Investigation of Aggregation By Comparing Fully Charged And Selectively Charged System.

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Abstract

The study of constant pH simulation systems plays an important role in the study of biological system. In this project we simplified the variable protonation state by assigning the charge selectively by skipping an atom. We then used LAMMPS to compute molecular modelling until the system is stable, which is checked using the stability of total energy change per time step. We compared the behavior of the system with the system which is fully charged. We also investigated the effect of epsilon and cut off distance toward aggregation. We concluded with a recommendation of increasing the aggregation of the system by using an additional atom type as an aggregation factor or nucleation site.

Introduction

Purpose

The purpose of this simulation is to understand the effect of of Lennard Jones and coulombic potential on aggregation on a fully charged and selectively charged system.

Lennard Jones and Coulombic Interactions

For non-ideal system, the potential energy of the system is the sum of the multi-bodies interaction. Other than low temperature and high density system, the pairwise, two-body interaction, dominates the overall total potential energy of the system. The interaction can be represented as a function of the distance between the two interacting bodies. [1][3]

When two atoms come close enough they will attract each other due to the momentary polarization of particles, which is called van der Waals attraction. This is due to the formation of dipole-dipole interaction due to the disturbance in the electronic cloud of the interacting atoms. As the atoms get too close to each other the attractiveness will be replaced by the repulsive force due to an overlap. [2]

This relationship is represented by a simple model of Lennard-Jones potential

$$V_{LJ} = 4 * \varepsilon * \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right)$$

where r_{ij} is an interaction radius between particle i and j, and V_{LJ} is the potential energy.

The parameters that are usually used to quantify the interaction are ε, σ and U(t). Epsilon, ε represent the depth of the interaction which attractiveness is directly proportional to the attractiveness between the atoms. Sigma is the distance where the total potential of the system is at zero.
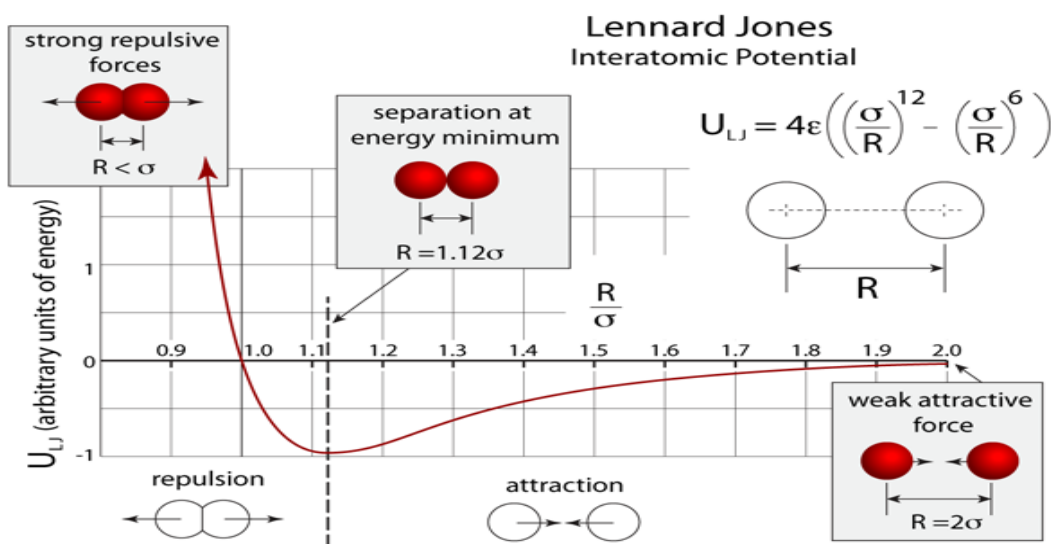

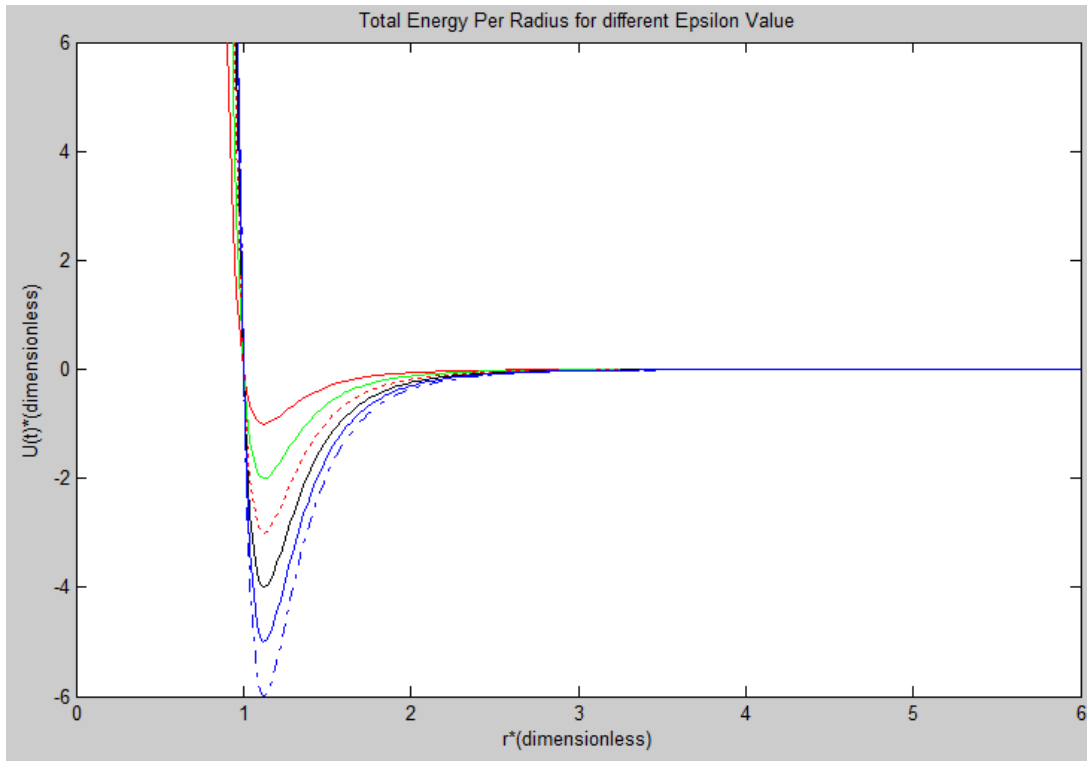Figure 1: detailed diagram of the Lennard Jones Interaction [1]

Figure 2: variation of total energy with epsilon change. Red line is for ε=1, green line for ε=2 and so on. As epsilon increase, the steepness of the total energy falling increases too.

Figure 2 shows that after the radius(r*) reaches to approximately 2.5, the value of the total energy become close to zero. This r* value is usually taken as a cutoff distance. After this radius, the interaction between two particles will be weaker but it won't be exactly to zero. The point where all the graph intersected with the U(t)=0 can be considered as the value of σ, which is equal to 1 from above graph. This project used the same assignment for the value of σ. The radius is where there is a significant drop in total energy is considered the maximum distance for the optimal interaction.

Another factor that affect the pairwise interaction is electrostatic interactions. This interaction can be described using Coulomb's law

$$u_{ele} = K * \frac{qi*qj}{r_{ij}}$$

Where K is $\frac{1}{4*\pi*\varepsilon*r_{ij}}$

For the charged atom, total potential energy of the system is the sum of all pair wise interaction, including electrostatic force and intramolecular terms.

Since we have radius of the interaction at the denominator of the Lennar Jones potential calculation, soft pair style is used to avoid potential computational error when the radius of interaction goes to zero. This helps to push apart the overlapping atoms. The soft pair style relates with the cut off distance with

$$E = A * \left[1 + \cos\left(\frac{\pi*r}{r_c}\right)\right] \qquad where\ r < r_c$$

A is the value of energy and r_c is the cut off for zero interaction atoms.

To create a system trajectory consistent with the microcanonical ensemble, performing a constant NVE integration to produce the position and velocity for each group of atoms in the time step is necessary. Performing constant NVE integration means keeping the total energy, volume and composition of the system constant with respect to the time step by using conservation of energy.

Constant pH Molecular Dynamics

In living systems, pH is an important means of regulating biological activity. This includes protein-folding, protein-protein interactions, and enzymatic activity. Many of the biological function occur at the constant, or close to constant, pH value. Having an accurate and reliable means to keep the pH constant in the simulation will highly increase the information that can be found from it.

In constant pH molecular dynamics simulation, the protonation of the atom is allowed to change during the system maintain the same protonation amount. This project tries to examine the overall challenges of allocating charges to the atom and tries to also get insight into the interaction with the lennard jones potential. For the detail of allocation of charges, refer to the method section below.

Method

The two dimension simulation, 30x30, is preferred to due to simplicity and for the sake of minimizing the computational cost for the behavior we want to study. This behavior was adjusted by enforcing the two dimension, setting z to 0, using enforce2d method. Only one bond type and four atom type are used in this simulation. The charge of the atoms are assigned manually after assigning the atomic style to full. We used the harmonic bond type with the multiplicity of the energy constant, specified as 50, with the square of the difference between

interaction between interaction radius and equilibrium radius of 0.75. The value of 1.2246 is used for r_c and 0.0 for value of A. Only 150 solvents are turned to be surfactant all runs we performed.

By setting the fix on NVE, the system performs constant NVE integration over the time step. Using the command fix temp/rescale, the temperature was kept close to constant over the time step by explicitly rescaling the velocities. The frequency of the temperature rescaling set to be performed every 100 step. It is important to note that we only applied a translational degree of freedom for the particles by setting this rescaling using the fix command.

The Lennard Jones interaction cut and columbic cut is used, using pair_style method, to manipulate the relationship between solvent and the micelle. Multiple runs were performed using different value for Lennard Jones and columbic potential force exchange. The results are included in the discussion section.

Acceptable number of run is verified by plotting the total energy and the temperature with respect to time step. The stability of the total energy against the change in time step is taken as an indicator for the stable over all system which verified the validity of the number of the run. These graphs are included in the appendix section.

We run the simulations in two sets as shown here and we compared the completion between electrostatic and Lennard Jones, as show in the discussion.
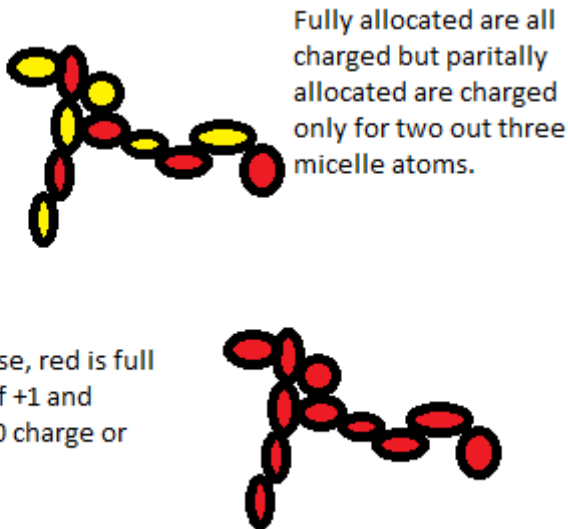
Partially Allocated		Fully Allocated	
ε	rc	ε	
6	1.25	6	1.25
6	9	6	9
1	9	1	9

Table 1: Sets of inputs

We arranged this this order to get a better comparison between epsilon and rc effect in the aggregation. This way we can compare the effect of changing the epsilon while keeping the cutoff radius and vice versa.

Charge allocation

We assumed the following model for the full and the partially allocated charged-

Fully allocated are all charged but paritally allocated are charged only for two out three micelle atoms.

In both case, red is full charged of +1 and yellow is 0 charge or neutral.

system.

Figure 3: Charge allocation

Result and Discussion

Expectations

Our expectation for our system is

1. If the system was not charged, then we will be see the set which has the highest value of ε and higher r_c value , as long as r_c is not too big from sigma, having higher total energy. This is due to the fact the when r_c value increase the sum will also increase up to certain point of r_c where it won't significantly matter. This should lead to larger aggregation of the pink, type 2, for the set of run with ε=6 and r_c=9. The fully charged system should also exhibit more or less similar behavior.

2. For the system with partially allocated charges, it is expected that the system will exhibit similar behavior, with a reasonable modification due to the added computation of between the charged and uncharged molecules. For the charge that are neutral, they are not affected by the columbic interaction directly. Considering this, we except higher interaction between charged/charged particles than charged/uncharged particles.

3. We expect the aggregated micelle might look like G-2/G-3 dendimer as we increase the epsilon value for 2-2 interaction, which we chose to be head interaction.

Stable System Result and Discussion

Six different set of parameters simulated to be used for the comparison. For all system, type 1 is blue, type 2 is pink, type 3 is purple, and type 4 is green. For partially allocated system, type 2 and type 2, or pink and purple, are charged +1 and green and blue left as uncharged.
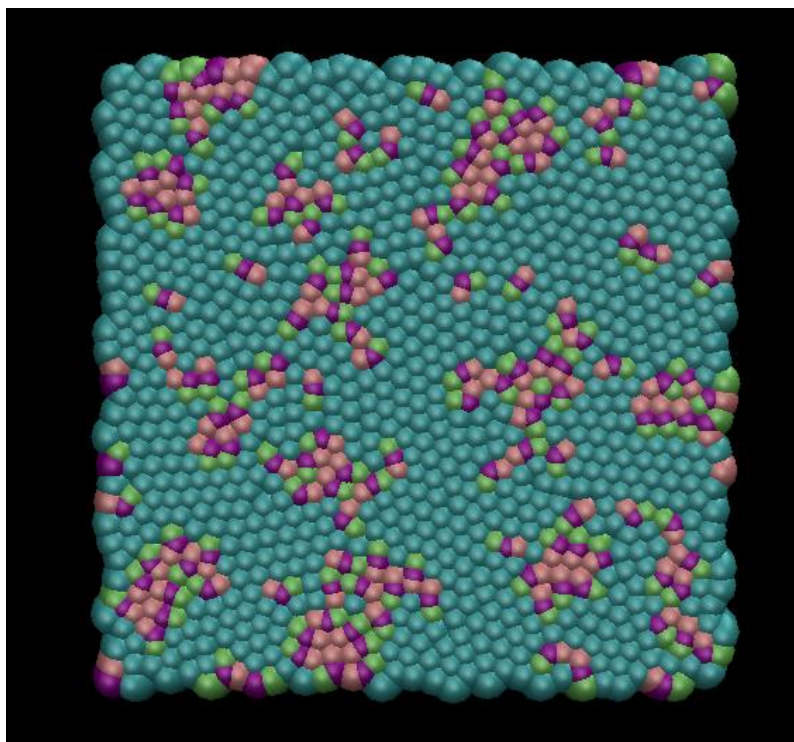

Figure 4 : for partially allocated charges where the head has epsilon of 6 and a cut off of 1.25

For this system, the pink and the purple tend to favor each other when green favor purple. Even if there is an expectation for the charged particle to repeal each other, we concluded that pink and purple were heavily interacting because of the coulomb cut off assigned, 2.5, and may also be due to the bond data provided. The uncharged particle are not affected by the coulomb potential and

affected by their proximity . They arranged with high preference for purple than pink. This high preference for purple were not expected due to the similar pair coefficient that was set for all types other than 2-2. We expected since pink and purple both charged, and green is not, there will be equal preference for green towards pink and purple. We suspected this behavior is due to bond data that we used as a default set up that we didn't change. Considering this bond data were design to create more organized my cell this suspicion seems reasonable. Pink atoms tend to favor each other due to the higher epsilon value they have.
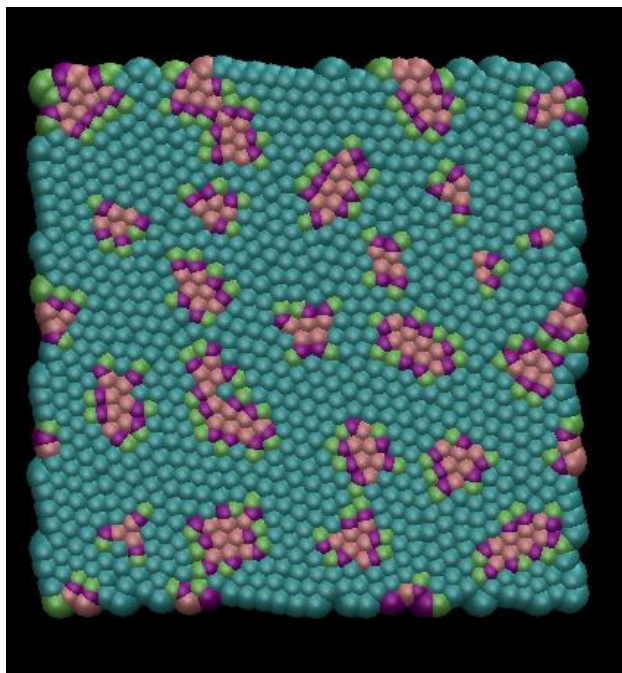
Figure 5: for partially allocated charges where the head has epsilon of 6 and a cut off of 9:

In this system there is a larger amount of aggregated pink atoms. This is due to the high epsilon and cut off value it has. Even if the pink atoms are positively

charged, their epsilon value, and also the fact that it is a 70% dense system, helped them aggregate better. There is a longer aggregation due to the higher attractions between the pink atom types.
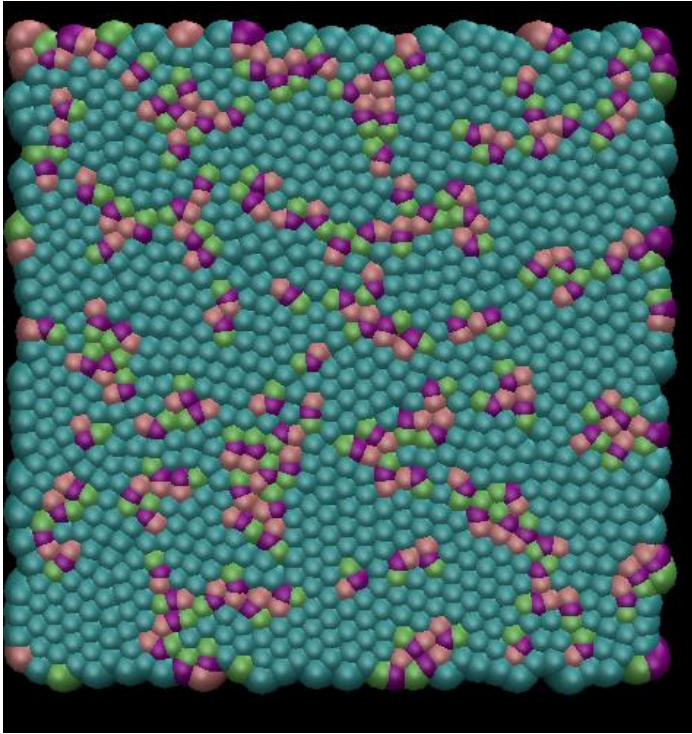

Figure 6:for partially allocated charges where the head has epsilon of 1 and a cut off of 9

This system didn't aggregate as both of the above system due to low epsilon value, which is translated as low attractive energy between them. So, for the same time step as above they formed more dispersed structure where the preference for each other is still slightly there, mainly due to amount since the cut off is large. This shows that epsilon value has significant effect in the aggregation than the cut off radius.
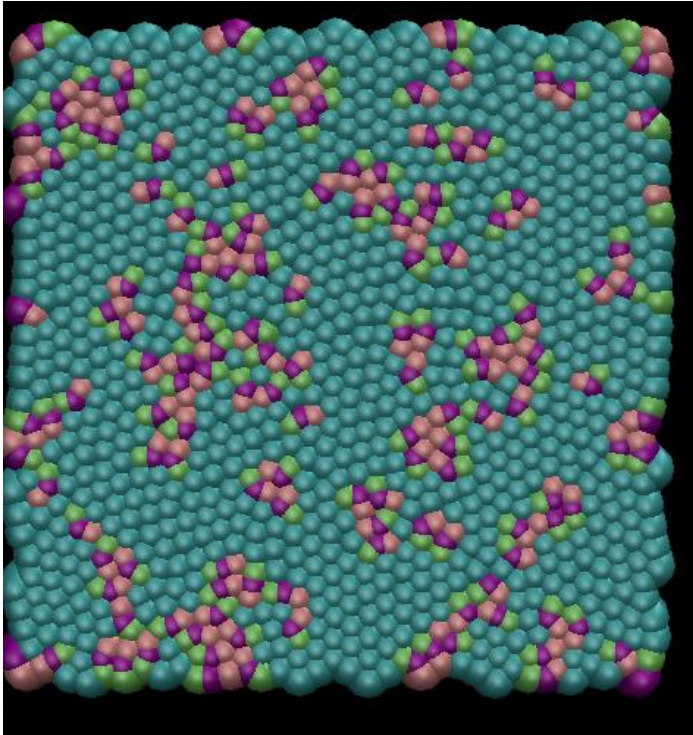
Figure 7: for fully allocated charges where the head has epsilon of 6 and a cut off of 1.25

In this system, all atoms have the same positive charge. Even if there is limited aggregation due to high epsilon value, they then to form longer chain than bulky structure. This is due to equal distribution of positive charges between the surfactants.
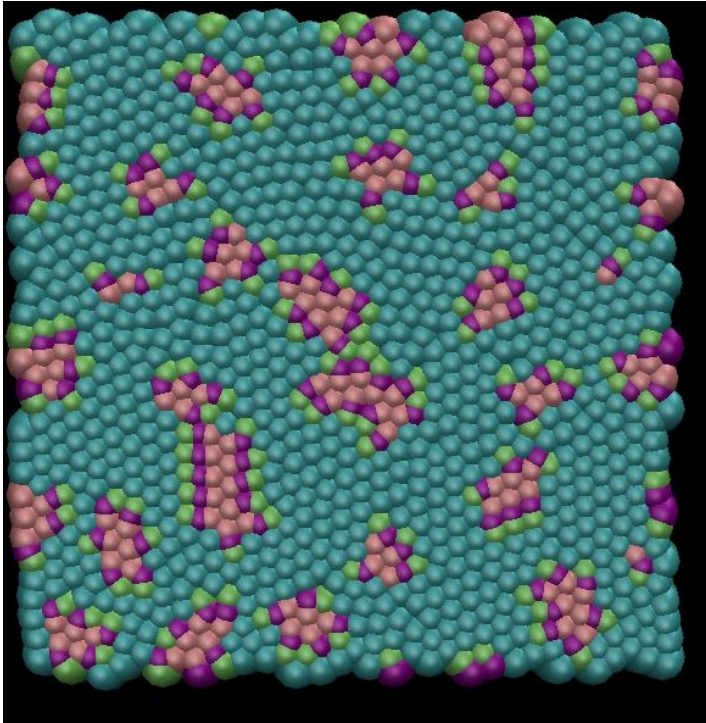
Figure 2: fully allocated charges where the head has epsilon of 6 and a cut off of 9

As shown in the above structure, the fully charged system tend to form longer chains than the partially allocated one. This is also due to the uniform distribution of charge between the surfactant.
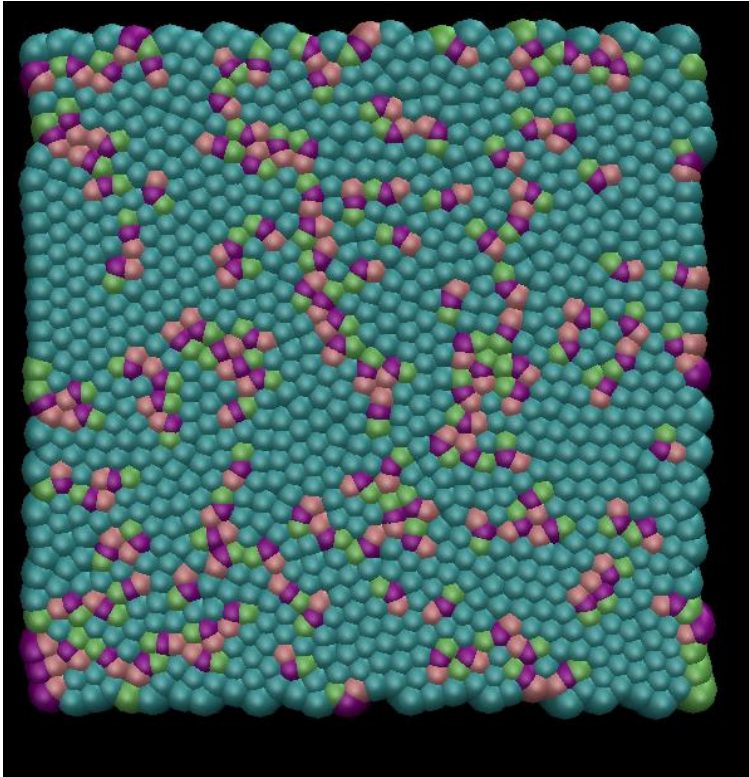
Figure 3: for fully allocated charges where the head has epsilon of 1 and a cut off of 9

As the above two systems where the fully charged surfactant preferred to create a longer chain rather than short bulky system, this system also preferred longer chain formation, but much longer chain due to low epsilon value.

Refereeing to our expectation, the system observed is consistent with our expectation, except the high preference of green and purple atoms.

Conclusion

To increase the aggregation of the selected atom, here type 2, we recommend keeping the epsilon value high for it while keeping the other atom type's epsilon value lower. It also help to decrease the pair wise interaction capacity of head

and tail to lower competition for the head aggregation. Keeping the different tail atoms interaction in the same chain strong and also decreasing the interaction between tail atoms of the same type will increase the formation of more symmetrical structure.

As we have seen in the above systems the pink were performing as nucleation site for the formation of a bulky, slightly symmetrical structure. This can also enhanced by adding other atom type whose primary purpose is to behave as a strong nucleation site for the pink atom to aggregate around. This will help to effectively limit the number of pink atoms that will serve as a group-nucleation site and produce more symmetrical structure.

Appendices

Partially Charged

Table 1
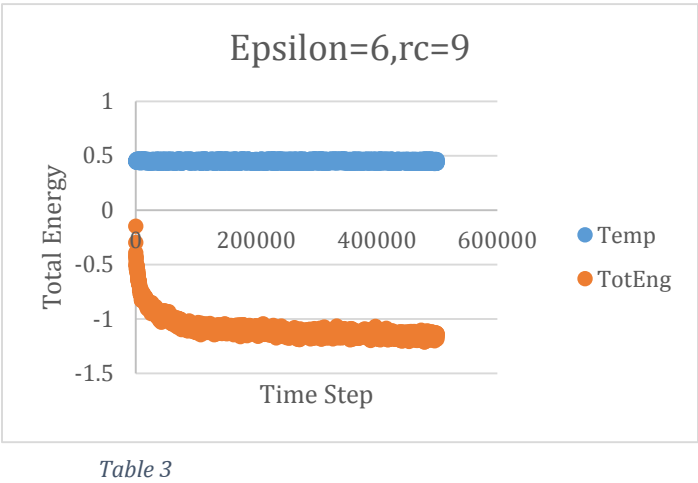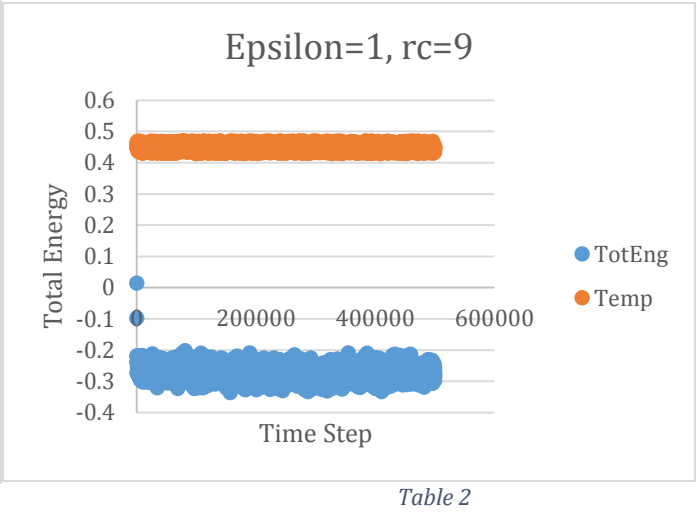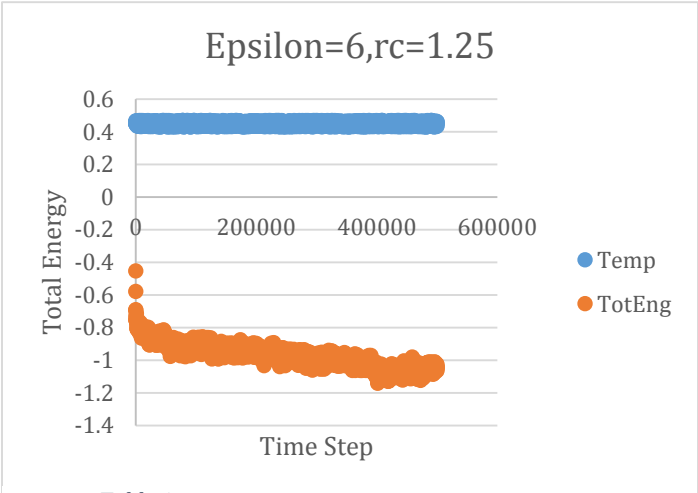
Table 2

Table 3

Fully Charged
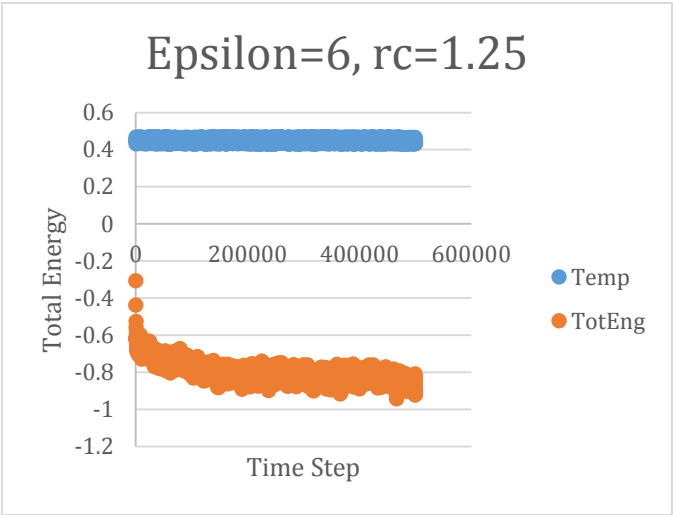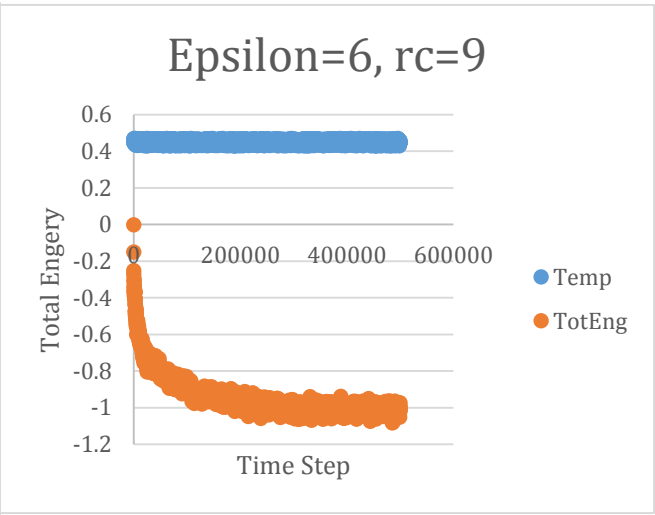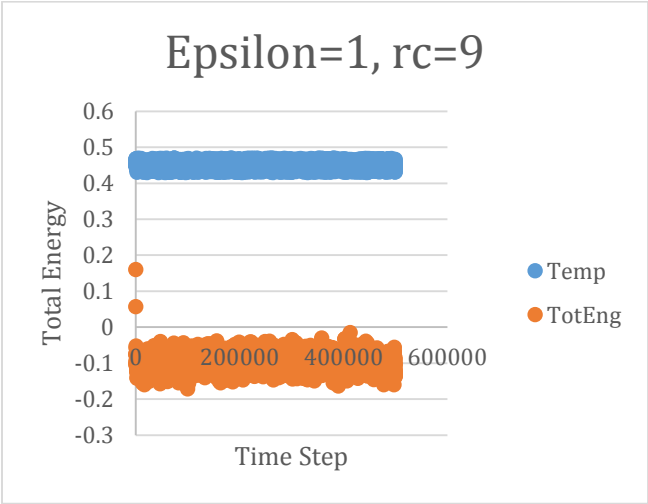

Table 5

Table 4

Table 6

Sample Input

```
# 2d micelle simulation

dimension      2
neighbor       0.3 bin
neigh_modify   delay 5
atom_style full
#***************************************************************
read_data      data111.micelle
special_bonds  fene
#***************************************************************
pair_style     soft 1.12246
pair_coeff     * * 0.0 1.12246
#***************************************************************
bond_style     harmonic
bond_coeff     1 50.0 0.75
#***************************************************************
velocity       all create 0.45 2349852
variable       prefactor equal ramp(1.0,20.0)
fix            1 all nve
fix            2 all temp/rescale 100 0.45 0.45 0.02 1.0
fix            3 all adapt 1 pair soft a * * v_prefactor
fix            4 all enforce2d

thermo         50
run            1000
unfix          3
#***************************************************************
pair_style lj/cut/coul/cut 2.5
dielectric 1
pair_coeff * * 1.0 1.0 1.125
pair_coeff     2 2 6.0 1.0 1.25
pair_coeff     3 4 1.0 1.0 1.25
pair_coeff     2 4 1.0 1.0 1.25
pair_coeff     2 3 1.0 1.0 1.25
pair_coeff     3 3 1.0 1.0 1.25
pair_coeff     4 4 1.0 1.0 1.25
#***************************************************************
thermo         100

dump           1 all atom 10000 c1dump.micelle
log c1log.txt

reset_timestep 0
run            500000
```

References

1. Goh, Garrett B., Benjamin S. Hulbert, Huiqing Zhou, and Charles L. Brooks. "Constant PH Molecular Dynamics of Proteins in Explicit Solvent with Proton Tautomerism." *Proteins: Structure, Function, and Bioinformatics* (2014): N/a. Print.

2. Kaznessis, Yiannis Nikolaos. *Statistical Thermodynamics and Stochastic Kinetics: An Introduction for Engineers*. Cambridge: Cambridge UP, 2012. Print. .

3. "LAMMPS Molecular Dynamics Simulator." *LAMMPS Molecular Dynamics Simulator*. N.p., n.d. Web. 02 May 2014.