

# Investigations of Freezing Pure Water

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May 2, 2013

## Abstract

We use a the molecular simulation package LAAMPS to simulate the freezing of water. We analyze the SPC and TIP3P potentials to simulate water at different temperatures to analyze the dynamics. Temperature is modified using a Nose-Hoover method or a Berendsen method. Structure Factors and energies versus times were calculated to attempt to locate a phase transition.

## 1 Introduction

Water covers most of the surface of the earth as both ocean water or ice. Life as we know it requires water as much of the chemistry of life takes place in solution. Because of its importance and simple structure water is commonly simulated in molecular dynamics. Its homogeneity and many other properties make water a frequent choice for simulation, however water remains difficult to simulate. There still isn't agreement in the literature about how water freezes and many simulations produce different answers.

Our project involves using the molecular dynamics simulation program LAMMPS. Developed at Sandia National Laboratory LAMMPS is a general purpose molecular dynamics program designed to work with many different potentials. For our experiment we modified the code to allow us to set up our own customized initial conditions and allow better temperature control. To visualize our data and set up initial conditions we used VMD, a molecular graphics software. This allowed us to watch our water as it changed from liquid to solid.

We describe the results of our molecular dynamics simulations and our many attempts to freeze water below.

## 2 Methods

We used two different water potentials. Our first and simpler potential is TIP3P which assigns each atom as a point charge. A Leonard-Jones Potential keeps the oxygen and hydrogen well positioned while a coulomb force attracts water molecules to one another. TIP3P depends on many parameters including

Table 1: TIP3P values for water

Variable	Value
r(OH),	0.9572
HOH, deg	104.52
A 103, kcal 12/mol	582.0
B, kcal 6/mol	595.0
q(O)	0.834
q(H)	+0.417

From the Literature[3] shows the melting temperature of water using the TIP3P model is 146K. The model is not optimized for freezing and freezes to ice 2 instead of the expected ice 1 observed when water freezes in the laboratory. Because of expected Histeris effects we expect our water sample to freeze at an even lower temperature. Overall TIP3P doesn't do a great job of simulating water however its simplicity makes it useful for other simulations.

A second method is SPC. SPC is a three point potential and takes into account an average polatization of the molecule. This model works better for pure water however is still an imperfect potential to use to simulate water.

$$E_{pol} = \frac{1}{2} \sum_i \frac{(\mu - \mu^0)^2}{\alpha_i}$$

is the dipole of the effectively polarized water molecule,  $\mu$  the dipole moment of an isolated water molecule (1.85 D from experiment), and  $\alpha_i$  is an isotropic polarizability constant, with a value of  $1.608 \cdot 10^{-40}$  F m<sup>2</sup>. This correction adds a noticable energy to the water sample which alters the dynamics. We ran the same experiments on this potential at TIP3P. In addition to the polarizability we have to include the standard parameters that go with any three point potential.

We used two different temperature controls. The first is Nose-Hoover which works by adding a frictional term to the Hamiltonian to simulate a heat reservoir. Heat is either added or subtracted based on the average kinetic energy of the particles and the desired temperature.

$$\mathcal{H}(P, R, p_s, s) = \sum_i \frac{\mathbf{p}_i^2}{2ms^2} + \frac{1}{2} \sum_{ij, i \neq j} U(\mathbf{r}_i - \mathbf{r}_j) + \frac{p_s^2}{2Q} + gkT \ln(s)$$

Second we used the Berendsen temperature control scheme to control water temperature. Berendsen thermostat couples the atoms to an external heat bath with a temperature derivation that is slowly corrected. A time constant  $\tau$  controls how quickly the system goes to equilibrium.

$$\frac{dT}{dt} = \frac{T_0 - T}{\tau}$$

Both methods came preprogrammed into LAMMPS. We ran both temper-

ature controls on both potentials. In both cases the temperature changed at about  $10^{13}$  K / sec an unrealistically fast rate but a nessisary to allow for the simulation of water.

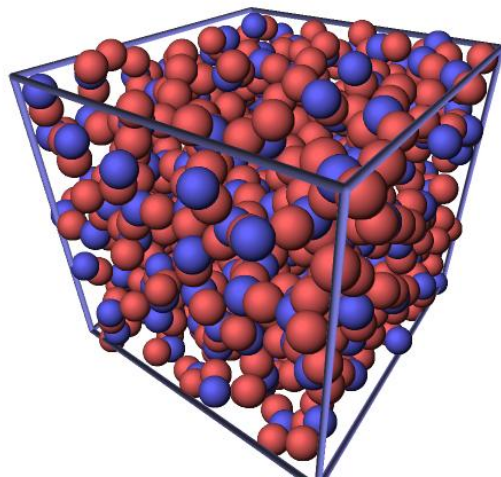


Figure 1: A simulated Box of Water

To visualize and manipulate our data we used ovito a graphics interface tool. Ovito is an open source visualisation software for molecular dynamics.

### 3 Comparison of potentials and thermostats

We started our project by comparing the different pair correlation function of water at 300K for the two different Potentials. Both were created using LAMMPS and allowed to run for a decent amount to time before measurement.

The Correlation functions are consistent with one another and are similar to the expected correlation function for water.

Both Potentials for water were initialized at 300K then cooled to 100K. Previous research indicates the phase transition would happen before this point. To Look for a phase transition we calculated the correlation function at 100K. Below are the correlation functions at 100K.

The pair correlation function has a larger peak and a larger gap before the next peak. Both of these indicate the water molecules are organized in a different way than they were at 300K. We conclude SPC-E froze between these temperatures. Our limited simulation time prevented us from acquiring additional data.

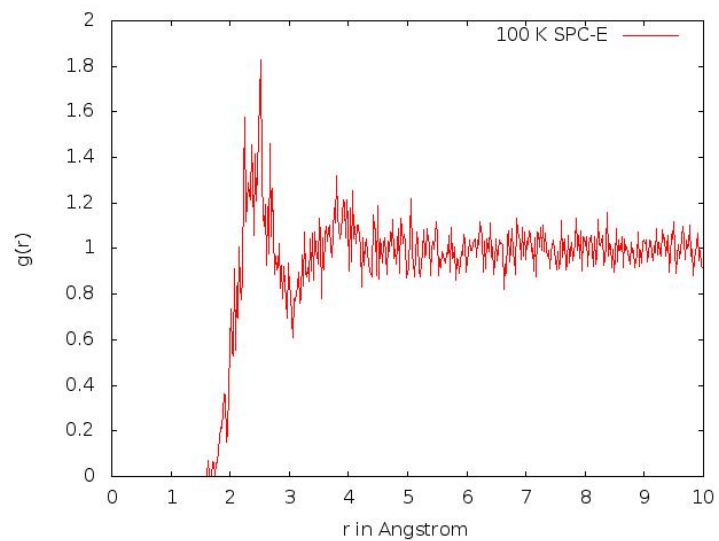


Figure 2: Correlation function using SPC-E potential At 300K

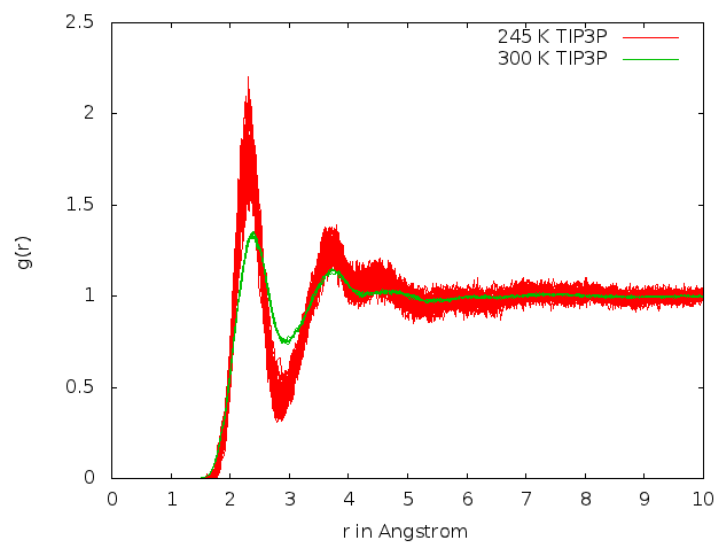


Figure 3: Correlation function using TIP3P potential At 300K

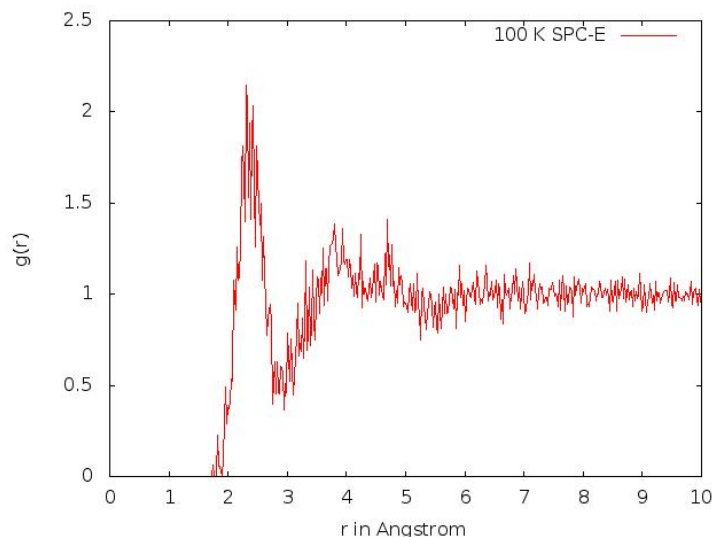


Figure 4: Correlation function using SPC-E potential At 100K

### 3.1 Total Energy while cooling

Additional evidence of a phase transition should be visible by examining the total energy as we cool our system. The degrees of freedom of a substance often decrease with a liquid to solid transition. Naively the energy as a function of temperature should have a noticeable change around the freezing temperature. Below is plotted energy as a function of time as we cooled our potential using the Nose-Hoover Algorithm.

The curve for TIP3P water shows a drop in energy at about 270 K. This is probably due to a phase transition. However the curve for SPC-E water has no such similar drop. This is likely a property of the potential itself and not a true phenomenon for water.

### 3.2 Berendsen Temperature Control

Our implementation of the Berendsen temperature control wasn't effective. The time scales required to implement a Berendsen thermometer require more computer time that we have. When we try to run the Berendsen temperature control at a faster rate we have to rebuild our neighbor table at every step requiring to much computer time to efficiently generate data.

## 4 References

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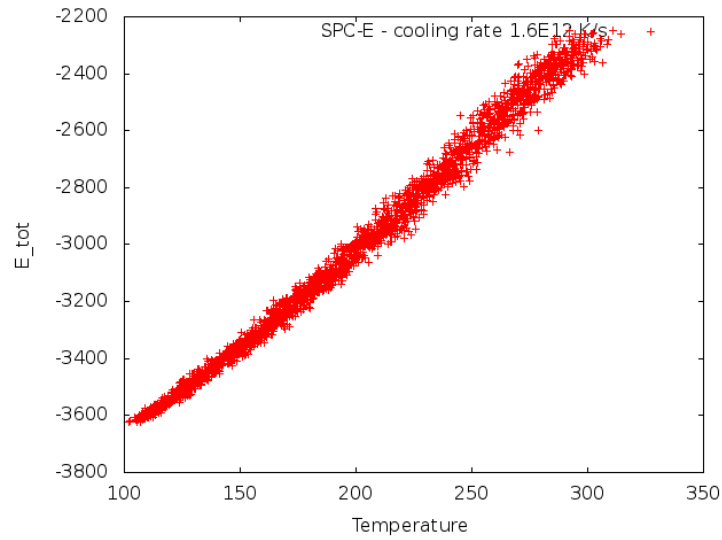


Figure 5: Measuring Energy versus temperature as SPC-E water cools

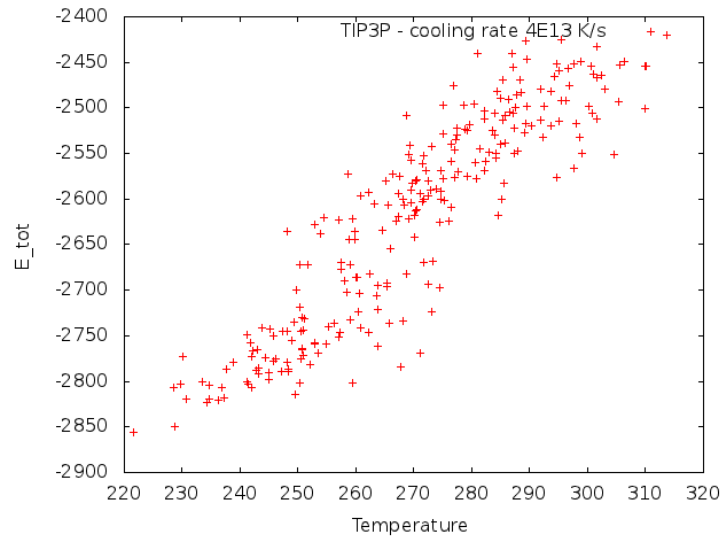


Figure 6: Measuring Energy versus temperature as TIP3P water cools

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