is due to the comparatively slow communications which predominate in the beginning steps of the SA.

The code in [12] was developed using C^*; in [10, 11] an earlier version of CM FORTRAN was used.

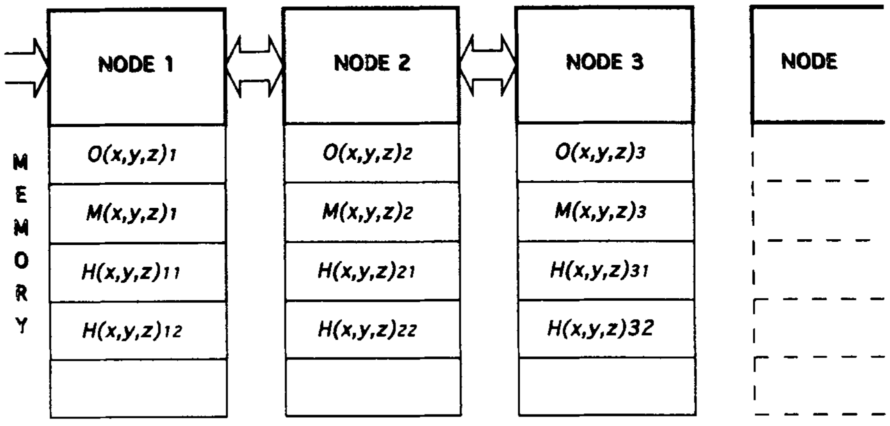
In view of the above factors we organized our programs to

a. reduce the internode communications;
b. reduce the VP ratio;
c. avoid I/O operations, which are slow;
d. use arrays of the same shape (or the same number of NEWS dimensions).

The most expensive part of the Monte Carlo simulation is the calculation of interaction energy between the given molecule and all others. For two TIP4P water molecules the total number of center-center interactions is 10 (nine electrostatic and one Lennard-Jones). Thus, to calculate the interaction of one molecule with N others, one has to evaluate $10N$ different distances. Calculation under the periodic boundary conditions makes this operation twice as long.

There are three basic ways to parallelise computation in molecular simulation on multinode machines [13]: one can map the molecules, interactions (as in SA), or space on the nodes. We choose the first method as the most convenient to the CM-2 architecture (Figure 5). After several attempts we accepted the one dimensional layout of the arrays with water center coordinates, to make all operations more economical. According to this idea, all centers of a given molecule are located in the memory of the corresponding node. In such a data layout, for example, the calculation of the distances (energy) between the oxygen center of molecule i with all other oxygen centers can be carried out in two steps: the first step is to spread the coordinates of O_i through all nodes at once, and the second is to calculate the distances (energy) on each particular node at the same time. The calculation of the total interaction energy can be carried out with the very fast intrinsic SUM function.

The second advantage of the one dimensional data layout appears when the correlation and distribution functions are calculated. In Figure 6 we represent the block scheme to calculate the distribution of water molecules between the graphite walls. The information about each molecule is updated in the histogram independently, and thus the time of this operation does not depend upon the number of molecules. In sequential computers the length of this operation is directly proportional to the number of molecules, N. The same method can be applied to the calculation of pair correlation functions; in this case the computation time will be reduced by $\frac{(N-1)}{2}$ times for the parallel code. This is because these calculations



CM FORTRAN code for distance calculation
with periodic boundary conditions:

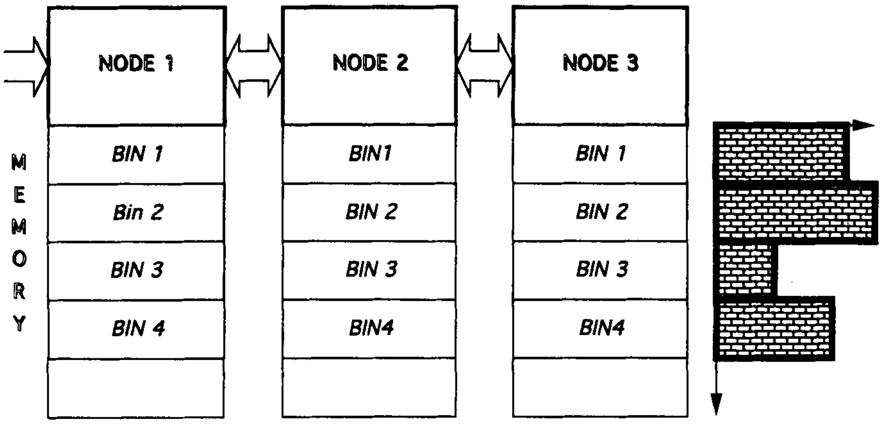
```
DO i=1, 3
  Dist(i,:)  = Os(i,:)-Os(i,mn)
  Shift(i,:) = Cell(i)*ANINT(Dist(i,:)/Cell(i))
  Dist(i,:)  = Dist(i,:)-Shift(i,:)
END DO

TDist(:) = SQRT(Dist(1,:)**2+Dist(2,:)**2+Dist(3,:)**2)
```

Figure 5 Data layout for the Monte Carlo algorithm on the Connection Machine.

are carried out only on the parallel unit of the CM, without any participation of the sequential front-end computer.

In Figure 7 we show the time for 10^6 CMC steps as a function of the number of water molecules in the water-pore system. The upper two curves represent the total calculation time and the busy time of the parallel unit, respectively. In our code we avoid sequential operations with the arrays. Thus, the busy time of the front-end computer (FE) is unchanged as the number of water molecules increases. When the number of molecules increases by 256 (256 is the number of processing units on one sequencer in slicewise mode), the virtual processor ratio is incremented by one, giving the step-like shape to the CM-time curve. The step-like shape is somewhat smoothed by optimization.

We have also developed the parallel code for two modifications of the GCMC method. The first one [2, 3] is based on the random insertion/deletion mechanism; the molecule insertion take place at a random point in space. This method doesn't take into account fluid structure, so that few insertion attempts are successful at high densities. The second method [4, 5] is based on preferential insertion in the cavities in the fluid structure. The main advantage of this algorithm is the increased



CM FORTRAN code for distribution calculation

```
FORALL(i=1:Number_of_Molecules)
  TD(IFIX(Os(3,i)/Dstep)+1,i) = TD(IFIX(Os(3,i)/Dstep)+1,i) + 1
.........................................
.........................................
DO j=1, Number_of_Distribution_Bins
  Distribution(j) = SUM(TD(j,:))
END DO
```

Figure 6 Water Molecule Distribution Calculation on the Connection Machine.

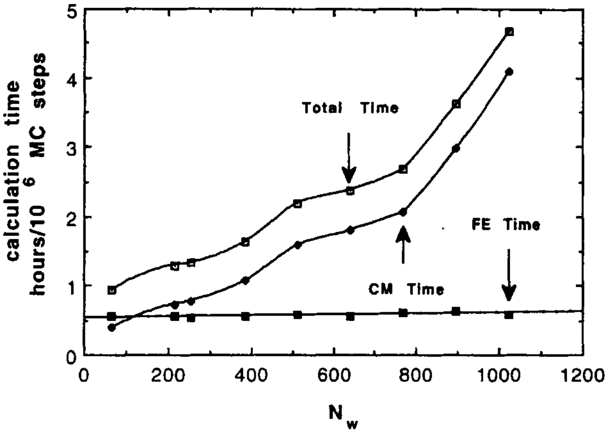


Figure 7 The Performance of the CM-2 for GCMC Simulation of Water Molecules between graphite walls.

Table 1 Time for 10^6 Monte Carlo steps for 512 TIP4P water molecules in bulk phase at 298K and density 1 g/cm^3 on different platforms.

Computer	*VAX 5000-400*	*CRAY Y/MP*	*RS/6000 M550 Cluster*	*CM-2*
Time (hours)	80–100	3–5	6–8[a]	0.9–1.7

[a] A cluster of 7 IBM RS/6000 workstations was used. This parallel algorithm ran 6 to 6.5 times faster on the cluster than the serial code on a single RS/6000 workstation.

number of accepted insertion/deletion steps. In this algorithm the simulation cell is mapped onto a three dimensional grid. The insertion attempt occurs only in grid centers which are not occupied by any other molecule. For each GCMC step one has to calculate the number of centers which satisfy the condition mentioned above. Due to the proposed data layout this operation takes very little time even when the number of grid centers is as high as 18,000–20,000.

The GCMC code implementation on the CM has approximately the same computation time as the CMC. The computational time for 1 million configurations for a system of 500 water molecules and 2016 carbon atoms is approximately 1.2 hours for 8K nodes equipped with floating point accelerator, and 2.0 hours for the 8K sequencer without floating point accelerator. The front-end computational time doesn't depend upon the number of molecules in the system, but only upon the size of the system (the size of the largest array in the code).

In Tables 1 and 2 we summarize the performance of different computers on Monte Carlo simulation codes for bulk and confined water systems. The code for the VAX 5000-400 was a sequential one, while those for the other three computers involved varying degrees of parallelization. The codes for the Cray Y/MP and RS/6000 were fully optimized (and vectorized in the case of the Cray Y/MP).

The principles mentioned above can also be used to improve the performance of the Square Algorithm. According to the description given in [10], at the beginning of each MD step, one has to 'spread' the one-dimensional array through two two-dimensional ones (say R and RT). This solution leads to a decrease in code performance, as the operation on the arrays involve *different shapes* and very complicated *internode communication*. The performance can be improved if one keeps and updates both two-dimensional arrays during the simulation, instead of creating them at each step. The integration of equations of motion takes place for both R and RT arrays independently. This method is preferable due to very long transposition times; even for two identical arrays, the operation $RT := TRANSPOSE(R)$, where 'TRANSPOSE' is the intrinsic CM FORTRAN function, takes approximately

Table 2 Time for 10^6 Monte Carlo steps for 512 TIP4P water molecules and 2016 carbon atoms at 298K and density 0.9 g/cm^3 on different platforms.

Computer	*VAX 5000-400*	*CRAY Y/MP*	*RS/6000 M550*	*CM-2*
Time (hours)	100–130	5–6	8–9[a]	1.–2.0

[a] A cluster of 7 IBM RS/6000 workstations was used.

2 seconds on the CM-2 for arrays of size (500 × 500). The improvements suggested above increase the performance of SA by a factor of five.

The second advantage of the improvements suggested above for the SA algorithm appear during the calculation of the pair correlation function. In this case the time of distribution updating does not depend on the number of molecules $\left(\text{for serial computers this time is proportional to } \frac{N(N-1)}{2}\right)$. The SA algorithm realization suggested here leads to a high memory requirement. However, the critical characteristic of the CM-2 is not the memory (which can reach 2GB) but the working frequency (7-8 MHz).

4 WATER BEHAVIOR IN SLIT GRAPHITE PORES

Here we present some results for water behavior in slit graphite pores of width $H = 20\,\text{Å}$ at 298K. Usually the length of calculation was from 10*10^6 to 50*10^6 GCMC steps. The first 3*10^6 to 10*10^6 were discarded.

In Figure 8 we show the total amount of adsorbed water as a function of the (increasing) configurational chemical potential. For low values of chemical potential the adsorption of water is ***negligibly*** small. The average number of molecules in this part of the phase diagram is less than one. The density of water molecules in the pore is only slightly higher than the number of molecules in the coexisting bulk phase.

The water in the pore exhibits a capillary condensation transition (gas-like to liquid-like state) at $\mu_c \approx -21.4\,\text{kJ/mol}$, well below the chemical potential of $\mu_c \approx -17.7\,\text{kJ/mol}$ for the gas-liquid transition for bulk water at 298K. The transition is that determined when μ_c is progressively increased, i.e. the adsorption (as

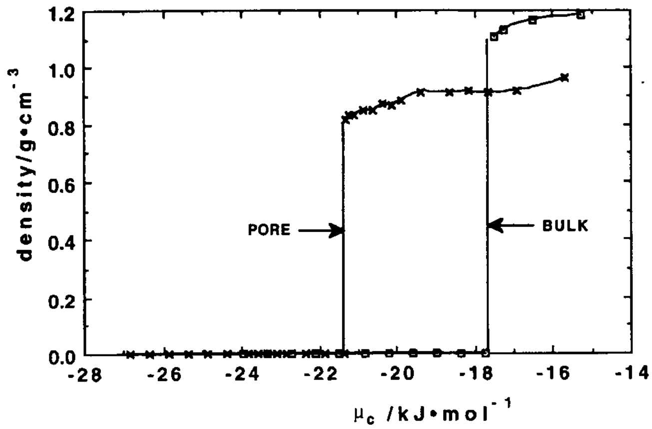


Figure 8 Water density (adsorption, i.e. curve for increasing μ_c) in the pore and bulk phases; $H = 20\,\text{Å}$, $T = 298\text{K}$.

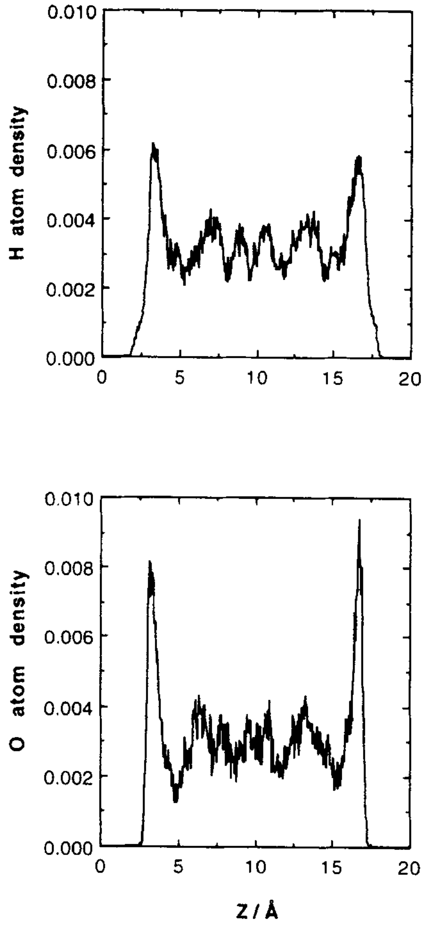


Figure 9 Distribution of *O* and *H* atoms in the pore.

opposed to desorption) curve. Since thermodynamic hysteresis is generally associated with these transitions, the transition shown is not expected to be the true thermodynamic one, but rather that shown by a metastable state. After the phase transition, the system consists of a water film confined between two structured carbon walls.

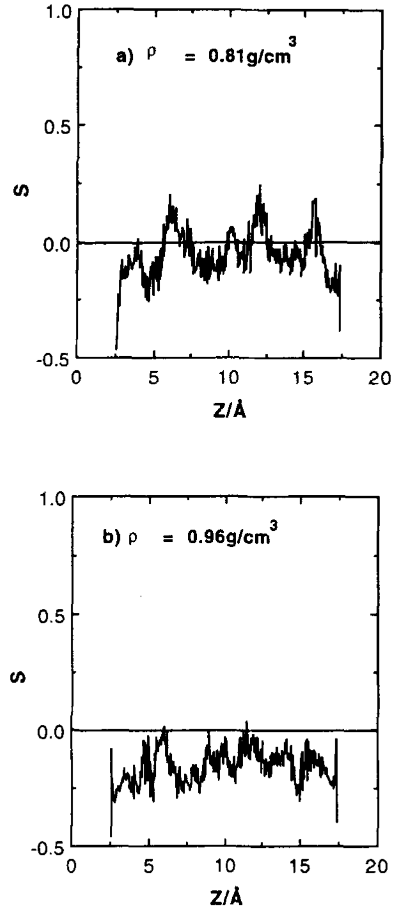
In Figure 9 we depict typical distributions of the water *H* and *O* atoms through the restricted direction. According to Figure 9 one can separate the adsorbed film in the pore into two parts. The first is the adsorbed layer of water molecules, with a width of 5 Å. The center part of the adsorbed phase can be treated as a disturbed bulk water phase.

The orientational properties of the restricted water film can be measured directly by using the order parameter [14, 15]:

$$S = \frac{3\langle\cos^2\theta\rangle - 1}{2} \tag{3}$$

where $\langle\cos^2\theta\rangle$ is the average value of $\cos^2\theta$, where θ is the angle between the molecular dipole moment and the Z axis perpendicular to the carbon wall. If all the molecules are orientaled with their dipoles parallel to the wall ($\theta = \pi/2$) then $S = -0.5$; if the molecular dipoles are all perpendicular to the wall ($\theta = 0$ or π) then $S = 1$; and for a disordered structure $S = 0$.

In Figure 10a we show a typical result for S as a function of the distance from the carbon walls. The water molecules are seen to prefer an orientation with their dipoles parallel to the wall in the adsorbed layer, and to be oriented nearly randomly in the central part of the pore. When the chemical potential is increased the molecules in the bulk part of the film also tend to adopt an orientation parallel to the pore surfaces (Figure 10b).



S	ORIENTATION
0	random
-0.5	parallel
1.0	perpendicula

Figure 10 Orientational order parameter $S = (3\langle\cos^2\theta\rangle - 1)/2$.

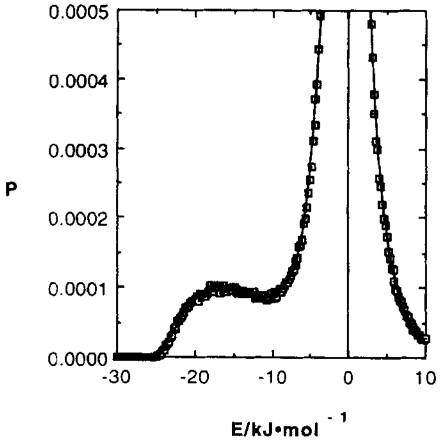


Figure 11 Water-water interaction energy distribution.

One of the main features of water is the network of hydrogen bonds, creating a polymer-like three dimensional structure in water and water solutions [16, 17]. In Figure 11 we depict the probability distribution, P, of the water-water pair energies for the molecules in the pore. The maximum of this distribution at approximately $-18\,\text{kJ/mol}$ corresponds to the hydrogen bonds in the system. This H-bond peak is somewhat less pronounced than for bulk water since some H-bonds must be broken when water enters the pore.

5 CONCLUSIONS

The CM-2 offers considerable advantages for Monte Carlo calculations, because MC does not require a lot of expensive internode communications. The speedup increases with the number of molecules in the system. For the system considered here (N TIP4P water molecules with two walls each containing 1008 carbon atoms) the parallel program on the CM-2 runs 2.5–3.5 times faster than a fully optimized and vectorized program on the Cray Y/MP for $N = 512$, and about 5 times faster for $N = 1024$. We have also used the parallel code to study vapor-liquid equilibria near the critical region (using Gibbs Ensemble MC) for large Lennard-Jones systems of up to 30,000 molecules, and find that the code runs at acceptable speeds [18]. The CM-2 appears to be less well suited to Molecular Dynamics calculations, because of the difficulty of avoiding substantial internode communications.

The parallel code has been used to study the behavior of TIP4P water in a graphitic slit pore of width $H = 20\,\text{Å}$ at $T = 298\text{K}$. The adsorption isotherms are of type V [19], showing little adsorption at low bulk gas pressure (because entry into the pore involves a net loss of H-bonding) and capillary condensation at somewhat higher pressures (chemical potentials); the capillary condensation pressure is well below the condensation pressure of the bulk liquid water. The water molecules near the walls tend to be oriented with their dipoles parallel to the surface, and this preference is still weakly felt by water molecules in the interior of the pore when the density of water is high. The hydrophobic graphite surface leads to the creation of two zones in the water film. The first adsorbed layer near the wall, about $2\sigma_w$ wide, is highly inhomogeneous and the water molecules are strongly oriented with their planes parallel to the wall, whereas the central zone has properties more similar to bulk liquid water.

Acknowledgments

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