

Chemical Potential of Water from Monte Carlo Simulation: The Fundamentals

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Abstract

Monte Carlo simulation was conducted using the Towhee software to calculate the chemical potential of water. The implementation is made simple and provides a clear demonstration of the concept of Monte Carlo simulation. This paper is targeted to new researchers interested in molecular modelling and can be used as a guide for beginners in the art of molecular modelling, specifically Monte Carlo simulation. The purpose of carrying out the calculation of the water chemical potential is that the value obtained can be implemented in the Grand Canonical (μVT) ensemble or Gibbs ensemble for further research. The result obtained from the Monte Carlo simulation for the chemical potential of water are in agreement with published water potential values, therefore validating the SPC water model and MCCCSTowhee software [1].

Keywords: Monte Carlo simulation, molecular modelling, water chemical potential

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INTRODUCTION

Molecular modelling is a set of techniques, which predict the properties of matter at the molecular level, which in turn can be used to determine macroscopic data. These include structural, thermodynamics and thermochemical properties [2]. Model systems, which are representative of the bulk system of interest, are studied. The efficiency of these models lies in the fact that a small number of particles can be representative of the bulk system [3]. These methods are now becoming innovative tools used by researchers due to the advancement and mass production of computers, which have made them accessible. It is now possible to run computer simulation using both, desktops and laptops. Soft wares are now available that can be used for visualisation, with a ready-made force field and data banks of ready-made models of molecules for running a simulation of choice.

Furthermore, molecular modelling is now being used more frequently to construct virtual experiments in cases where controlled laboratory experiments are difficult, too dangerous, impossible or expensive to perform

[4, 5]. They are also used to check the reliability of analytical methods. The vision for molecular modelling was conceived long ago even before the advent of computers as reported by Jabbarzadeh *et al.* [6]. They pointed out that Laplace described the idea as “Given for one instant an intelligent being which could comprehend all the forces by which, nature is animated and the respective situation of the beings who compose it, an intelligence sufficiently vast to submit these data to analysis; it would embrace in the same formula, the movements of the greatest bodies of the universe and those of the lightest atoms, nothing would be uncertain and the future, as the past, would be present in its eyes”.

Rapport points out that a philosophical concept by Greek theorist in the 5th century BC, in which the universe is believed to be composed of tiny indivisible particles, which are the basis for the foundation of molecular dynamics [7]. The earliest work in atomic scale simulation was accomplished by Metropolis *et al.* [8]. This work was fundamental to the so-called Monte Carlo (MC) method. Early models were idealised

using hard spheres (three-dimensional) and two-dimensional hard disks [9]. The molecular dynamic method was first introduced by Alder and Wright in the late 1950s, to study the interaction of hard spheres [10, 11]. Many insights concerning the behaviour of simple liquids emerged from their research [12, 13]. The next significant advance was in 1964 when Rahman carried out the first simulation using a realistic potential for liquid argon [14]. The first molecular dynamic simulation of a practical system was done by Rahman and Stillinger in their simulation of liquid water in 1971 [15]. Today, molecular models, for example, multicomponent mixtures are typical [16], or prediction of structural and thermodynamic properties for large molecules are considered reliable [17].

MC and MD are equivalent methods that take a similar approach [18, 19]. Molecular dynamics modelling is a computational technique in which the physical movement of atoms and molecules and their interactions are studied with respect to time. The path of the motion of atoms and molecules are defined mathematically and solved following Sir Isaac Newton's equation of motion. The atomic and molecular properties such as interaction forces and potential energy are determined by the behaviour of motion, which are then used to compute the macroscopic properties such as energy, pressure and heat capacities of the given material system. Monte Carlo simulations involve the generation of random numbers, and the sampling of phase space of a model system by generating a series of configurations of particles and measuring the average of the desired quantity [1].

Molecular modelling has made huge strides lately and is bit by bit turning into a pervasive device in science and engineering [20]. There is a rise of educational interest in these computer-based laboratories due their accuracy and cost. However, most journals in the art of molecular modelling are too complicated for the new researcher or undergraduate student to understand. In this paper, the implementation of Monte Carlo simulation is made simple and provides a clear demonstration of the concept of Monte Carlo simulation. Furthermore, this paper is targeted to new researchers interested in molecular

modelling and can be used as a guide for beginners in the art of molecular modelling, specifically Monte Carlo simulation.

THEORY

Molecular Dynamics

The classical mechanics that we know today is attributed to Sir Isaac Newton. The Newton equation of motion is given by:

$$F=ma \quad (1)$$

Where, F is the resultant force acting on an object, m is the mass of the object and a , is the acceleration of the object moving in the direction of force F . By applying Newton's equation of motion of atoms, if we know the force that is acting on each atom, we can determine the acceleration of each atom. Integrating of the acceleration over a period starting from an initial velocity yields a trajectory of the position, velocities and acceleration of each particle within the time frame. Once the velocities and position of each atom are known, the state of the system at the microscopic level can be predicted regarding the properties of all atoms involved. Expressing the force as the gradient of potential energy (V) i.e. energy as a result of a body's position in a given space gives:

$$F = -\nabla V \quad (2)$$

Combining the two equations gives:

$$-\frac{dV}{dr} = m \frac{d^2x(t)}{dt^2} \quad (3)$$

Where, (v is the velocity), x is the coordinates of the atoms, and m is the mass of the atoms and t is the time.

Velocity Verlet Algorithm

The potential energy is a function of the atomic positions (3D coordinates) of all the atoms in the system, and due to the complicated nature of the function, there is no analytical solution to Eq. (3); therefore it has to be solved numerically using integration method. The integration of Newton's equation of motion can be performed using different types of algorithms with the aid of finite difference method, where the Taylor series is used to approximate the position, velocities and acceleration at any time, such as:

$$r(t + \delta t) = r(t) + \delta t v(t) + \frac{1}{2} \delta t^2 a(t) + \frac{1}{6} \delta t^3 b(t) + \dots \quad (4)$$

$$v(t + \delta t) = v(t) + \delta t a(t) + \frac{1}{2} \delta t^2 \delta t^2 b(t) + \frac{1}{6} \delta t^3 c(t) + \frac{1}{24} \delta t^4 d(t) + \quad (5)$$

$$a(t + \delta t) = a(t) + \delta t b(t) + \frac{1}{2} \delta t^2 c(t) \quad (6)$$

Where, v is the velocity (the first derivative with respect to time), a , the acceleration (the second derivative with respect to time), b is the third derivative with respect to time and r is the position of the atom. The Velvet algorithm is the most widely used method for integrating the trajectories of motion in MD simulations. To derive the algorithm, we use the following two forms of Taylor series:

$$r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2} a(t)\delta t^2 \quad (7)$$

$$r(t - \delta t) = r(t) - v(t)\delta t + \frac{1}{2} a(t)\delta t^2 \quad (8)$$

Combining Eqs. (7) and (8) gives:

$$r(t + \delta t) = 2r(t) - r(t - \delta t) + a(t)\delta t^2 \quad (9)$$

As can be seen from the Eq. (9), the equation does not apply when we need to calculate velocity. We need the velocity to calculate the kinetic energy. Therefore, we use the position of the atoms in the following way to calculate the velocity. Subtracting Eq. (8) from Eq. (7) yields an algorithm for calculating the velocities:

$$v(t) = \frac{r(t + \delta t) - r(t - \delta t)}{2\delta t} \quad (10)$$

Force Field

Atomic parameters and functional forms, such as dynamic force fields are the vital infrastructures for a molecular mechanic [21, 22]. They are essential to determine the total energy of a system and usually are derived from experiments and quantum mechanics calculations. The simplest representation of the atomic force field can be described using the following equation:

$$E_{\text{molecularmechanics}} = E_{\text{Stretching}} + E_{\text{Bending}} + E_{\text{non-bondedinteractions}} \quad (11)$$

Where, $E_{\text{molecularmechanics}}$ is the molecular mechanics energy due to the interaction between the component atoms, $E_{\text{Stretching}}$ is the stretching energy or bond stretching between atoms, E_{Bending} is the bending energy due to angle of bending, and $E_{\text{Non-bondedinteractions}}$ is the non-bonded

interaction energy. The bonded terms in Eq. (11) are the angle bending and bond stretching, while the non-bonded interactions are the van der Waals and electrostatic forces. Eq. (11) can be simplified as:

$$E_{\text{forcefield}} = E_{\text{Bonded}} + E_{\text{non-bonded}} \quad (12)$$

Intra-Molecular Potentials

Angle Bending

The bending angle is calculated using the Hooke's law or harmonic potential. The bending energy is the result of elasticity between two or more bonded atoms but concerning their ideal bond angle. The Hooke's law or harmonic potential below is used to calculate the energy change due to the bending:

$$E_{\text{Bending}} = \frac{k}{2} (\theta - \theta_0)^2 \quad (13)$$

Where, E_{Bending} is the energy of angle bending, θ is the normal angle bending, θ_0 is the angle as a result of elasticity, and k is a force constant.

Bond Stretching

If we consider the atomic bonds to act like a spring, which can be stretched or compressed, then the energy required to compress or stretch the bond can be calculated using the Hooke's law:

$$E_{\text{Stretching}} = \frac{k}{2} (r - r_0)^2 \quad (14)$$

Where, r is the distance between the two atoms and k is the force constant.

Intermolecular Potentials

These are weak forces of attraction or repulsion which act between atoms or molecules, the non-bonded interactions can be defined by the equation below:

Van der Waals Term

$$E_{\text{Vanderwaals}} = \sum_{\text{Non-bondedpairs}} \left(\frac{A_{ik}}{r_{ik}^{12}} - \frac{C_{ik}}{r_{ik}^6} \right) \quad (15)$$

The most commonly used of these potentials is the Lennard-Jones (L-J) potentials [23]. It defines a pair of interactions based on the assumption that there exists a general potential function, which is different only for the different molecules through one, two, or more parameters [24]. The L-J potential describes a

two-body interaction of uncharged atoms or molecules. The attractive part of the potential is given by Van der Waals forces where the repulsive part is caused by the so-called exchange interaction [25]. The L-J potential is a simple model of mathematics founded by Sir Edward Lennard-Jones [23]. The Lennard-Jones potential can be defined as:

$$V = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (16)$$

Where, r is the distance between the centres of the two interacting atoms or molecules and ϵ is the well-depth of the interaction potential, and σ is the collision diameter.

Electrostatic Potentials

Coulomb's law is used to determine the electrostatic potential between molecules. It can be written as:

$$V_{elect} = \frac{q_i q_j}{4\pi\epsilon_{eff} r_{ij}} \quad (17)$$

q_i and q_j are the atomic charges; ϵ_{eff} is the effective dielectric constant, and r_{ij} is the relative distance between the two particles.

Periodic Boundary Conditions

The periodic boundary condition is a technique for diminishing surface effects. It is applied to a simulation such that a limited number of molecules display the bulk properties of the system. As seen in Figure 1, the highlighted box represents a unit cell containing a small number of the particles we are simulating.

The surrounding molecules mirror all the properties of the outlined limited particles i.e. they include the same bulk properties. The concept used here is that when an atom exits from the simulated domain (simulation cell), an atom with the same configuration from the neighbour will enter the simulation cell. The highlighted box at the centre is the simulation unit/domain. Figure 1 is an example of periodic boundary condition technique.

Monte Carlo Simulation

The phrase Monte Carlo was coined by Metropolis [8]. However, because of the extensive use of random numbers in the calculation, the Monte Carlo simulation is a technique where a large set of configuration is

generated randomly, and the averages of a particular quantity are produced from the settings [26].

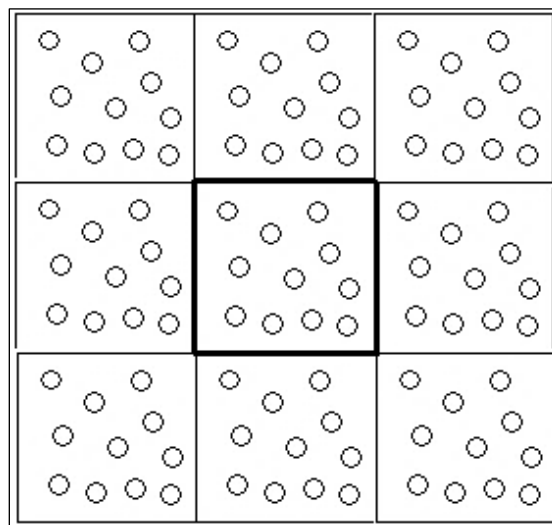


Fig. 1: Periodic Boundary Conditions.

These sampling experiments involve the generation of random numbers followed by a limited number of arithmetic and logical operations; these tasks are well suited to a computer; and the arrival of the MANIAC computer in Los Alamos prompted the study of many body problems [27]. The canonical ensemble (NVT) that is an ensemble with a constant number of particles N , constant volume and temperature and was the ensemble used by Metropolis *et al.* in their paper of 1953 [8]. The review below takes the same form. Consider a system described by Hamiltonian:

$$\kappa(P^N, r^N) = \sum_{i=1}^N \frac{p_i^2}{2m} + U(r^N) \quad (18)$$

Where, the Hamiltonian (κ) is the sum of the potential, and kinetic energy of the system, the canonical partition function Z (NVT) of such a system is given by:

$$Z(NVT) = \frac{1}{\Lambda^{3N} N!} \int dr^N \exp[-\beta U(r^N)] \quad (19)$$

Where, $U(r^N)$ is the total energy of the system with certain number of molecules N at position (r^N), β is the inverse of KT (Boltzmann constant) and the thermal wavelength (also called the De Broglie wavelength) results directly from the integration over the momenta and is defined by:

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

The free energy of the system equals:

$$F(N, V, T) = -k_B T \ln Z(NVT) \quad (20)$$

Quantities like the pressure and energy can be computed by employing partial derivatives of $F(NVT)$. The canonical ensemble of momentum-independent observable i.e. quantities that only depend on r^N can be expressed as:

$$\langle A \rangle = \frac{\int dr^N A(r^N) \exp[-\beta U(r^N)]}{\int dr^N \exp[-\beta U(r^N)]} \quad (21)$$

In order to sample the phase space efficiently and adequately, the core idea in the Metropolis Monte Carlo method is that phase point is generated according to the desired probability. In this way, one avoids the numerical evaluation of the integrand on a high dimensional grid where most of the grid points result in configuration with an extremely low Boltzmann weight. Consider for example a sequence of configuration $r_1^N, r_2^N, r_3^N, \dots, r_n^N$. If the sequence consists of random configuration the ensemble average $\langle A \rangle$ is simply:

$$\langle A \rangle = \lim_{n \rightarrow \infty} \frac{\sum_{i=1}^n A(r_i^N) \exp[-\beta U(r_i^N)]}{\sum_{i=1}^n \exp[-\beta U(r_i^N)]} \quad (22)$$

Again computing $\langle A \rangle$ in this way is often not meaningful, as the Boltzmann weight is nearly always zero. However, suppose that we can generate r_i^N is proportional to $\exp[-\beta U(r_i^N)]$, then the ensemble average is simply:

$$\langle A \rangle = \lim_{n \rightarrow \infty} \frac{\sum_{i=1}^n A(r_i^N)}{n} \quad (23)$$

This sampling is called Metropolis sampling. As we can generate an infinitely large sequence of configuration on the computer, we estimate the average by taking a large value of n . To visit points with the correct frequency, the algorithm generates random trial moves from the old state (o) to the new state (n). The primary challenge of designing a Monte Carlo molecular simulation lies in devising ways to adequately evaluate the equilibrium distribution of the correct statistical mechanical ensemble [28].

Metropolis *et al.* showed that you could sample such a distribution by treating it as if it is a Markov chain [8]. In a Markov chain, each event in a sequence depends on the event that occurred directly before it as shown below:

$$P = (x_5 \mid x_4, x_3, x_2, x_1) = P(x_5 \mid x_4) \quad (24)$$

That is x_5 depends on x_4 and so on, so that the probability of a certain state being reached depends only on the present state of the chain. Let us say three states are x_1, x_2 and x_3 are connected by a transition probability (π) that is the probability of going from one state to the next (Figure 2). The matrix below illustrates the properties of a Markov chain:

$$\pi_{ij} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0.2 & 0.8 \\ 0.3 & 0.7 & 0 \end{bmatrix} \quad (25)$$

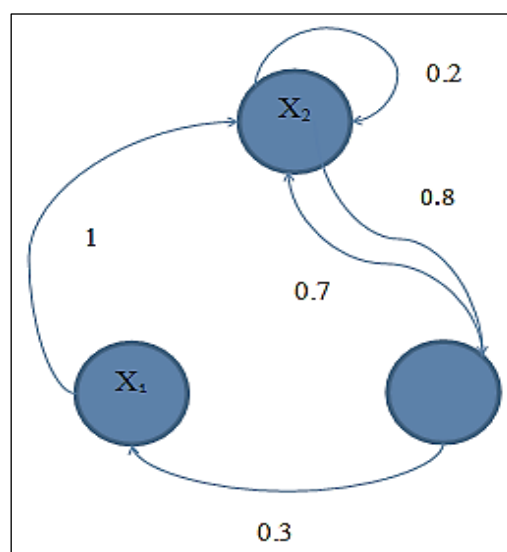


Fig. 2: Transition Graph.

It is easy to visualise Markov chain using a transition matrix or chart. From the model above, we can see that the next step of the system depends solely on the current state. If we are at x_2 , there is a probability of 0.1; the next step will be back to the same state and at a probability of 0.9, the next step will be x_3 . The primary objective of using this method is to design the move in such a way that the system intersects to a stationary distribution as given in Eq. (25). This chain has the important property that it is ergodic, meaning that it will visit every point in the domain and it will visit them a proportionate amount to their probability. To be ergodic the chain must be:

- Irreducible, that is from every state there is a positive probability of moving to any other state.
- Aperiodic, that is the chain must not get trapped in a cycle.

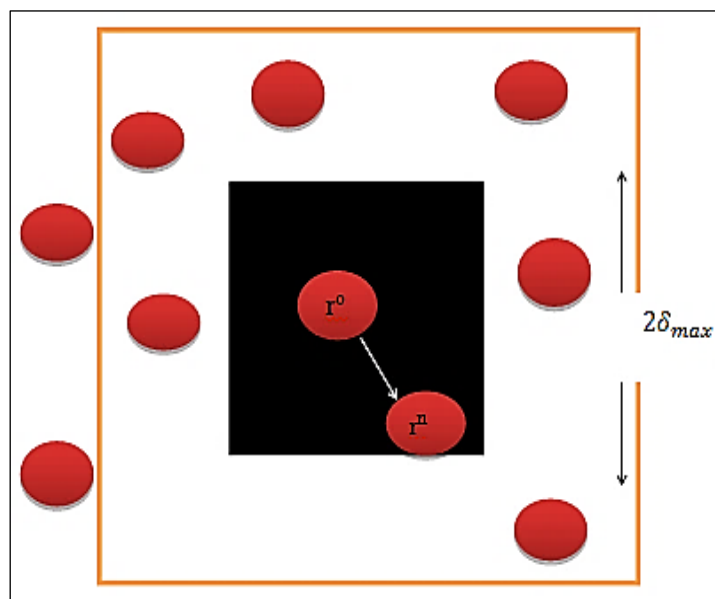


Fig. 3: Metropolis Sampling Method, a New Configuration is obtained by Moving an Atom with Uniform Probability to Any Point in the Square Box.

There are three types of moves or changes that have to be considered to generate a new configuration for a system. These are translation and rotation of the molecules and volume changes for a system where the volume is not constant.

The diagram above (Figure 3) shows six atoms in an initial state (o) to move a single atom in the phase space to the final state (n), a translational step is performed in a system, at the beginning of an MC move, an atom is picked at random and given a uniform displacement. The maximum displacement (δ_{max}) is an adjustable parameter that governs the length of possible translation of the molecule (Shaded Region) and controls the convergence of the Markov chain. If this value is large, there will be a high probability that the atoms of two molecules will overlap, making the molecules possess a significant, and positive interaction energy due to the repulsive part of the Lennard-Jones potential.

Such configuration is likely to be rejected by the Metropolis criterion for deciding whether to accept new states. If the parameter is too small, then the probability of accepting the state will be high, but it will take a long time for the configuration space of the system to be sampled adequately. In practice, the Metropolis algorithm to compute ensemble

averages of a system of a given number of particles in volume V is as follows:

1. Generate an initial configuration.
2. Start with a configuration, o and calculate its energy $U(o)$.
3. Select a particle at random.
4. Give the selected particle a random displacement, $x_n = x_o + \xi \delta_{max}$, where, δ_{max} is the particle maximum displacement and ξ is a random number between the interval (0, 1).

Calculate the energy $U(n)$ of the configuration n, where, $U(n)$ is the potential energy of the configuration.

1. Accept the trial move with a probability $acc(o \rightarrow n) = \min(1, \exp[-\beta(U(n) - U(o))]) = \min(1, \exp[-\beta(\Delta U)])$

Monte Carlo Simulation in the NPT Ensemble

In the NPT ensemble, starting from an initial distribution of molecules in an inner box, a new configuration is generated by randomly translating and rotating a randomly chosen molecule along Cartesian coordinate. New configurations are also produced by scrutinising the density of the liquid with volume changes. After a volume change, the centres of mass of all molecules in the reference box are scaled. The Monte Carlo

extension to the NPT ensemble is by Woods [29]. It was later applied to gas mixtures by McDonalds and samples the phase space of a constant N, constant P, and constant T ensemble with appropriate phase-space probability [3] (Figure 4). The NPT-ensemble average of a function $f(r^N, v)$ is given by:

$$\langle f(r^N, v) \rangle = \frac{\int_0^\infty dv \exp(-\beta PV) \int_v dr^N f(r^N, v) \exp(-\beta \Phi(r^N))}{\int_0^\infty dv \exp(-\beta PV) \int_v dr^N \exp(-\beta \Phi(r^N))} \quad (26)$$

The details of the Monte Carlo procedure to calculate the average are thus, let the potential energy of a given array of N particles within a cube of volume v' be Φ' , a test array is generated according to the rules.

$$\alpha_i \rightarrow \alpha_i + \lambda R^\alpha \quad (27)$$

$$L \rightarrow L + \mu R^L \quad (28)$$

Where, the particle i is chosen either recurrently or at random, the quantities $R_x^\alpha, R_y^\alpha, R_z^\alpha$ and R^L are chosen randomly and uniformly within the interval $(-1, +1)$, λ is a displacement parameter, and μ is a volume change parameter.

Let the total potential energy of the new configuration be Φ'' and let the new volume of the cube be v'' .

$$w = (\Phi'' - \Phi') + P(v'' - v') - N\beta^{-1} \ln \left(\frac{v''}{v'} \right) \quad (29)$$

The above quantity is calculated, and the new configuration is chosen to replace the old one with a probability P given by:

$$P=1, \text{ if } W \leq 0 \quad (30)$$

$$P=\exp(-\beta w), \text{ if } w > 0 \quad (31)$$

Repetition of the above procedure gives rise to a chain of configuration, which sample the whole phase space of the system. In this study, the Monte Carlo simulation in the NPT ensemble has been used to compute the chemical potential of a fluid at certain pressure and temperature.

The Widom Insertion Method is based on the thermodynamic definition of chemical potential, which involves insertion of a test particle into the N-particle simulation system at desired temperature and pressure [30].

The interaction energy of the virtual test particle with the N-particle system during the insertion move is used to calculate the chemical potential of the fluid. The chemical potential can be computed by:

$$\beta\mu = \ln(\Lambda^3 \beta \rho) - \ln \left\langle \frac{\beta PV}{N+1} \int ds_{N+1} \exp(-\beta \Delta U) \right\rangle \quad (32)$$

Where, μ is the chemical potential, β is the inverse of KT, Λ is the de Broglie wavelength, V is the volume of the simulation box, S_N is the scaled coordinates and ΔU is the system energy change induced by the insertion of the test particle.

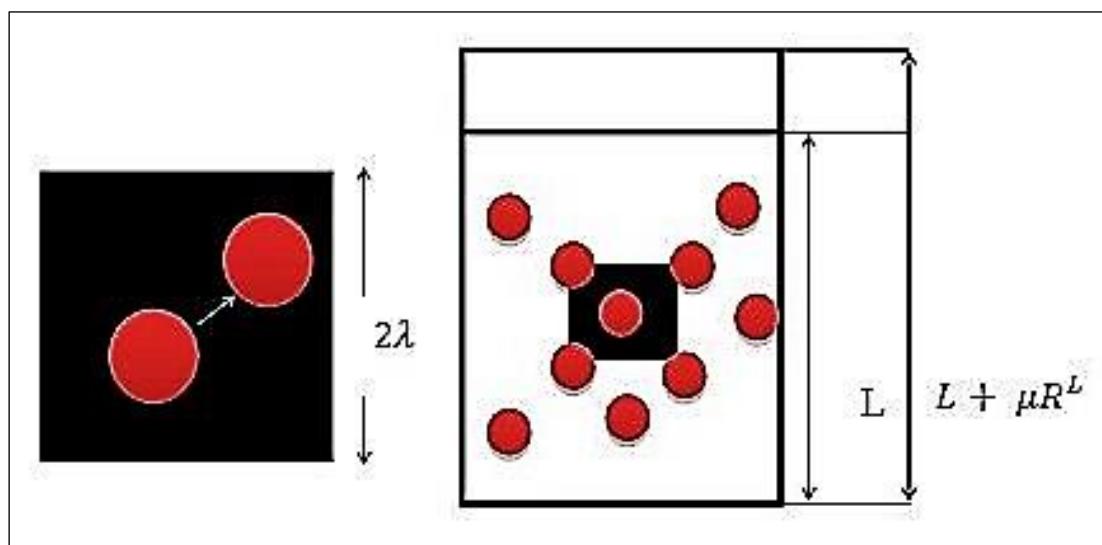


Fig. 4: Monte Carlo Sampling Method in the NPT Ensemble, Particle Moves and Volume Changes.

MATERIALS AND METHODS

Simulation Setup

Single box NPT Monte Carlo simulation was carried out using the computational program MCCS Towhee, to calculate the chemical potential of water at 298 K and 100 KPa [1]. Once the potential energy equilibrates, the Widom Insertion Method is employed in order to calculate the chemical potential. The primary use of the single box MC simulation in the NPT ensemble is to evaluate a property of a fluid at a certain point. In this study, MC simulation in the NPT ensemble is used to compute the chemical potential of water at a temperature of 298 K and 100 kpa (Figure 5). The evaluated chemical potential will be utilised in the GCMC or grand canonical ensemble to obtain isotherm of the fluid in an adsorbent over a range of temperature and pressure.

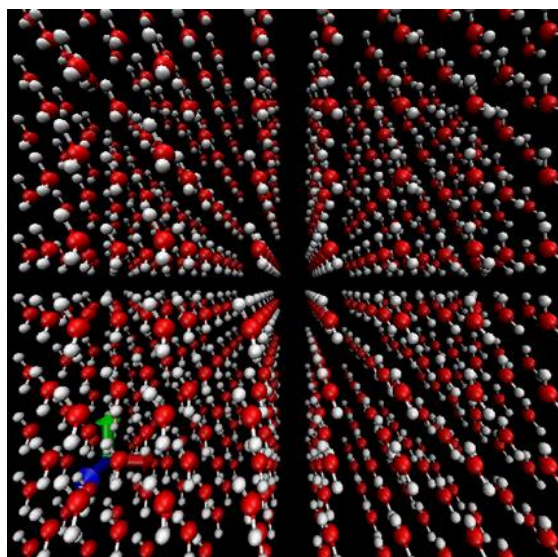


Fig. 5: Snapshot of Water Molecules in a Cubic Box Used in the Simulation; the Red Atoms Represent the Oxygen Atoms while the White Molecules are Hydrogen Atoms.

Potential Functions

The water force field interaction was described using SPC water model [31]. It is a three-point charge model where the charges on H are at 1.000 Å from the Lennard-Jones centre at O, the negative charge is at the oxygen site, and

the HOH angle is 109.47. The pair potential has the form:

$$v = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \quad (33)$$

Where, $\sigma = 3.1656\text{Å}$ and $\epsilon = 78.1970\text{ K}$ are the Lennard-Jones parameters between oxygen atoms on different water molecules, q_i is the charge in oxygen molecule of water, q_j is the charge in the hydrogen molecule ($q_O = -0.8476\text{ e}$ and $q_H = 0.4238\text{ e}$), and r_{ij} is the distance between charge site i and j in two or more water molecules.

Simulation Parameters

Monte Carlo simulation was carried out in a single box isobaric-isothermal ensemble (NPT) ensemble, in which the number of particles, pressure and the temperature is kept constant. The Monte Carlo simulation was executed using cubic samples of 645 monomers in a box of length 30 Å, periodic boundary conditions and Metropolis sampling at a temperature of 298 K and pressure of 100 kpa. Spherical cut-off at 15.0 Å was used in evaluating the energy including interactions with monomers nearest neighbour. New configurations were generated by randomly translating and rotating a randomly chosen monomer.

Also, the volume of the system was randomly selected and increased by a maximum displacement of 0.01 Angstroms, and all coordinates were scaled approximately. The ranges for the translations (0.5 Angstrom), rotations (0.4 degrees) and volume changes (0.05 Angstroms) were chosen to provide acceptance rate of 50% for the new configuration. In each case equilibrium involved at least 1,000,000 (1 M), while production runs and analysis was carried out over an additional 1,000,000 (1 M) settings. All simulations were performed using an Apple Mac Pro computer, OSX version 10.9.3., with a processor 2 GHz Intel Core 2 Duo.

Table 1: Conditions of Monte Carlo Simulation for SPC Water at 298 K and 100 Kpa.

N	Equilibrium	Average	$r_{cut}(\text{Å})$	$\Delta r(\text{Å})$	Δq	$\Delta V(\text{Å}^3)$
645	1×10^6	1×10^6	15.0	0.5	0.4	0.05

N is the number of molecules used in this study, equilibrium and average are the number of Monte Carlo steps for various runs respectively, r_{cut} is the cut-off ratio employed in this study and Δr , Δq and ΔV are the ranges for translation, rotation and volume respectively.

RESULTS AND DISCUSSION

Equilibrium Plot

Equilibration runs consisted of at least 10×10^6 MC moves during which the potential energy and pressure were monitored for convergence. Convergence meaning that equilibration had been achieved once the trends in these properties did not change with increasing simulation time. Figures 6 and 7 below show the Monte Carlo step at which the system reached equilibrium.

Chemical Potential

The isothermal-isobaric (NPT) ensemble Monte Carlo simulation values of the chemical potential of water at 298 K and 100 kPa are presented in Table 2. A value of -43.15 kJ/mol was obtained from this study while a value of -45.56 kJ/mol was published by Rao *et al.* [32]. In another study, a value of -44.5 was obtained for the TIP3P water [33]. All simulations were carried out using the MCCC Towhee software, the difference in values reported was only about 1%, the principal cause of variation in the result is due to the Monte Carlo steps, a longer running step will lead to the production of a more converged result. Furthermore, a recent study has confirmed that the algorithm used in the MCCC Towhee software has the capability of calculating the chemical potential accurately [1].

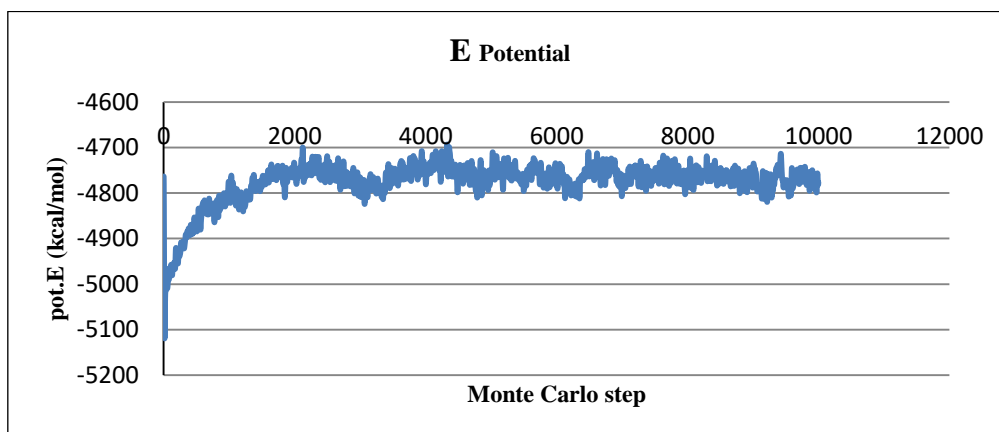


Fig. 6: Plot of Energy versus Monte Carlo Step.

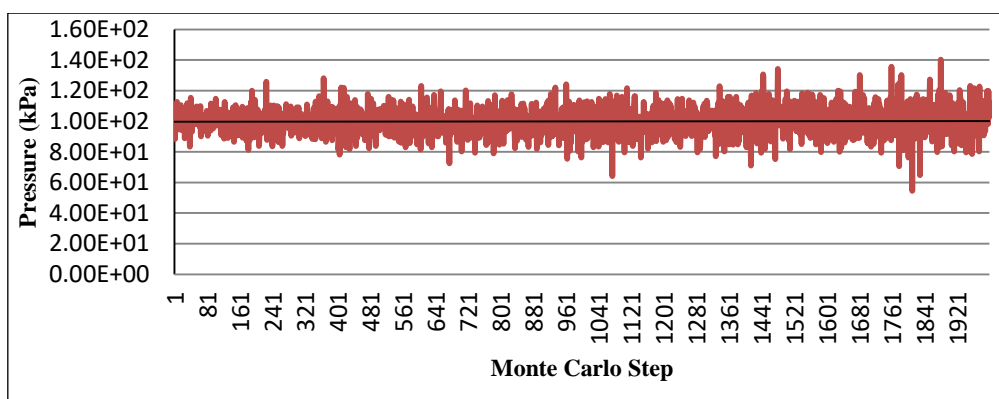


Fig. 7: Plot of Pressure versus Monte Carlo Step.

Table 2: Chemical Potential Values of Water at 298 K and 100 Kpa.

Temperature (K)	Pressure (KPa)	Water Model	Chemical Potential (kJ/mole)
298	100	SPC TIP3P	-45.56^a , -43.15^b -44.5^c

The value of subscript b represents the value of chemical potential obtained from this study, while the value with the subscript a, and c was taken from the work of reference.

CONCLUSION

Monte Carlo simulation in the NPT ensemble was conducted to determine the chemical potential of water and also to validate the MCCCSTowhee software.

The conclusions drawn from the research so far can be summarised as:

1. The previous study conducted reported a value of -45.56 kJ/mol for chemical potential, for the SPC water model, and -44.5 kJ/mol for the TIP3P water model, while from this study, a value of -43.15 KJ/mol was obtained [32]. The result obtained is quite close to the published result.
2. The purpose of carrying out the calculation of the water chemical potential is to use the value in the grand canonical (μVT) ensemble or Gibbs ensemble for further research.
3. From the study carried out, the SPC water model and software have been validated. Published studies have been conducted to verify the ability of the MCCCSTowhee software to calculate the chemical potential [1].

ABBREVIATIONS

MD: Molecular Dynamics

MC: Monte Carlo

NPT: Isobaric-Isothermal Ensemble

GCMC: Grand Canonical Monte Carlo

SPC: Simple point charge

TIP3P: Transferable Intermolecular Potential

NVT: Canonical Ensemble

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REFERENCES

1. Martin MG. MCCCSTowhee: A Tool for Monte Carlo Molecular Simulation. *Mol*

Simul. 2013; 39(14–15): 1212–1222p. doi:10.1080/08927022.2013.828208

2. Ayappa K, Malani A. Molecular Simulations: Probing Systems from the Nanoscale to Mesoscale. *J Indian Inst Sci.* 2012; 87. Retrieved from <http://journal.library.iisc.ernet.in/index.php/iisc/article/view/193/0>
3. McDonald IR. NpT-Ensemble Monte Carlo Calculations for Binary Liquid Mixtures. *Mol Phys.* 1972; 23(1): 41–58p. doi:10.1080/00268977200100031
4. Bonnaud P, Coasne B, Pellenq RJ-M. Molecular Simulation of Water Confined in Nanoporous Silica. *J Phys Condens Matter: An Institute of Physics Journal.* 2010; 22(28): 284110p. doi:10.1088/0953-8984/22/28/284110
5. Jin Z, Firoozabadi A. Methane and Carbon Dioxide Adsorption in Clay-Like Slit Pores by Monte Carlo Simulations. *Fluid Phase Equilib.* 2013b; 360: 456–465p. doi:10.1016/j.fluid.2013.09.047
6. Jabbarzadeh A, Tanner R. Molecular Dynamics Simulation and its Application to Nano-Rheology. *Rheology Reviews.* 2006. Retrieved from <http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:MOLECULAR+DYNAMICS+SIMULATION+AND+ITS+APPLICATION+TO+NANO-RHEOLOGY#0>
7. Rapaport DC. *The Art of Molecular Dynamics Simulation.* *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki.* 2004. Retrieved from <http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:No+Title#0>
8. Nicholas Metropolis, Rosenbluth Arianna W, et al. The Equation of State Calculation by Fast Computing Machines. *J Chem Phys.* 1953; 21(6).
9. Alder BJ, Wainwright TE. Phase Transition in Elastic Disks. *Phys Rev.* 1962; 127: 359–61p.
10. Alder BJ, Wainwright TE. Phase Transition for a Hard Sphere System. *J Chem Phys.* 1957; 27(5): 1208p. doi:10.1063/1.1743957
11. Alder BJ, Wainwright TE. Studies in Molecular Dynamics. I. General Method. *J*

- Chem Phys.* 1959; 31(2): 459p. doi:10.1063/1.1730376
12. Shroll RM, Smith DE. Molecular Dynamics Simulations in the Grand Canonical Ensemble: Application to Clay Mineral Swelling. *J Chem Phys.* 1999; 111(19): 9025p. doi:10.1063/1.480245
 13. Zhou Q, Lu X, Liu X, *et al.* Hydration of Methane Intercalated in Na-Smectites with Distinct Layer Charge: Insights from Molecular Simulations. *J Colloid Interface Sci.* 2011; 355(1): 237–42p. doi:10.1016/j.jcis.2010.11.054
 14. Rahman A. Correlation in the Motion of Atoms in Liquid Argon. *J Phys B: Atomic, Molecular and Optical Physics.* 1964; 136.
 15. Rahman A. Molecular Dynamics Study of Liquid Water. *J Chem Phys.* 1971; 55(7): 3336p.
 16. Nath SA, Escobedo FA, de Pablo JJ. On the Simulation of Vapour-Liquid Equilibria for Alkanes. *J Chem Phys.* 1998; 108: 9905p.
 17. Karayiannis NC, Mavrantzas VG, Theodorou DN. A Novel Monte Carlo Scheme for the Rapid Equilibration of Atomistic Model Polymer Systems of Precisely Defined Molecular Architecture. *Phys Rev Lett.* 2002; 88(10). doi: 10.1103/physrevlett.88.105503.
 18. Boek ES, Coveney PV, Skipper NT. Monte Carlo Molecular Modeling Studies of Hydrated Li-, Na-, and K-Smectites: Understanding the Role of Potassium as a Clay Swelling Inhibitor. *J Am Chem Soc.* 1995; 117(50): 12608–12617p. doi:10.1021/ja00155a025
 19. Dubbeldam D, Torres-Knoop A, Walton KS. On the Inner Workings of Monte Carlo Codes. *Mol Simul.* Taylor & Francis; Dec 2013. doi:10.1080/08927022.2013.819102
 20. Diaz-Campos M, Akkutlu IY, Sigal RF. A Molecular Dynamics Study on Natural Gas Solubility Enhancement in Water Confined to Small Pores. *SPE Annual Technical Conference and Exhibition.* 2009. doi: 10.2118/124491-MS
 21. Cygan RT, Liang J-J, Kalinichev AG. Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field. *J Phys Chem B.* 2004; 108(4): 1255–1266p. doi:10.1021/jp0363287
 22. Rappe AK, Casewit CJ, Colwell KS, *et al.* UFF, A Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *J Am Chem Soc.* 1992; 114(25): 10024–10035p. doi: 10.1021/ja00051a040.
 23. Lennard-Jones J. The Equation of State of Gases and Critical Phenomena. *Physica.* 1937. Retrieved from <http://www.sciencedirect.com/science/article/pii/S0031891437801913>
 24. Mourits F, Rummens F. A Critical Evaluation of Lennard-Jones and Stockmayer Potential Parameters and of Some Correlation Methods. *Can J Chem.* 1977; (2). Retrieved from <http://www.nrcresearchpress.com/doi/abs/10.1139/v77-418>
 25. Jorgensen WL. Quantum and Statistical Mechanical Studies of Liquids. 10. Transferable Intermolecular Potential Functions for Water, Alcohols, and Ethers. Application to Liquid Water. *J Am Chem Soc.* 1981; 103(2): 335–340p. doi: 10.1021/ja00392a016.
 26. Yazaydin O. *Molecular Simulation of the Adsorption of Organics.* Worcester Polytechnic Institute; 2007.
 27. Allen MP, Tildesley DJ. *Computer Simulation of Liquids.* Oxford, United Kingdom: Clarendon Press; 1987.
 28. Martin MG, Siepmann JI. Transferable Models for Phase Equilibria 1. United-Atom Description of n-Alkanes. *J Phys Chem B.* 1998; 102: 2569p.
 29. Wood WW. Monte Carlo Calculations for Hard Disks in the Isothermal-Isobaric Ensemble. *J Chem Phys.* 1968; 48: 415–34p.
 30. Widom B. *J Chem Phys.* 1963; 39: 2808–2812p.
 31. Berendsen H. The Missing Term in Effective Pair Potentials. *J Phys Chem.* 1987; 6269–6271p. Retrieved from <http://pubs.acs.org/doi/abs/10.1021/j100308a038>
 32. Rao Q, Xiang Y, Leng Y. Molecular

- Simulations on the Structure and Dynamics of Water-Methane Fluids between Na-Montmorillonite Clay Surfaces at Elevated Temperature and Pressure. *J Phys Chem C*. 2013; 117(27): 14061–14069p. doi:10.1021/jp403349p
33. Tambach TJ, Bolhuis PG, Hensen EJM, *et al.* Hysteresis in Clay Swelling Induced by Hydrogen Bonding: Accurate Prediction of Swelling States. *Langmuir*. 2006; 22(3): 1223–1234p.

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