

# Equilibrium Structure of Electrolyte calculated using Equilibrium Monte Carlo, Molecular Dynamics and Boltzmann Transport Monte Carlo Simulations

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## ABSTRACT

The pair correlation function is a measure of the microscopic structure of matter. Thermodynamic quantities that depend on the pair potential can be directly extracted from the pair correlation function, thus it provides suitable benchmark calculation for validating molecular scale simulations. Here we simulate simple homogeneous equilibrium electrolytes at concentrations of physiological interest using three quite different simulation methodologies – Equilibrium Monte Carlo (EMC), Molecular Dynamics (MD), and Boltzmann Transport Monte Carlo (BTMC). Ion-ion pair correlation functions computed for both monovalent and divalent electrolytes compare very well between the three different methodologies.

**Keywords:** pair correlation function, electrolyte, Lennard-Jones, Monte-Carlo, Molecular Dynamics.

## 1 INTRODUCTION

The recent availability of large-scale computational resources and methodologies has made possible the direct simulation of biological ion channel systems at the atomistic level of detail provided by Molecular Dynamics (MD) simulations. Nonetheless, the CPU time required to simulate ion permeation and observe measurable current is still prohibitive, even on massively parallel machines [1]. Here we propose an alternative, computationally less intensive approach – Boltzmann Transport Monte Carlo (BTMC).

The BTMC method is a numerically efficient way to solve the Boltzmann Equation for semi-classical transport. It has been used routinely in the semiconductor community over the past two decades to simulate charge transport in electron devices [2]. However, its application to ionic solutions is very recent and therefore requires validation. For this purpose we calculate the ion pair correlation function  $g(r)$  for several homogeneous electrolytes, for comparison with benchmark calculations obtained by MD

and Equilibrium Monte Carlo (EMC) simulations [3]. The function  $g(r)$  plays a central role in describing the microscopic structure and thermodynamic state of a system. For homogeneous isotropic systems it is proportional to the probability of finding two atoms separated by a distance  $r$ . Thus, for any molecular scale simulation to be thermodynamically correct it must reproduce the correct pair correlation function.

In section 2 we describe briefly the three methods used in this comparative study. In section 3 we compare the ion pair correlation function calculated via these three approaches for several electrolytes. Section 4 concludes with a discussion of this work.

## 2 METHODS

We consider a generic bulk electrolyte at equilibrium consisting of two ionic species interacting via the Coulomb potential and a modified form of the Lennard-Jones pairwise potential that retains only the repulsive component *viz.*

$$U_{LJ}(r_{ij}) = \begin{cases} 4\epsilon_{LJ} \left( \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) + \epsilon_{LJ}, & r_{ij} < 2^{1/6} \sigma_{ij} \\ 0, & r_{ij} > 2^{1/6} \sigma_{ij} \end{cases} \quad (1)$$

where  $\epsilon_{LJ}$  is the Lennard-Jones energy parameter and  $\sigma_{ij} = (\sigma_i + \sigma_j) / 2$  is the average of the individual Lennard-Jones distance parameters for particles  $i$  and  $j$ . For this work we set  $\epsilon_{LJ} = kT$  and  $T = 298.15K$ . The pair correlation function  $g(r)$  is defined as

$$g(r) = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle \quad (2)$$

where  $V = L \times L \times L$  is the system volume,  $N$  is the number of particles,  $r_{ij}$  is the distance between particles  $i$  and  $j$ , and the angular brackets denote a time or ensemble average.

Since all three simulation methods provide particle coordinates in real space,  $g(r)$  is readily computed by a simple counting procedure [3].

## 2.1 Equilibrium Monte Carlo

EMC simulations involve sampling the phase space of a system in thermodynamic equilibrium. For this work the canonical ( $NVT$ ) ensemble is used. Particles are distributed randomly in the phase space of a fixed volume and periodic boundary conditions are imposed to mimic bulk conditions.  $g(r)$  is computed by attempting to alter the system configuration. Each EMC step involves displacing a single ion randomly in the simulation volume. The change is accepted with probability  $\exp(-\Delta U/kT)$  where  $\Delta U$  is the energy cost of the change, determined from the Coulomb and Lennard-Jones interaction potentials. The long-range component of the Coulomb interaction is determined in Fourier Space using an Ewald sum and the Lennard-Jones interaction is determined directly in real space. The process is repeated until  $g(r)$  is sufficiently sampled.

## 2.2 Molecular Dynamics

MD simulations usually follow the motion of all particles in the system as it evolves according to Newtonian Mechanics [4]. Particle trajectories in real space are integrated in time using a fourth-order predictor-corrector scheme [5]. The total force acting on the particles includes the Lennard-Jones interaction and an electrostatic interaction. Electrostatic fields are evaluated using the Particle-Particle-Particle Mesh ( $P^3M$ ) scheme [6]. The particle-mesh component was computed in Fourier space using Ewald Sum techniques while the short-range particle-particle component was computed directly from Coulomb's Law in real space [6]. The system is brought to steady state then sampled at a fixed rate to acquire the pair correlation function. More details on the EMC and MD methods can be found in [3].

## 2.3 Boltzmann Transport Monte Carlo

BTMC simulates ion transport as a sequence of trajectories interrupted by random scattering events, which thermalize the ions [7]. Water is treated as a continuum dielectric background and ion-water interactions are accounted for by a scattering rate. Trajectory flight times between collisions  $T_f$  are generated statistically according to

$$-\ln r = \int_0^{T_f} \lambda(p(t)) dt \quad (3)$$

where  $\lambda(p(t))$ , the total scattering rate for all collision mechanisms, is a function of particle momentum  $p$ . For this work we use a constant scattering rate based on the

mass and diffusion coefficient of  $\text{Na}^+$  and  $\text{Cl}^-$  in water:  $\lambda_+ = 8.1 \times 10^{13} \text{ s}^{-1}$  and  $\lambda_- = 5.3 \times 10^{13} \text{ s}^{-1}$  [8].

Ion trajectories are integrated in time and space according to the local electric field, obtained from Poisson's equation, discretized using finite differences on a rectilinear grid. The resulting linear system is solved using a conjugate gradient approach [9], subject to Dirichlet boundary conditions applied at two points on opposite sides of the domain. In general applications injecting/absorbing boundary regions may be included to simulate an open system. In this particular application the BTMC system is closed – ions are reflected off hard-wall domain boundaries.

Discretization of Poisson's Equation leads to an unavoidable truncation of the short-range component of the electrostatic force, which can be corrected using the  $P^3M$  scheme to evaluate short-range interactions explicitly [10]. The total force acting on each ion is obtained by adding the contribution from the Lennard-Jones interaction.

## 3 RESULTS

In all three simulations, water is treated as a dielectric continuum with a permittivity  $\epsilon = 78.46$ . The EMC and MD simulations use a box of length  $L = 69.251 \text{ \AA}$ . A larger ( $L = 96 \text{ \AA}$ ) box was used for the BTMC simulations to reduce edge effects associated with the closed system. For a 1M monovalent solution these dimensions give ensembles of 400 (MD and EMC) and 1066 (BTMC) ions.

Each EMC simulation was run long enough to yield a relatively smooth function  $g(r)$ , sampled at every iteration in discrete bins of width  $h=0.3 \text{ \AA}$ . CPU requirements on a single processor SGI Origin2000 are of the order of a couple of hours.

The MD simulations were run for 1ns using a trajectory integration time step of  $\Delta t=2.5\text{fs}$ . The system is sampled every 10ps, after 100ps of equilibrium, yielding a total of 100 samples. Particle-particle short-range Coulomb forces were updated every  $100\Delta t$  and particle-mesh forces were updated every  $5\Delta t$  on a  $64 \times 64 \times 64$  grid (grid spacing  $\Delta = 1.1 \text{ \AA}$ ) with  $g(r)$  sampling bin width of  $h=0.37 \text{ \AA}$ . Run-times on a single processor SGI Origin2000 are  $\sim 60$  hours.

Unless otherwise specified, the BTMC simulations were run for 0.5ns, with  $\Delta t=10\text{fs}$ , particle-mesh forces were updated every  $10\Delta t$ .  $g(r)$  is sampled every 0.1ps in bins of width  $h=0.3 \text{ \AA}$ . Grid dimensions are specified individually for each result. All BTMC simulations were performed on a single processor 600MHz Dec Alpha. As we show in Section 3.3, run-times are strongly dependent on the choice of grid spacing, varying between about 1 to 10 hours for a 500ps simulation.

### 3.1 Monovalent Electrolyte

We consider first a simple monovalent electrolyte of two ion species having  $\sigma_+ = \sigma_- = 3 \text{ \AA}$ , at a concentration of 1M. Cation-cation  $g_{++}(r)$ , anion-anion  $g_{--}(r)$  and cation-

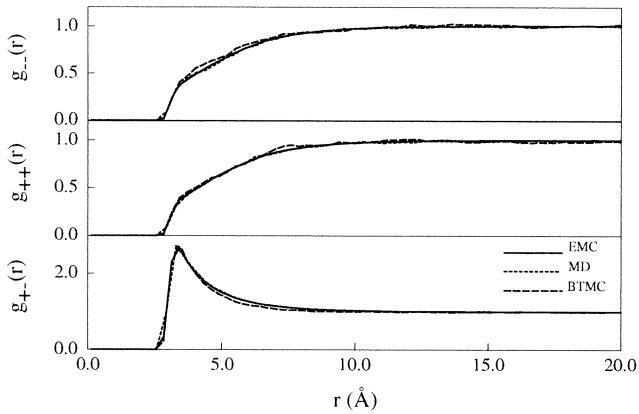


Figure 1. Anion-anion, cation-cation and cation-anion pair correlation functions computed from EMC, MD and BTMC simulations for a 1M solution of a simple monovalent electrolyte.

anion  $g_{+}(r)$  pair correlation functions computed using the three different simulation techniques are shown in Figure 1. The comparison between all three simulations is excellent. For this result the BTMC simulation was run for 100ps and electrostatic fields were obtained using only the particle-mesh scheme [10] (i.e., no correction term for the truncation of short-range forces) on a  $48 \times 48 \times 48$  ( $\Delta = 2 \text{ \AA}$ ) grid. The repulsive interaction described by (1) ensures that the minimum ion separation is greater than the distance over which truncation of short-range Coulomb interactions become important. The slight discrepancy between the BTMC simulation and the other two simulations is attributed to the fact that the BTMC system does not use periodic boundary conditions to mimic bulk electrolyte and is therefore sensitive to edge effects.

### 3.2 Divalent Electrolyte

We next consider a 0.75M solution of a divalent electrolyte consisting of ions of dissimilar sizes,  $\sigma_{+} = 1.9 \text{ \AA}$ ,  $\sigma_{-} = 3.62 \text{ \AA}$ ,  $z_{+} = +2$ ,  $z_{-} = -1$ . In this case the BTMC simulation was performed on a relatively coarse grid  $\Delta = 4 \text{ \AA}$  ( $24 \times 24 \times 24$  grid points) using the  $P^3M$  scheme to include the short-range Coulomb forces. The agreement between all three simulations is again very good.

### 3.3 Computational Issues

At present the computational bottleneck in the BTMC simulations is the solution of Poisson's Equation in real space. For the  $48 \times 48 \times 48$  grid used in Figure 1, roughly 75% of the total CPU ( $\sim 2$  hours for 100ps simulation) was spent solving Poisson's Equation. Since the CPU cost of the Poisson solution scales linearly with the total number of grid points there is clear motivation to use the coarsest possible mesh. In this section we return to the 1M monovalent electrolyte ( $\sigma_{+} = \sigma_{-} = 3 \text{ \AA}$ ) described in

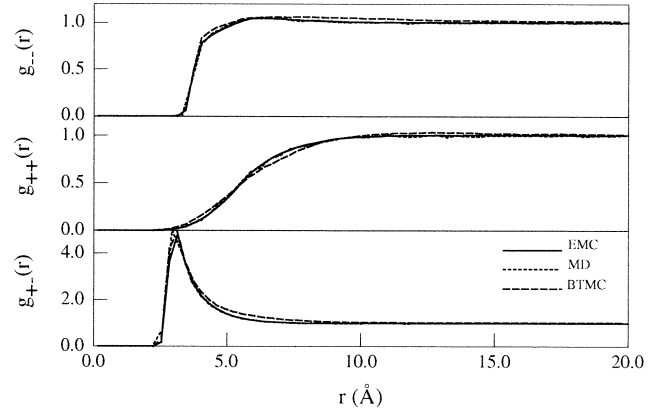


Figure 2. Anion-anion, cation-cation and cation-anion pair correlation functions computed from EMC, MD and BTMC simulations for a 0.75M solution of a divalent electrolyte ions of dissimilar size.

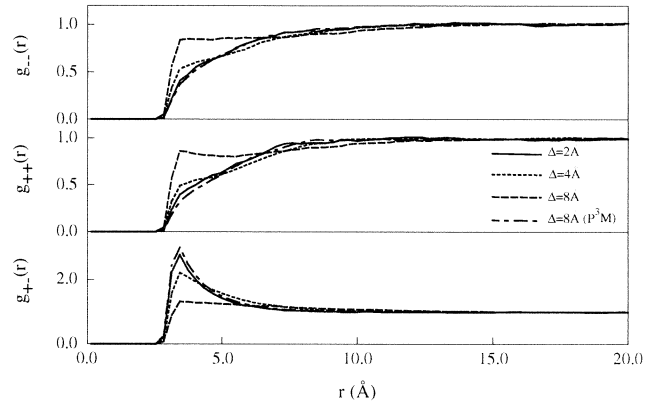


Figure 3. Anion-anion, cation-cation and cation-anion pair correlation functions computed from BTMC simulations using the particle-mesh scheme on progressively coarser grids. Distortions to  $g(r)$  at larger values of  $\Delta / \sigma_{LJ}$  can be recovered by using the  $P^3M$  scheme to evaluate the short-range coulomb forces

section 3.1, and examine the effect of mesh truncation of short-range forces.

Figure 3 shows pair correlation functions computed from the BTMC simulations using progressively coarser grids:  $\Delta = 2 \text{ \AA}$ ,  $\Delta = 4 \text{ \AA}$  and  $\Delta = 8 \text{ \AA}$ . Electrostatic forces were evaluated using the particle-mesh scheme. The truncation of short-range Coulomb forces by the mesh becomes critical at inter-particle distances  $r \sim 1.5\Delta$  [10]. Therefore, as we saw in Figure 1, if the grid is sufficiently fine ( $\Delta < \sigma_{LJ}$ ) the repulsive interaction in (1) the event of two ions occupying the same or neighboring mesh cell at the same time is extremely unlikely and thus the force truncation by the mesh does not affect the results. When  $\Delta$  is increased to  $4 \text{ \AA}$  the pair correlation functions are slightly distorted. Since we now have  $\Delta > \sigma_{LJ}$  it is possible to find

two or more ions in the same or neighboring mesh cells, hence the truncation of the electrostatic force by the mesh starts to be important. At  $\Delta = 8\text{\AA}$  the force truncation is clearly very important as evidenced by the severe distortion of the pair correlation function. The increase in  $g_{++}(r)$  and  $g_{-}(r)$ , and decrease in  $g_{+}(r)$  at short interaction distances ( $r = 3 - 6\text{\AA}$ ) indicates that the electrostatic interaction is grossly underestimated by the particle-mesh scheme. However, by using the P<sup>3</sup>M scheme to evaluate the short-range component of the Coulomb interaction explicitly the original pair correlation functions are recovered even on a very coarse  $\Delta = 8\text{\AA}$  grid, as is also shown in Figure 3.

The CPU required per 500ps of BTMC simulation using the particle-mesh scheme on a single processor 600Mhz Dec Alpha is approximately 605, 77 and 50 minutes for the 2, 4 and 8 $\text{\AA}$  grids, respectively. The dramatic speed-up observed when the grid spacing is increased from  $\Delta=2\text{\AA}$  and  $\Delta=4\text{\AA}$  saturates at larger grid spacing, because the computational burden is now dominated by the sampling of the pair correlation function (every 10ps in this case) and the particle transport. Evaluation of the short-range Coulomb force on a sub-domain surrounding each ion using the P<sup>3</sup>M scheme on the  $\Delta=8\text{\AA}$  grid increases the run-time to 72 minutes.

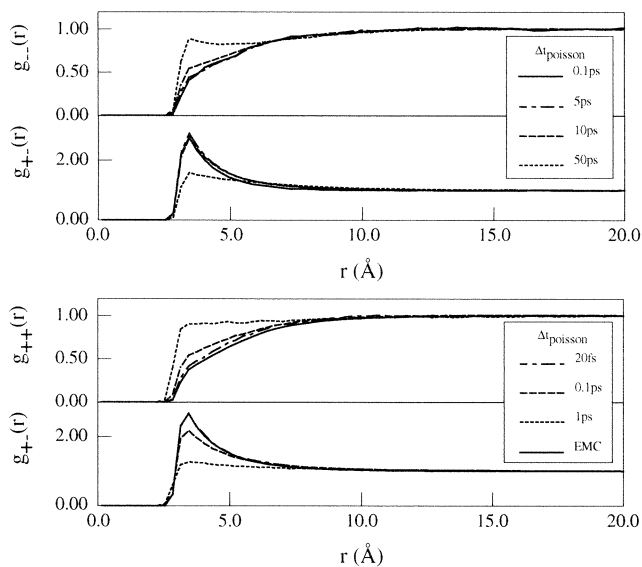


Figure 4. Effect of increasing the time between successive field updates on the pair correlation function for a highly collisional (top) and less collisional (bottom) system.

In addition to reducing the number of grid points, substantial reduction in the computational load can be achieved by relaxing the time interval between successive solutions for the electrostatic field. Ion transport in electrolyte is highly collisional and under bulk equilibrium conditions ion transport is largely diffusive [1]. The ion root-mean-square displacement scales with time as  $x_{rms} = \sqrt{6Dt}$ , where  $D$  is the diffusion coefficient [11].

Over a time scale of 1ps the ion diffusion length in a typical bulk electrolyte is about 1 $\text{\AA}$ . Therefore, in a realistic transport that is damped by water the charge configuration changes relatively slowly over time and the frequency of field updates can be relaxed without appreciably perturbing the results.

Careful benchmarking is necessary to determine the optimal frequency of field updates. Figure 4 (top) shows the anion-anion and cation-anion pair correlation functions for a 1M monovalent solution, computed via the BTMC method on a 2 $\text{\AA}$  grid, using the particle-mesh scheme, with progressively longer time intervals between solutions of Poisson's Equation. The time between field updates can be relaxed out to more than 5ps before any significant distortion in the pair correlation function is evident. Also shown in Figure 4 (bottom) are cation-cation and cation-anion pair correlation functions computed using ion-water scattering rates reduced by a factor of 100, with the EMC result plotted for comparison. As expected, the lower scattering rate allows the ions to diffuse much further over the same time scale, necessitating a much more frequent field update.

## 4 DISCUSSION

We have described three very different computational methods to simulate the equilibrium structure of both monovalent and divalent electrolytes. The agreement between all three models is very good. Each methodology has its own advantages and drawbacks depending on the particular application. The EMC method is computationally very efficient but, through its assumption of equilibrium conditions, is limited to providing information on the system configuration. The MD simulation follows the detailed ion transport in the electrostatic and Lennard-Jones potentials. For applications in which the periodicity of the system can be exploited the Ewald sum technique has been shown to be numerically quite efficient but cannot be extended practically to a general device structure in which periodic boundary conditions are not applicable. The BTMC method is well suited for simulating ion transport in non-periodic structures with very modest computational requirements.

We have also demonstrated that the computational performance of the BTMC method can be dramatically improved if the P<sup>3</sup>M scheme is implemented carefully. This has extremely important implications for realistic simulations of computationally large systems such as those encountered in ion channel systems with salt baths *in situ*. A good compromise must be achieved in the choice of mesh size so that the overhead of evaluating the Coulomb forces explicitly on a short-range domain for each particle does not outweigh the speedup achieved from using a coarser mesh for the particle-mesh scheme. The P<sup>3</sup>M scheme is currently implemented in such a way that while the distance over which the Lennard-Jones ion-ion interaction is included is greater than the range over which

the particle-particle Coulomb interaction is calculated explicitly, the overhead associated with searching for ions in the latter domain is negligible.

Finally, we have shown that by including a high ion-water scattering rate, estimated from ion diffusion coefficients in solvent, the charge configuration changes sufficiently slowly to relax the time interval between successive solutions of Poisson's Equation to several picoseconds without any noticeable change to the pair correlation function.

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