

Long-range Interactions in Monte Carlo Simulation of Confined Water

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Abstract

We investigate methods for the treatment of long-range interactions in the context of grand canonical Monte Carlo (GCMC) simulations of water adsorption in slit-shaped activated carbon pores. Several approaches, ranging from the simple minimum image convention to the more complex two-dimensional Ewald summations, are implemented and compared with respect to accuracy and speed of computation. The performance of some of these methods in GCMC is found to be significantly different from that in molecular dynamics applications. Of all the methods studied, one proposed by Heyes and van Swol was the most promising, providing the best balance between accuracy and speed. In our application, it was shown to be about 2 times faster than the fastest of the two-dimensional Ewald methods. We expect this conclusion to apply in general to systems that are periodic in two dimensions and finite in the third.

1 Introduction

Our interest in the calculation of long-range interactions in confined phases arises from the grand canonical Monte Carlo simulation of water adsorption in carbon pores containing polar surface sites. The simulation of polar molecules such as water requires the calculation of the electrostatic potential between two point charges, as given by Coulomb's law. The total potential in a system comprised of a set of point charges involves two nested sums over all charges:

$$U^{Total} = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{q_i q_j}{4\pi\epsilon_0 |\mathbf{r}_{ij}|} \quad (1)$$

where the factor $\frac{1}{2}$ is applied because each interaction is counted twice.

In the above equation, q_i is the charge on site i , \mathbf{r}_{ij} is the distance vector between sites i and j and ϵ_0 is the vacuum permittivity ($8.85419 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$). This potential is long-ranged, that is to say, it does not vanish at a relatively short distance, as is the case with dispersion interactions. In simulations of bulk systems, the simulation cell is usually replicated periodically in all three space dimensions, in order to reproduce an infinite medium. In this type of system, the sum over all pairs of charges, as calculated from equation (1), is conditionally convergent. Therefore, more elaborate procedures, such as the Ewald summation technique are required. In three-dimensional periodic systems, this technique is well established [1,2]. In the Ewald method, each point charge is surrounded by a charge distribution of equal magnitude and opposite sign, which is conveniently chosen to be Gaussian. The width of the distribution is controlled by an arbitrary parameter, κ , which can be optimised for speed of convergence. In principle, the final result of the sum is independent of κ . The potential due to this new set of screened charges is short-ranged and can be summed efficiently. However, this screening effect has to be cancelled, which is done by adding a compensating charge distribution. This compensating distribution is a smoothly varying periodic function, which can be represented by a rapidly converging Fourier series. After it is summed in reciprocal (Fourier) space, the total is transformed back into real space. Since this scheme includes the interaction of the charge i with itself, this self-term must be subtracted from the total. The final result is

$$\begin{aligned}
U^{Total} = & \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{4\pi\epsilon_0} \left[\sum_{|\mathbf{n}|=0}^{\infty} \left(\frac{\text{erfc}\left(\frac{|\mathbf{r}_{ij} + \mathbf{n}|}{\kappa}\right)}{|\mathbf{r}_{ij} + \mathbf{n}|} + \frac{4\pi}{V} \sum_{\mathbf{k} \neq 0} \frac{\cos(\mathbf{k} \cdot \mathbf{r}_{ij})}{k^2} \exp\left(-\frac{k^2 \kappa^2}{4}\right) \right) \right] \\
& + \frac{1}{\kappa \sqrt{\pi}} \sum_{i=1}^N q_i^2
\end{aligned} \tag{2}$$

In equation (2), V is the volume of the simulation cell, given by $V = L_x \times L_y \times L_z$, \mathbf{n} are the real space lattice vectors, given by $\mathbf{n} = (n_x L_x, n_y L_y, n_z L_z)$ with n_x , n_y , and n_z integers, and \mathbf{k} are the reciprocal space vectors, given by $\mathbf{k} = (2\pi n_x / L_x, 2\pi n_y / L_y, 2\pi n_z / L_z)$. The prime over the summation indicates that we omit $i = j$ for $\mathbf{n} = 0$.

The Ewald summation method is fast and, in principle, exact, so it has been widely used to calculate the potential energy in systems which are periodic in all three dimensions. However, we are interested in simulating adsorption in slit-shaped pores (infinite in two dimensions and finite in the third). Therefore, the simulation cell must be replicated in only two dimensions. In contrast to 3D systems, in systems with slab geometry the sum of the Coulomb interactions is absolutely convergent. Nevertheless, the summation converges very slowly and special methods must be employed to make the potential calculations practical. An additional complication arises from the anisotropy of the system, which invalidates the straightforward use of the 3D Ewald sum. Several methods have been proposed over the years for dealing with this problem [3-16] and various comparative studies have also been presented [17-22]. In these studies, the various methods have been compared on the basis of their performance in the calculation of the total potential and/or the forces between the molecules, mostly with application to molecular dynamics (MD) simulations. The conclusions drawn from the comparisons of the methods with respect to accuracy will be equally valid for Monte Carlo simulations. However, the comparison with respect

to speed of computation is different in Monte Carlo simulations, where the total potential in the cell need not be calculated, and a method that is very suitable for MD applications might not have the same advantages in MC. In this paper, we present a comparison between a series of methods for the treatment of long-range interactions in the context of grand canonical Monte Carlo (GCMC) simulation of water adsorption in a slit-shaped carbon pore. To our knowledge, this is the first investigation of its type with GCMC applications in mind.

2 Simulation and Potential Models

2.1 Molecular models

Water is represented by the TIP4P potential [23]. This model is composed of a Lennard-Jones site at a location corresponding to the oxygen atom in the water molecule, two positive point charges located at the positions of the hydrogen atoms and a negative point charge placed a short distance away from the oxygen atom (“site M”). The potential between two molecules is given by:

$$U_{ij} = 4\varepsilon_{ff} \left[\left(\frac{\sigma_{ff}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ff}}{r_{ij}} \right)^6 \right] + \sum_{a_i} \sum_{b_j} \frac{q_a q_b}{4\pi\varepsilon_0 r_{ab}} \quad (3)$$

The first term on the right hand side of equation (3) represents the short-range interaction between the Lennard-Jones (L-J) sites of molecules i and j , while the second term describes the Coulombic interaction between all point charges in both molecules (sum over charges a in molecule i and charges b in molecule j). σ_{ff} is the fluid-fluid L-J site diameter and ε_{ff} is the L-J well depth. Geometric and potential parameters were taken from reference [23].

In this work, water is confined in a parallel, slit-shaped pore. Each pore wall is described by an infinite number of graphitic layers composed of Lennard-Jones sites. Furthermore, it is assumed that the walls are structureless, that is to say that the carbon atoms are smeared out uniformly over the graphitic layer. The potential between an adsorbate molecule and this smooth carbon surface is thus given by the 10-4-3 potential of Steele [24]:

$$U_{is} = 2\pi\epsilon_{sf}\rho_s\sigma_{sf}^2\Delta\left(\frac{2}{5}\left(\frac{\sigma_{sf}}{z_i}\right)^{10} - \left(\frac{\sigma_{sf}}{z_i}\right)^4 - \frac{\sigma_{sf}^4}{3\Delta(z_i + 0.61\Delta)^3}\right) \quad (4)$$

where ρ_s is the number of carbon atoms per unit volume in the graphitic layer (114 nm^{-3}), Δ is the separation distance between layers of graphitic carbon (0.335 nm) and z_i is the distance between the adsorbate site and the surface. Solid-fluid Lennard-Jones parameters were calculated using the Lorentz-Berthelot combining rules. The simulation cell is rectangular, bounded in the z direction by the pore walls and replicated in the x and y directions. The length of the simulation cell in both directions parallel to the wall was chosen to be 30 Å and periodic boundary conditions are used in these directions.

We have studied configurations in which polar carbonyl groups are grafted to the graphite wall. A carbonyl site is constituted by one L-J site for the oxygen atom and two point charges (one on the oxygen and one on the carbon atom in the basal plane). Parameters for this type of group were taken from the OPLS potential model [25]. In table 1, we show the potential parameters for water, graphite and carbonyl groups. [Insert table 1 about here]

2.2 Grand Canonical Monte Carlo

We have performed simulations in the Grand Canonical Ensemble, in which the temperature (T), volume (V) and chemical potential (μ) are kept constant. The statistical mechanical basis and the algorithm for GCMC simulations are well documented [1,2], and we have used the standard methodology.

In GCMC, there are three types of random trials: movements, creations and destructions. The outcome of each trial depends on the difference in potential energy between the old and new states [2]. In the case of long-range interactions, such as the potential between two point charges, one has to sum over a series of periodic boxes (counting only interactions that involve at least one molecule of the centre box – where we want to calculate the potential). The efficient implementation of this calculation is most easily explained with the help of a simplified diagram (figure 1). As an example, we take a creation trial in the centre box. Before the creation (figure 1a), the total potential in the centre box is given by the sum of the interactions between the particle already there and its periodic images (we assume, for simplicity of illustration, that only interactions with the two nearest images are significant). Along with the particle in the centre box, an infinite number of periodic images is also created in the trial (represented by only two images in the diagram). The total potential after the creation is, thus, the result of all the interactions depicted in figure 1b. [Insert figure 1 about here]

As we are only interested in the energy difference, the interactions before the creation are subtracted (figure 1c). To make the program simpler, it is convenient that all interactions be centred on the recently created molecule. Therefore, we use the fact that the potential calculations depend only on the separation of the sites to obtain an

equivalent scheme, with all interactions centred on the created molecule (figure 1d). The above discussion is also valid for destruction and move trials.

In order to sample configurations that are characteristic of equilibrium, the system must be allowed to equilibrate. This is done by starting from a random configuration and discarding a large number of initial steps. The number of equilibration steps varied according to the operating conditions, but was never less than 2×10^6 and as large as 10^7 for the highest densities. The sampling period was divided into 20 blocks of at least 10^5 steps, so as to obtain a set of independent samples. From these values, an overall average density and a standard deviation were calculated. Each type of MC trial was chosen randomly with the same probability. In the case of water (a multi-site molecule) the move trial entailed a random rotation as well as a translation of the molecule. Calculations were performed on Sun Ultra 10 workstations.

3 Long range interactions.

The approaches studied here are:

- Minimum Image Convention (MI)
- 2D Ewald method of Heyes, Barber and Clarke. [8] (HBC)
- 2D Ewald method of Rhee, Halley, Hautman and Rahman [10] (RHHR)
- 2D Ewald method of Hautman and Klein [11] (HK)
- Method of Nijboer and de Wette [12] (NdW)
- 3D Ewald Summation for slabs [14] (3DEW)
- Method of Heyes and van Swol [15] (HvS)
- Method of Lekner [16] (LK)

As all methods examined are well documented, we will not describe them in detail, but rather give a simplified description of each procedure, while assessing each method's advantages and disadvantages.

The simplest choice for the simulation of confined water is to simply ignore the long-range character of the potential by making the simulation cell sufficiently large. The minimum image convention with a cutoff radius can then be employed. This was the method used in the earlier simulations of water in carbon pores [3,4], when the lower computer power available made any more complex treatments impractical. It has been shown by several authors [14,17,21] that the results obtained using this procedure are significantly less accurate than those obtained with 2D versions of the Ewald sum. Furthermore, the calculations seem to depend on the type of cutoff scheme employed [14]. (An alternative, and quite distinct approach to the simulation of water was taken by Müller and coworkers [5-7] who modelled hydrogen bonding by a square-well potential.)

The first derivation of the Ewald sums for 2D periodic systems that we have considered is that due to Heyes et al. [8], also derived independently by de Leeuw and Perram [9]. They used an approach analogous to the original (3-D) Ewald method, but the in-plane (\mathbf{s}_{ij}) and out-of-plane (z_{ij}) distances are separated in the Fourier part. The potential energy between a molecule i and all other molecules j is given by

$$\begin{aligned}
 U_i^{HBC} = \frac{1}{2} \sum_{j=1}^N \frac{q_i q_j}{4\pi\epsilon_0} \left[\sum_{|\mathbf{m}|=0}^{\infty} \frac{\operatorname{erfc}\left(\frac{|\mathbf{r}_{ij} + \mathbf{m}|}{\kappa}\right)}{|\mathbf{r}_{ij} + \mathbf{m}|} + \frac{\pi}{A} \sum_{\mathbf{h} \neq 0} \frac{\cos(\mathbf{h} \cdot \mathbf{s}_{ij})}{h} \right] \exp(hz_{ij}) \operatorname{erfc}\left(\frac{h\kappa}{2} + \frac{z_{ij}}{\kappa}\right) \\
 + \exp(-hz_{ij}) \operatorname{erfc}\left(\frac{h\kappa}{2} - \frac{z_{ij}}{\kappa}\right) \left[-\frac{\pi}{A} \left[z_{ij} \operatorname{erf}\left(\frac{z_{ij}}{\kappa}\right) + \frac{\kappa}{\sqrt{\pi}} \exp\left(-\frac{z_{ij}^2}{\kappa^2}\right) \right] \right] - \frac{q_i^2}{\kappa\sqrt{\pi}} \quad (5)
 \end{aligned}$$

where \mathbf{m} and \mathbf{h} are the two-dimensional real and reciprocal lattice vectors and A is the area of the simulation cell in the periodic dimensions, given by $A = L_x \times L_y$. We have neglected the sum over different sites in the same molecule for simplicity of notation.

A similar treatment, but with a different screening function, is the basis of the method due to Rhee *et al.* [10], who also included a multipole expansion in the z direction (for details, see [10]). Another Ewald method is due to Hautman and Klein [11], who used a Taylor series expansion of the inverse inter-particle distance $1/r_{ij}$ in powers of z_{ij}/s_{ij} . This function is used in both the real- and the Fourier-space summations. Full equations are given in references [11] and [19]. Nijboer and deWette [12] devised a formulation that computes the whole potential in Fourier space. Although simple, this method cannot in practice be used on its own, since it diverges as $z_{ij} \rightarrow 0$. Smith [13] proposed the use of a hybrid HBC-NdW method, which makes use of the HBC formulation at small out-of-plane separations and uses the NdW expressions at large z_{ij} .

An entirely different approach is to use the standard 3D Ewald Summations but including a sufficiently large empty space between successive boxes in the z direction, in order to avoid an artificial influence of the periodic images in this direction. This method has been used by Shelley and Patey [14] to simulate water confined between planar walls. However, it was shown by Spohr [17] that the results from the 3D Ewald method converged to the values obtained from the 2D methods only when the length of the simulation box in the z direction was very large (more than 5 times larger than the length in the x and y directions). The addition of a correction term to the 3D Ewald method was proposed by Yeh and Berkowitz [18]. This term is appropriate for a slab geometry and is given by

$$U^{Corr} = \frac{2\pi}{V} \left(\sum_{i=1}^N q_i z_i \right)^2 \quad (6)$$

where z_i is the cartesian coordinate of molecule i . It is easy to see that the contribution from this term to the potential on a single molecule i is given by

$$U_i^{Corr} = \frac{2\pi}{V} q_i z_i \sum_{j=1}^N q_j z_j \quad (7)$$

Thus, to calculate the potential energy between a molecule i and all other molecules j in the corrected 3DEW, one must simply use equation (2) (without the sum over i) and add the correction term in equation (7). By performing these calculations for several test cases, Yeh and Berkowitz concluded that the corrected method would converge to the desired results for an empty space equal to the length of the simulation box in the x and y directions.

We have also looked into two other non-Ewald methods, the first of which was proposed by Heyes and van Swol [15]. This method calculates the sum of the simple Coulomb expression over a small number of periodic boxes (up to a truncation radius R_c) and then includes a correction term for the rest of the boxes up to infinity. The expression for this correction term is obtained by expanding the potential from each image charge about $\mathbf{r}_{ij} = 0$ and then replacing the periodic discrete charges with a uniform charge density distribution (this is equivalent to replacing the double sum over the two periodic dimensions with a two-dimensional integral in that plane). The full expressions for the potential in HvS with a unit box length in the x and y dimensions (once again neglecting the sum over different sites in the same molecule for simplicity of notation) are:

$$U_i^{HVS} = \frac{1}{2} \sum_{j=1}^N \frac{q_i q_j}{4\pi\epsilon_0} \left[\sum_{n_x=0}^{n_c} \sum_{n_y=0}^{n_c} \frac{1}{|\mathbf{r}_{ij} + n_x + n_y|} + \frac{\pi}{n_c} (x_{ij}^2 + y_{ij}^2 - 2z_{ij}^2) \right] \quad (8)$$

In the above equation, n_x and n_y are the components of the unit lattice vector in the x and y directions, n_C is the number of cells in each direction over which the lattice sums are performed, and x_{ij} , y_{ij} and z_{ij} are the cartesian components of \mathbf{r}_{ij} . The last term in Equation 8 accounts for the contributions from molecules in replicas further than n_C cells from the simulation cell.

The last method considered is originally due to Lekner [16] and was published in a corrected form by Grønbech-Jensen *et al.* [26]. It is based on a representation of the forces acting on the particles in terms of a sum of trigonometric and Bessel functions. Expressions for the potential are then obtained from integration of the forces (see [16] and [26] for full equations).

4 Results and Discussion

We will start by comparing the performance of the simplified MI convention with the full 2D Ewald summation (we have chosen HBC for this comparison, since it is considered the most accurate of the Ewald methods [19]). The MI methodology has been recently revived for the simulation of water/methanol mixtures by Shevade *et al.* [27,28]. As a justification for the use of this algorithm, they have suggested that the difference in potential between the MI convention and a full 2D Ewald summation was below 1%. We have found this to be true only for very close packed systems with a large number of molecules (in which case the potential in the vicinity of a water molecule is dominated by the interactions with its nearest neighbours). For low densities, the difference in potential increased in some cases above 50%, which is clearly non-negligible. We have compared adsorption isotherms obtained with both the MI convention and HBC, and have observed the results to be significantly different. One of those comparisons, for a pore width of 9.5Å and a surface site density of 2.67 sites/nm², is shown in figure 2. The discrepancies are clear, especially

in the pressure at which pore filling occurs (lower with MI) and in the density of water after pore filling (higher with MI). This leads us to conclude that the MI convention should not be used in simulations of confined water. [Insert figure 2 about here]

Moving on to the more accurate, but more computationally demanding Ewald methods, we have started by looking at the version of the 3DEW for slab geometry. figure 3 shows the potential on a water molecule as a function of the ratio L_z/L_x for the two different methods (3DEW with and without the correction term). It is clear that the result converges to the value obtained using the full HBC summation in both cases, but the correction term significantly improves this convergence, particularly at low values of L_z . We can see that the 3DEW method plus the correction term is able to calculate an essentially accurate value for the potential (error below 1% relative to the full HBC result) if we use $L_z=2$. The reason for the success of this method lies in the fact that the correction term effectively compensates for the contributions of the replicas of the simulation cell in the z direction, which are unphysical in two-dimensional periodic systems [18]. [Insert figure 3 about here]

We now compare the performance of the Ewald methods described in the previous section (HK, HBC, RHHR and 3DEW plus correction term). In terms of accuracy, we have observed that HBC produces the most accurate results, which agrees with a previous comparison between HK, HBC and NdW by Widmann and Adolf [19]. The results for computer time as a function of the screening parameter, κ , for those four methods are shown in figure 4. The number of real- and reciprocal-space vectors used in the summations were fine-tuned in order to obtain a maximum error of 1% in the potential, relative to the full HBC result. We can see that at the optimum value of κ , all the methods have comparable speeds, with HBC being the

fastest. In contrast, Widmann and Adolf [19] found HBC to be the slowest method. This reflects the fact that the total potential was calculated in their MD simulations, requiring two nested sums over all molecules in the box. In the standard 3DEW (and, indeed, in the HK, NdW and RHHR methods), it is possible to replace these two summations by only one, using complex algebra [1]. This apparent disadvantage of the HBC method disappears in our MC simulations. Since it is only necessary to calculate the difference in potential energy when one molecule is affected, there is no need to compute the double sum over all molecules. Hence, the HBC method becomes much more competitive. [Insert figure 4 about here]

Direct comparisons between all methods were made for a series of test cases (changing the number of molecules, pore width, and box length). Results for one of these test cases are shown in table 2. All parameters for each method were optimised to give the fastest computing time for an error in potential smaller than 1% (relative to the full HBC result). All test cases have shown the same trend. By looking at the table we can confirm that HBC is indeed the fastest of the Ewald methods. Both RHHR and HK suffer from accuracy problems, particularly at large z , and in the case of HK an approximate expansion must be used as $s \rightarrow 0$ [19]. As for the 3D version, the efficiency of the method is hindered by the fact that the summations have to be performed over three dimensions instead of two. However, it is reasonable to expect that this method will become more competitive in MD simulations, due to its simplicity. [Insert table 2 about here]

The Lekner method suffers from divergence problems at very small r and this problem is overcome only by including a prohibitively large number of terms in the summation. Some authors [29] have suggested the development of a combined method that takes advantage of the good properties of HK at small z and makes use of

the fast convergence of the Lekner method at larger z separations, but this possibility was not investigated further.

HvS is seen to be the fastest method by a factor of 2 (relative to HBC) in the example presented here (a similar performance was found in other test cases), which represents a significant improvement. Even though this method is still about 5 times slower than the MI convention, it is the optimal method for our work, since it is capable of producing an essentially accurate potential in a relatively short time. We have chosen the cutoff number of boxes, n_C , to be 3, since it provides us with a suitable balance between accuracy and speed of computation.

5 Conclusions

We have compared several methods for the treatment of long-range interactions in grand canonical Monte Carlo simulation of water adsorption in slit-shaped pores. The method of Heyes and van Swol [15] had the best performance in this application. We see no reason to believe that this conclusion is specific to our particular system, but rather that it is likely to apply in general to long-range interactions in phases confined in spaces that are unbounded in two dimensions.

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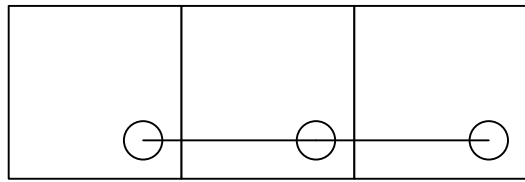
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table 1: Potential parameters for water molecules, graphite walls and carbonyl sites.

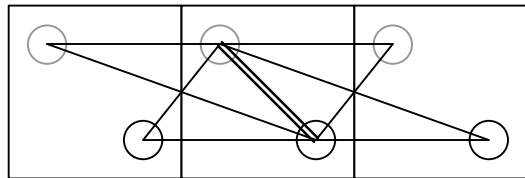
	Site	σ/nm	$\epsilon/(\text{J}\cdot\text{mol}^{-1})$	q/e
Water	H	0.0	0.0	+0.52
	O	0.3154	649.3	0.0
	M	0.0	0.0	-1.04
Graphite	C	0.340	232.8	0.0
Carbonyl	C	0.0	0.0	+0.5
	O	0.296	879.6	-0.5

table 2: Comparison of several methods for treatment of long-ranged interactions. All methods are optimised for a maximum error of 1% in the potential energy.

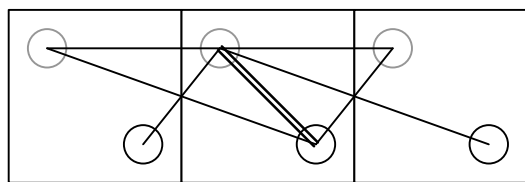
Method	Computing time/s
HBC	3.0
RHHR	7.4
HK	4.0
3D Ewald + correction	7.7
HvS	1.6
Lekner	55.6



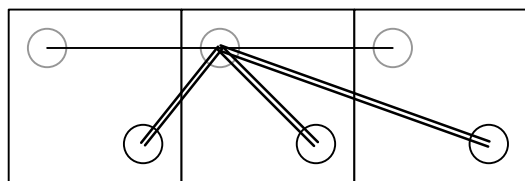
a) Potential before the creation



b) Potential after the creation



c) Potential difference



d) Final potential

figure 1: Diagram describing the calculation of the potential energy difference in a GCMC creation trial.

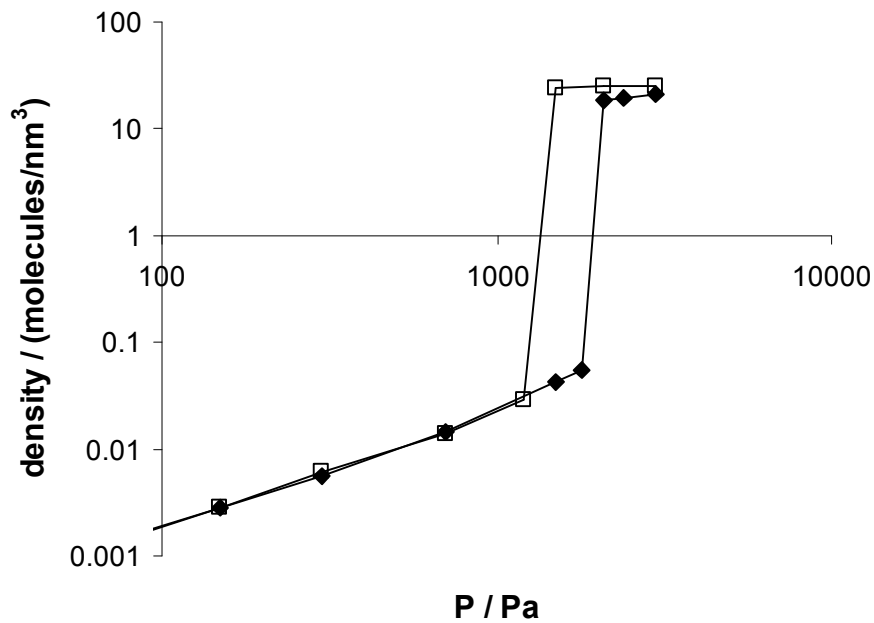


figure 2: Water adsorption isotherms in a pore of width 9.5\AA with a density of 2.67 carbonyl sites/ nm^2 on the surface. The two curves represent results obtained with the 2D Ewald sum (diamonds) and with the MI convention (open squares). Error bars are the size of the symbols used.

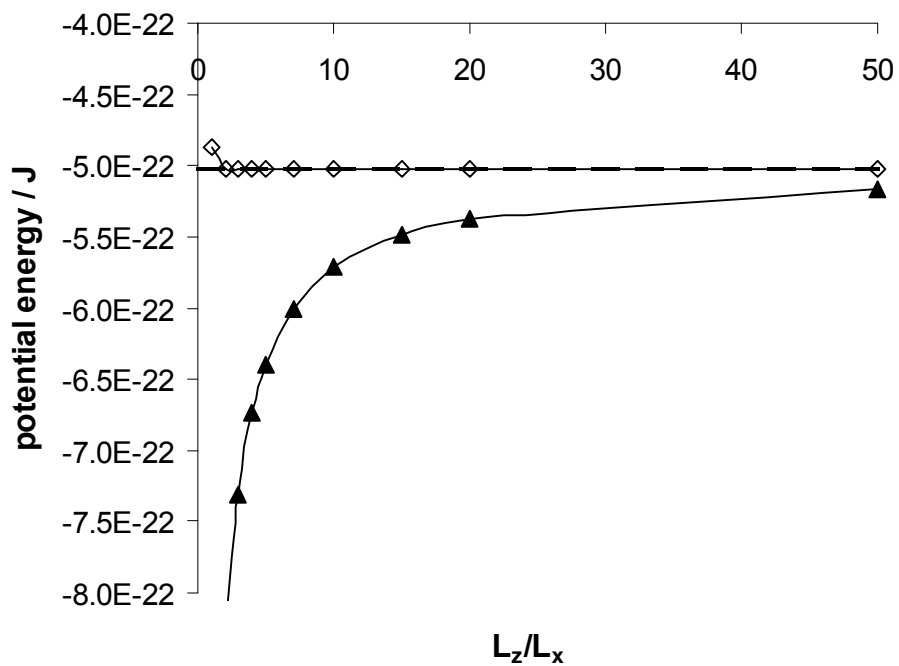


figure 3: Potential energy on a water molecule as a function of the relative dimension of the simulation cell in the z direction. Triangles are for the 3D Ewald sum, open diamonds for the 3D Ewald sum plus the correction term and the dashed line is the result obtained using the full 2D Ewald sum (HBC).

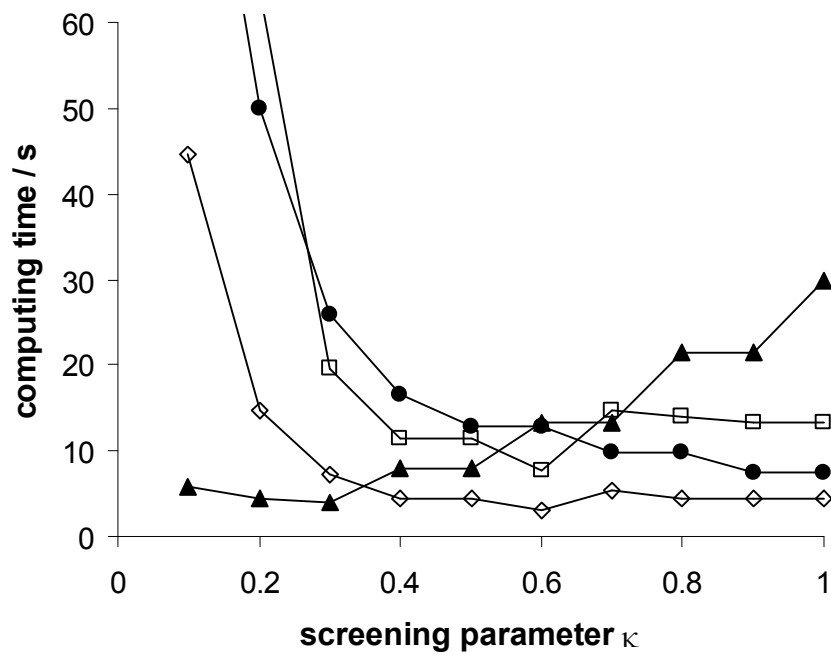


figure 4: Computing time as a function of the screening parameter κ for four different Ewald methods: HK (triangles), HBC (open diamonds), RHHR (circles) and 3D+correction (open squares). Lines are a guide to the eye.