

A novel Monte Carlo algorithm for polarizable force fields: Application to a fluctuating charge model for water

Marcus G. Martin, Bin Chen, and J. Ilja Siepmann^{a)}

Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455-0431

(Received 17 October 1997; accepted 23 December 1997)

In this Monte Carlo algorithm for polarizable force fields, the fluctuating charges are treated as special degrees of freedom subject to a secondary low-temperature thermostat in close analogy to the extended Lagrangian formalism commonly used in molecular dynamics simulations of such systems. The algorithm is applied to Berne's SPC-FQ (simple point charge-fluctuating charge) model for water. The robustness of the algorithm with respect to the temperature of the secondary thermostat and to the fraction of fluctuating-charge moves is investigated. With the new algorithm, the cost of Monte Carlo simulations using fluctuating-charge force fields increases by less than an order of magnitude compared to simulations using the parent fixed-charge force fields. © 1998 American Institute of Physics. [S0021-9606(98)51409-2]

Most standard molecular force fields model the electronic structure of atoms, ions and molecules using partial point charges located on well-defined sites in the molecular frame. Commonly, the values of these charges remain fixed throughout the simulations, i.e. they do not change depending on their environment. Thus the fixed charges are effective parameters reflecting the average environment of the particular phase for which they have been derived. This limits the applicability and transferability of fixed-charge models. For example, the failure of fixed-charge water models to deal with changes in environment has now been well documented.¹⁻⁴ For situations where the electronic fields are strong and heterogeneous, the next level of transferable and accurate force fields has to incorporate models in which the electronic structure of molecules can respond to environmental changes. In the case of water, this demand has now been met with the upsurge of many dipole-polarizable⁵⁻⁹ and fluctuating-charge^{10,11} models.

In polarizable and fluctuating-charge models it is assumed that the system remains always in its electronic ground state (adiabatic limit). There are two principle alternatives to satisfying this requirement. The first is to use an iterative procedure to minimize the electronic energy at every change of configuration (molecular dynamics time step or single Monte Carlo move).^{8,12-14} As has been pointed out by Frenkel and Smit,¹⁵ the iterative procedure has to be carried out to high accuracy to avoid a systematic drag force in molecular dynamics simulations. Similarly, a very high accuracy is required in Monte Carlo simulations to satisfy the detailed balance condition. Iterative schemes have been used in Monte Carlo simulations, but the fact that the electronic structure should be optimized at every move (i.e. N times per cycle) makes this method extremely computer intensive and compares very unfavorably to molecular dynamics where it-

erations are required only once for every time step. Medeiros and Costas¹³ have suggested a Monte Carlo scheme which updates the electronic structure of only the molecule which is displaced. However, polarizability is a many-body effect, and Medeiros and Costas do not show that their procedure satisfies the detailed balance condition.

The more elegant solution to maintaining the adiabatic limit in molecular dynamics simulations is the "on-the-fly" optimization pioneered by Car and Parrinello.¹⁶ In this approach, the fluctuating charges (or the electronic density) are treated as additional dynamical variables (with fictitious mass and kinetic energy) and an extended Lagrangian formalism is used to solve the equations of motion.^{5,16-19} The electronic configuration fluctuates around the adiabatic value, i.e. it is not exactly in its ground state. However, the fluctuations are random and can be made small by maintaining a sufficiently low (kinetic) temperature for the fluctuating charges.²⁰ The use of an electronic temperature of 5 K is typical in molecular dynamics simulations of fluctuating-charge models.^{10,20}

The underlying idea of the algorithm proposed here is to mimic the Car-Parrinello approach in the context of a Monte Carlo framework. Like in the molecular dynamics case, the fluctuating charges are treated as additional degrees of freedom and two different temperatures (nuclear, T , and electronic or fluctuating-charge, T_{fq} , with $T_{fq} \ll T$) are specified. In addition to conventional moves (say, translations and rotations) for the nuclear degrees of freedom, a new type of move has to be used to update the electronic configuration, such as fluctuating charges or dipole polarizabilities. The acceptance probability for nuclear moves is calculated using T , while T_{fq} is used for fluctuating-charge moves. In the following description of the fluctuating-charge move, we focus on the use of Berne's SPC-FQ (simple point charge-fluctuating charge) model for water, which contains three fluctuating charge sites.¹⁰ However, it should be pointed out that the principle is very general and can easily be adapted to other

^{a)} Author to whom correspondence should be addressed.
E-mail: siepmann@chem.umn.edu

TABLE I. Potential energy, E , Lennard-Jones energy, E_{LJ} , Coulombic energy, E_C , and polarization energy, E_{fq} , (in units of kJ mol^{-1}) and average dipole moment (in units of Debye) for different temperatures of the secondary thermostat, T_{fq} (in units of K), and for different ratios of fluctuating-charge versus standard moves, R_{fq} . The subscript gives the statistical uncertainty in the last digit(s).

T_{fq}	R_{fq}	E	E_{LJ}	E_C	E_{fq}	μ
5.0	1	-47.8 ₁	+20.4 ₆	-119.4 _{1,8}	+51.2 _{1,1}	3.132 ₁₄
5.0	10	-47.8 ₂	+19.9 ₄	-118.4 _{1,3}	+50.7 ₈	3.123 ₁₀
0.5	1	-47.7 ₂	+20.0 ₅	-117.6 _{1,8}	+50.0 _{1,0}	3.117 ₁₅
0.5	10	-48.4 ₁	+21.9 ₄	-124.6 _{1,2}	+54.3 ₈	3.167 ₈
0.05	1	-48.0 ₁	+19.8 ₄	-116.6 _{1,2}	+48.9 ₇	3.113 ₉
0.05	10	-48.4 ₂	+21.4 ₅	-123.1 _{1,5}	+53.3 ₉	3.155 ₇

polarizable force fields. The fluctuating-charge move employs a *symmetric* underlying Markov matrix, so that the standard Metropolis acceptance rules can be applied to satisfy the detailed balance condition.^{21,22} The first step is to randomly select the type of move to be attempted. For a system consisting of rigid water molecules in the canonical ensemble, translational, rotational, and fluctuating charge moves are required. The second step is the random selection of the trial molecule. If the fluctuating-charge move has been selected in the first step, the third step is the random selection of one of the three partial charges (on the water molecule). The value of this charge is now changed by an amount, dq , uniformly selected from the range $(-dq_{\max}; +dq_{\max})$, where dq_{\max} is the maximum displacement, which can be adjusted to yield a desired acceptance rate. If we use the constraint that each water molecule has to be neutral, the other two charges on the selected molecules are changed by $-dq/2$.²³ This constrained charge transfer constitutes the trial displacement. Now the change in Coulombic and polarization energies caused by the trial displacement has to be evaluated and the move is then accepted/rejected using the standard Metropolis acceptance rule with T_{fq} .²¹

In this work we have used the SPC-FQ water model proposed by Berne and co-workers.¹⁰ The model contains three fluctuating charges located on the hydrogen and oxygen atomic sites, one Lennard-Jones site on the oxygen and has the same (fixed) internal geometry as the popular SPC model.²⁴ The potential energy of an N -molecule system is the sum of the Lennard-Jones part, the intermolecular Coulomb part, and the intramolecular polarization energy as given by Eq. 2.16 of Ref. 10. A molecule-based spherical potential truncation at $r_{OO} > 10.5 \text{ \AA}$ is employed for the Lennard-Jones and Coulomb interactions and analytical tail corrections are added for the Lennard-Jones part.²⁵ In addition, an inner cut-off is used which prevents any two non-bonded sites from approaching to closer than 1.5 \AA . All simulations were carried out in the canonical ensemble with 500 molecules at $T = 298.15 \text{ K}$ and $\rho = 1.00 \text{ g cm}^{-3}$. Production periods consisted of 10^5 Monte Carlo cycles (or 5×10^7 Monte Carlo moves). Standard deviations were calculated by dividing the simulations into 10 blocks.²⁶

Six sets of simulations were performed in which the fluctuating-charge temperature ($T_{fq} = 5, 0.5, \text{ or } 0.05 \text{ K}$) and the ratio fluctuating-charge versus standard moves ($R_{fq} = 1 \text{ or } 10$) were varied. For $R_{fq} = 1$ and 10 the computer time in-

crease by factors of 1.9 and 9.6, respectively, compared to a simulation of the fixed-charge SPC model,²⁷ and the increase is independent of system size. This small increase in computer time compares very favorably with Monte Carlo simulations using an iterative procedure for which an increase by a factor of 60 has been reported for a system containing 128 polarizable molecules.¹²

The calculated energies are reported in Table I. The average potential energies of all simulations are close to -48 kJ/mol and the difference between the largest and smallest value is less than 2%. However, the spread in the individual contributions to the potential energy is larger. In comparison, Rick *et al.*¹⁰ reported an average potential energy of -42 kJ/mol and a polarization energy of $+32 \text{ kJ/mol}$ for their molecular dynamics simulations of the SPC-FQ model. The differences are most likely caused by the different treatments of the long-range electrostatic interactions.²⁵ For $T_{fq} = 5 \text{ K}$, the results for $R_{fq} = 1$ and 10 are indistinguishable, whereas for the lower T_{fq} the higher ratio seems to yield a lower potential energy, and the results for $T_{fq} = 0.5$ and 0.05 K are in good agreement. The distributions of the fluctuating charges are shown in Fig. 1. First of all, the distributions for the two hydrogens are indistinguishable which is a good indication for sufficient sampling of the fluctuating-charge degrees of freedom. Secondly, the widths of the distributions are very similar irrespective of the values of T_{fq} and R_{fq} . Thus, the width is mainly caused by the heterogeneous liquid environment and not by thermal

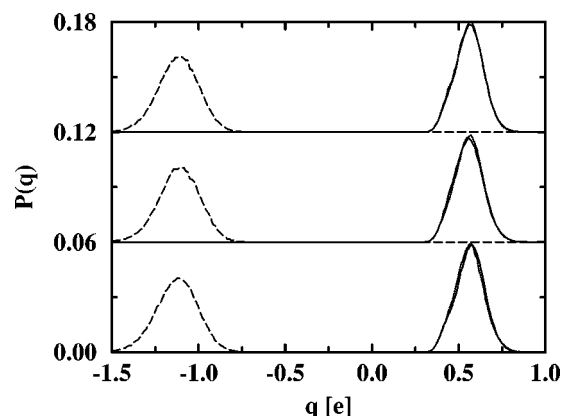


FIG. 1. Distributions of the fluctuating charges for $T_{fq} = 5 \text{ K}$ and $R_{fq} = 1$ (upper part), for $T_{fq} = 5 \text{ K}$ and $R_{fq} = 10$ (middle part), and for $T_{fq} = 0.05 \text{ K}$ and $R_{fq} = 10$ (lower part). Solid, dotted and dashed lines are used for the fluctuating charges on hydrogen 1, hydrogen 2, and oxygen.

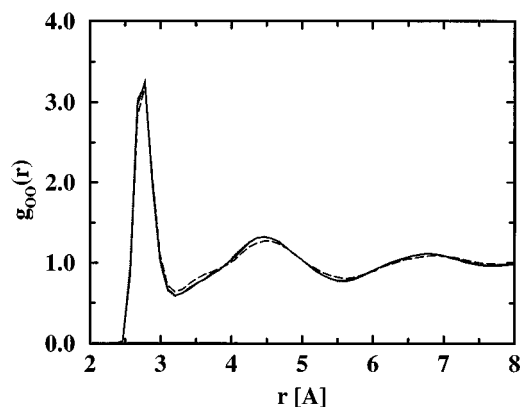


FIG. 2. Oxygen-oxygen radial distribution functions for $T_{fq}=5$ K and $R_{fq}=1$ (solid line), for $T_{fq}=5$ K and $R_{fq}=10$ (dashed line), and for $T_{fq}=0.05$ K and $R_{fq}=10$ (dotted line).

fluctuations. Thirdly, the magnitude of the fluctuating charges is slightly larger at $T_{fq}=0.05$ K and $R_{fq}=10$, as could also be inferred from the lower E_C . As a consequence, the dipole moment also increases for lower T_{fq} (see Table I). Thus, using the lower electronic temperature results in a slightly larger polarization of the fluctuating charges. Figures 2 and 3 show the corresponding oxygen-oxygen and oxygen-hydrogen radial distribution functions (RDFs). Despite the fact that differences in E_{LJ} are observed for different T_{fq} , it is hard to distinguish between the oxygen-oxygen RDFs. It is also worth noting that the first minima in the oxygen-oxygen RDFs fall around 0.6 in good agreement with the neutron diffraction data of Soper and Phillips.²⁸

In conclusion, a novel fluctuating-charge Monte Carlo algorithm has been demonstrated to satisfy the detailed balance condition and to be remarkably efficient for simulations using polarizable force fields. Simulations were carried out for the polarizable SPC-FQ water model in the canonical ensemble. The overall agreement between the simulations at

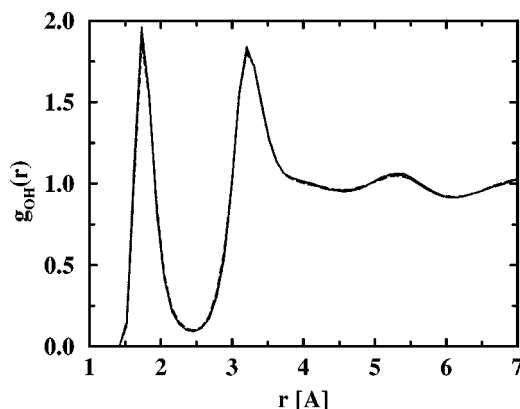


FIG. 3. Oxygen-hydrogen radial distribution functions for $T_{fq}=5$ K and $R_{fq}=1$ (solid line), for $T_{fq}=5$ K and $R_{fq}=10$ (dashed line), and for $T_{fq}=0.05$ K and $R_{fq}=10$ (dotted line).

different electronic temperatures is very satisfactory. Lower electronic temperatures yield a slightly lower potential energy caused by increased polarization of the fluctuating charges.

We would like to thank Michiel Sprik and John Shelley for many stimulating discussions on water simulations. Financial support from the Petroleum Research Fund, administered by the American Chemical Society, a Camille and Henry Dreyfus New Faculty Award, and a Department of Energy Computational Science Graduate Fellowship (M.G.M.) is gratefully acknowledged. Part of the computer resources were provided by the Minnesota Supercomputer Institute.

- ¹K. Watanabe, M. Ferrario, and M. L. Klein, *J. Phys. Chem.* **92**, 819 (1988).
- ²J. C. Shelley, K. Watanabe, and M. L. Klein, *Langmuir* **9**, 916 (1993).
- ³H. J. Strauch and P. T. Cummings, *J. Chem. Phys.* **96**, 864 (1992).
- ⁴P. A. Kollman, *Acc. Chem. Res.* **29**, 461 (1996).
- ⁵M. Sprik and M. L. Klein, *J. Chem. Phys.* **89**, 7556 (1988).
- ⁶P. Ahlström, A. Wallqvist, S. Engström, and B. Jönsson, *Mol. Phys.* **68**, 563 (1989).
- ⁷P. Cieplak, P. Kollman, and T. Lybrand, *J. Chem. Phys.* **97**, 2659 (1992).
- ⁸A. Wallqvist and B. J. Berne, *J. Phys. Chem.* **97**, 13841 (1993).
- ⁹A. A. Chialvo and P. T. Cummings, *J. Chem. Phys.* **105**, 8274 (1996).
- ¹⁰S. W. Rick, S. J. Stuart, and B. J. Berne, *J. Chem. Phys.* **101**, 6141 (1994).
- ¹¹I. M. Svishchev, P. G. Kusalick, J. Wang, and R. J. Boyd, *J. Chem. Phys.* **105**, 4742 (1996).
- ¹²J. Gao, J. J. Pavelites, and D. Habibollahzadeh, *J. Phys. Chem.* **100**, 2689 (1996).
- ¹³M. Medeiros and M. E. Costas, *J. Chem. Phys.* **107**, 2012 (1997).
- ¹⁴K. Kiyohara, K. E. Gubbins, and A. Z. Panagiotopoulos (preprint).
- ¹⁵D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, San Diego, California, 1996).
- ¹⁶R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ¹⁷H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).
- ¹⁸M.-L. Saboungi, A. Rahman, J. W. Halley, and M. Blander, *J. Chem. Phys.* **88**, 5818 (1988).
- ¹⁹M. Wilson and P. A. Madden, *J. Phys.: Condens. Matter* **5**, 2687 (1993).
- ²⁰M. Sprik, *J. Phys. Chem.* **95**, 2283 (1991).
- ²¹N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
- ²²M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).
- ²³If the sampling of intermolecular charge transfer is desired, then the corresponding constraint is that the entire system has to be neutral. In this case, we could simply change the value of all other charges by $-dq/(N_{fq}-1)$, where N_{fq} is the total number of fluctuating charges in the system.
- ²⁴H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, and J. Hermans, in *Intermolecular Forces*, edited by B. Pullman (Reidel, Dordrecht, 1981), p. 331.
- ²⁵In Ref. 10 an Ewald sum is used for the long-range electrostatic energy. Since this paper is only concerned with the testing of the fluctuating-charge Monte Carlo algorithm, we have not included the Ewald sum. Use of an Ewald sum is straightforward in Monte Carlo calculations and it has been used, for example, in Refs. 13 and 14.
- ²⁶A second production period was carried out in all cases and the results of the two production periods agree to better than the reported standard deviations from the block averages.
- ²⁷Fluctuating charge moves are less expensive than translations or rotations, since the former do not require the evaluation of the Lennard-Jones energy. 10^5 Monte Carlo cycles for the fluctuating-charge model with $R_{fq}=1$ take approximately 60 hours on a Silicon Graphics R10000 processor.
- ²⁸A. K. Soper and M. G. Phillips, *Chem. Phys.* **107**, 47 (1986).