

# Classical dynamics model of water and benzene interactions and phase separation

## **Abstract:**

Benzene is one of the most complex small organic structures, and therefore very interesting. Since it also is an organic solvent, the phase separation between benzene and water can be used in extractions. The conditions to create this separation are not well known. Since experimental research involves many variables, a model can be of help, provided that it's a good one. The purpose of this research is to create a model of water and benzene with ClassicalDynamics and then evaluate the accuracy of this model. We started by modelling only one benzene molecule. The next step was to add more molecules with a script. Finally, we extended the script to generate water molecules as well and create all the interactions between the different molecules. The interaction characteristic values were retrieved from literature. Due to unavailability of sufficient calculation power of the used cpu, no actual experiments to determine phase separation were performed. However visualisation of the model proved that in ClassicalDynamics the basic values provide a decent description for this system.

## Introduction

Benzene is one of the most interesting organic structures known today. Although its composition is quite simple, its structure and the forces that contribute to benzene's ring-shape certainly are not. The alternating single and double bonds create an average bond length that lies between the normal values, and the aromaticity makes the molecule rigid and extremely stable. But, when this compound is brought into contact with other chemical substances, even more interesting phenomena, namely interactions, can occur.

When separating mixtures of chemicals, a frequently used method is extraction by solubility. Hydrophilic compounds will solve well in aqueous fluids, hydrophobic in organic fluids. This extraction method depends on the phase separation of the polar and non-polar fluid. In order to optimize the extraction, fundamental knowledge of the driving forces behind the separation of the two liquids in different layers is crucial.

Modelling a system allows the testing of a wide range of parameters, such as experimental conditions and substance concentrations, where traditional research would use large quantities of chemicals or would be interfered by human errors.

Theoretical chemistry is even more important when the scale of observation is considered. A model can simulate on the level of individual atoms or molecules or even macro-molecules, but also predict behaviour of large quantities of solids, liquids and gases. Lab research on the other hand, can only discern on the substantial scale.

This model is used to investigate whether it is possible to simulate a phase separation between benzene and water, starting from a mixed state. And simultaneously, which interactions are necessary to create these different liquid phases.

The model is based on the Newtonian classical dynamics and uses different interaction types. Since Quantum Mechanics is too complex for larger molecules and corresponds quite well with classical dynamics for molecules of this size, the latter provides a useful basis for simulations.

The next section in this article (method), will explain the program we used and its syntax and how the input files were created procedurally will also be explained. In the third chapter (experiment) will be described which steps were taken to design the final model and will be mentioned which other models it is derived from. Observations of the several simulations can be found in the results section. Finally, in the conclusion and discussion, the results will be explained and reviewed. Also, recommendations regarding additional research can be found here.

## Method:

This first part of this section describes the tools, procedures and parameters used to create the model. The simulation program will be introduced, its principle and functionality described and the content of the input files explained. After that, the graphical tool will be briefly commented on. The final part of this section explains what the advantages of generating input files through a script are and describes the functioning of the script.

All simulations were carried out with ClassicalDynamics<sup>1</sup>, “a program written in C++, offering general classical dynamics for students and researchers in science”<sup>2</sup>. This software determines the movement of the individual atoms through an application of the classical Newtonian mechanics in a force field. An explanation with derivation of the transition from potential to particle movement can be found in ‘An application of grid computing in surface science’ by M. Somers<sup>1</sup>.

The mentioned force field consists of the potentials that are created by interactions between the atoms in the molecules and between the different molecules. Since there are many different kinds of interatomic forces, for instance bonding or repulsive interactions, there are also various equations to describe them. ClassicalDynamics supports eight of these interactions, they are listed below. The five that we used are described in detail.

1. Gravitational interaction. 
$$F_G = \frac{m_x * m_y}{m_x + m_y}$$

2. Coulomb interaction. 
$$F_C = \frac{f_Q * q_x * q_y}{r_{xy}}$$

This interaction describes a force due to the charge difference of the particles. Here  $f_Q$  is a unit-less Coulomb prefactor,  $q_x$  and  $q_y$  are the charges of particle  $x$  and  $y$  and  $r_{xy}$  is the distance between particles  $x$  and  $y$ . Only  $f_Q$  needs to be filled in,  $q_x$  &  $q_y$  are stated in the particle definition and  $r_{xy}$  is taken from the simulation.

3. 12-6 Lennard-Jones interaction. 
$$F_{LJ} = f_{LJ} * \left( \left( \left( \frac{r_0}{r_{12}} \right)^{12} \right) - 2 * \left( \left( \frac{r_0}{r_{12}} \right)^6 \right) \right)$$

In this equation for an anharmonic bond,  $f_{LJ}$  is a unit-less Lennard-Jones prefactor,  $r_0$  is the equilibrium distance (or ‘well-depth’) and  $r_{12}$  the distance between particle 1 and 2. On definition,  $f_{LJ}$  and  $r_0$  must be provided.

4. Morse interaction. 
$$F_M = f_M * \left( 1 - e^{-B(r_{12} - r_0)} \right)^2 - f_M$$

5. Rydberg interaction. 
$$F_R = f_R - f_R * (1 + A_1 * (r_{12} - r_0) + A_2 * (r_{12} r_0) + A_3 * (r_{12} - r_0))$$

6. Harmonic stretch interaction. 
$$F_H = \frac{1}{2} * f_H * (r_{12} - r_0)^2$$

This interaction describes the linear attraction and repulsion of two atoms with the harmonic oscillator. Parameter  $f_H$  is the unit-less harmonic stretch prefactor,  $r_0$  the equilibrium distance and  $r_{12}$  the distance between particle one and two. The prefactor and equilibrium distance must be defined.

7. Harmonic bend  $F_B = f_B * (\cos(\alpha_{123}) - \cos(\alpha_{234}))^2$  interaction.

It determines the angle between three atoms. Here  $f_B$  is the force parameter,  $\alpha_{123}$  the equilibrium angle between atom 1, 2 and 3 in degree or radians and  $\alpha_{234}$  the current angle. The current angle is measured, the other parameters must be provided.

8. Periodic torsional  $F_P = f_P * \left(1 - \left(\cos(N * \beta_{1234})\right)\right)$  interaction.

This interaction determines the movement of molecules in a plane. It involves at least four atoms. In this equation,  $f_P$  is the amplitude,  $N$  the period of the interaction and  $\beta_{1234}$  the angle between the planes of particles 1, 2, 3 and particles 2, 3, 4 in degree or radians. All parameters have to be defined.

The values of the explained variables can be entered in any desired unit. However, for obvious compatibility reasons, these units must be consistent throughout the simulation. Because of the atomic working scale, we choose to use the atomic units. This results in a.u.m. (electron mass) for mass, a.u.c (electron charge) for charge and a.u.l (Bohr) for length.

We used the coulomb interaction to simulate the interaction between the water molecules, because these molecules are charged by the electro negativity of the oxygen atom. To describe the interaction between all the benzene molecules and between the benzene and water molecules, the 12-6 Lennard-Jones interaction was necessary, because these interactions have to be attractive at large distances and repulsive at short distance. Between the oxygen atoms of the water molecules we also defined a Lennard-Jones interaction, to keep the water molecules separated.

Within the molecules we defined harmonic bend and stretch interactions between the O-H, C-C and C-H, to simulate the vibrations that are present in these non-rigid molecules. The periodic torsion was also used in benzene to enhance the planar aspect of this molecule.

Simulations for ClassicalDynamics are built in a .cbs (Classical Builder Sheet) file, where all the atoms, interactions and other simulation parameters are defined. The build-up and syntax of such a simulation file will be explained in this section.

A .cbs file starts with a list of colour definitions. These colours will be used on the particles during the simulation. As shown below, the 'color' statement is followed by 'id' (used to refer to the colour), rgb (RedGreenBlue code) and 'name' (used in Classical Builder).

```
color id=0 rgb=[0.0,1.0,1.0] #!CB name="Aqua"
```

After 'color', the box in which the simulation takes place has to be defined. The 'cell' box will stop simulating when a particle leaves the defined space, while a 'periodic' one will continue to run by replicating the out-of-the-box particle on the opposite side of the box. An example:

```
box periodic=[18.7595310032,18.7595310032,18.7595310032]
```

When the box is defined, the atoms can be created. A 'particle' has a unique 'id' (used in interactions), 'c' refers to the colour id, the physical properties 'm' (mass), 'q' (charge) and 'r' (radius), a 'x' (position) and 'p' (momentum) and also a 'name' for CB. When several similar atoms are defined, only the 'particle' statement

and differing parameters (mainly 'x') have to be typed. ClassicalDynamics will then re-use the previous values for the unstated parameters and increase 'id' by 1. Stated below is the code for two carbon atoms.

```
particle id=0 c=0 m=21894.71 q=-0.115 r=1.46 x=[4.5,0.0,0.0]
p=[0.0,0.0,0.0] #!CB name="0 C1"
particle id=1 x=[2.25,-4.0,0.0] p=[0.0,0.0,0.0] #!CB name="0 C2"
```

When all the particles are defined, the interactions can be created. All interactions have a name and several parameters, lastly the concerning atoms by their 'id'. An example of every used interactions can be found below.

```
interaction harmonic f=0.4792 r0=2.642 { 5 0 } #!CB name="HS 0 C1C2"
interaction bending f=0.285 rad=2.094395102 { 1 0 6 } #!CB name="HB 0
C2CH1"
interaction torsional n=3.0 f=0.0004464 deg=180.0 { 0 1 2 8 } #!CB
name="PT 0 C123H3"
interaction coulomb f=1.0 { 15 16 .. 94 95 } #!CB name="Coulomb All
Water Molecules"
interaction lennardjones f=9.887E-4 r0=5.96 { 15 18 .. 90 93 } #!CB
name="LJ All Oxygen"
```

After the interactions, the 'conformation' statement is found. This optional statement tells ClassicalDynamics to find in 'n' iterations the most stable conformation (with lowest energy) within the 'error' margin, while not moving particles distances greater than 'maxstep'.

```
conformation n=10000 error=1.0E-4 maxstep=2.5
```

Then the starting temperature and method of temperature regulation can be picked with the 'temperature' statement. Here 'k' is the Boltzmann constant in atomic units and 'constant' ensures that the particle velocities are rescaled continuously to stabilize the temperature.

```
temperature k=3.166829E-6 constant=2.9315E+02
```

Finally, the simulation is started with the 'dynamics' statement. The time difference per calculation is regulated with 'dt', the duration of the simulation with 'tend', the starting point with 't' and the 'error' option is for the energy conservation. The 'snapshots' parameter prints the simulation status in the output file at regular intervals.

```
dynamics dt=4.13411 tend=4.1341105461E7 t=0.0 error=3.67493E-6
snapshots=10
```

A complete ClassicalDynamics input file can be found in appendix A.

A .cbs file can be created manually, but also with the graphical interface of the Classical Builder<sup>3</sup>. This software gives an overview of the particles in the box, their properties and the interactions between them. All these elements can be selected and edited. This is very useful in the testing of small models.

For larger, many atom models however, this program is not functional, since it is not possible to generate series of atoms and their interactions. Each atom and interaction still needs to be selected and specified by the user, which is very repetitive and extremely time-consuming. So instead we wrote a script in BASH (Bourne Again Shell) to fulfil our needs.

This script, Water\_Benzene\_Generator.sh (Appendix B) consists of an interactive part, where the desired number of benzene and water molecules can be entered. If these desired values are possible, the script uses Python to calculate the dimensions of the

box and the space each molecule can get in that box. Then all the necessary particles are created and placed in the box and the interactions that connect them into molecules are added. Then the interactions between the molecules are generated and wrapped between a header, with the colours and box definition, and footer, containing the temperature and dynamics control, and stored in a .cbs file.

The primary goal of this script is to enable simulations with many different compositions in an easy way. But the script also puts the molecules in a regular roster, so that the simulation forms a substance with a realistic density. And the final advantage is that the molecules are placed at a random orientation, which ensures that each simulation is different.

## Experiment

The experiment was conducted in several phases. It started with a single benzene molecule simulation. Then, from a simulation with several benzene molecules, it evolved into a molecular system with many water and benzene molecules. These different phases will be described below.

First, the single benzene molecule was simulated with the properties of an existing hexane model of Somers<sup>4</sup> and from the article Calculations of force field parameters<sup>5</sup>. The plane in the benzene ring was created with a periodic torsion, force parameters were taken from A Molecular Dynamics simulation in Benzene derivatives<sup>6</sup>.

Second, the model was expanded to a model with two benzene rings. Only one intermolecular interaction was built into the model, the Lennard-Jones(L-J) interaction, with parameters from Friedrich and Lustig<sup>7</sup>. The L-J interaction was defined between all the carbon atoms of the two molecules. No L-J interaction between hydrogen and oxygen was taken into account.

The third model was created with the first version of the BASH script. It could autonomously generate a chosen number of benzene molecules and their intra- and inter molecular interactions. The script was able to place the atoms of the benzene molecules in a liquid roster with a random orientation angles.

The fourth model, which contained one benzene molecule and one water molecule, was created with water-benzene interactions as Raschke and Levitt used from the GROMACS TIP4P model<sup>8</sup>. This model had been chosen because it has the same energy potential function as the water model used, made by M.F. Somers<sup>9</sup> from Fergusons model<sup>10</sup>, and it had values for Lennard-Jones interaction between carbon atoms and oxygen atoms. The values may differ slightly because it is a '4-Point-model' while our model is a '3-point-model'. Nevertheless, the properties of L-J interaction of the 4P-model between the oxygen atoms of different water molecules did not vary much from the 3P-model.

The fifth model differs only from the fourth with respect to the number of water molecules; it contained two water molecules instead of one. Another difference was the extra Coulomb interaction between the oxygen atoms of the water molecules.

Penultimate, the benzene generation script was extended to a script that created benzene and water molecules with all five different interactions, as described in the method section.

So our final model consisted of an approximately 1M solution of benzene in water, which means that each benzene molecule was surrounded by 27 different water molecules, and all molecules were interacting with each other. The parameters used in this final model are listed in tables 1 to 3.

Parameter & unit	Carbon	Hydrogen (benzene)	Oxyge n	Hydrogen (water)
Mass(AUM)*	21894,7 1	1827,81	29165, 1	1827,81

Charge(AUC)**	6	1	0,8476	0,4238
Radius(Bohr)	1,46	0,701	1,38	0,701

Table 1: Parameters of particles of a benzene and water molecule. \*= Atomic Unit of Mass | \*\*= Atomic Unit of Charge

Parameter & unit	Lennard- Coulom		L-J	Harmonic stretch (HS)	HS
	b HHO	Jones (L-J) H2O	(C-C)	C-H	C-C
Force (Hartree)	-1	0,00024757	0,0010	0,3505	0,47
Equilibrium distance (Bohr)	-	6,71554729	2	6	92
		9	6,3697	2,06	2

Table 2: Parameters of the Coulomb, Lennard-Jones and harmonic stretch interactions.

Parameter & unit	HS	Harmonic bend (HB)	HB	HB	Periodi c
	O-H	C-C-H	C-C-C	H-O-H	Torsion
Force (Hartree)	1,7461611	25	0,285	1,173	0,026
Equilibrium distance (Bohr)	1,8897259	89	-	-	-
Angle (degree)	-	-	120	120	109,47
Period	-	-	-	-	1

Table 3: Parameters of the harmonic stretch, harmonic bend and periodic torsional interactions

## Results

In following section, the results of the simulations with the different models will be described.

The single benzene ring model kept its original hexagonal structure, without being stiff. The stretch and bend interactions were clearly present. The planar aspect of the benzene molecule was not quite maintained, carbon and hydrogen atoms would move out of plane in opposite directions.

In the multiple benzene molecules model the molecules would remain in either a parallel conformation or changed to a T-shaped conformation. The attractive and repulsive interactions were visible. One moving molecule made the others move as well and the molecules kept apart at a fixed distance, without colliding.

The first benzene-water model showed a larger distance between the benzene and water molecule than expected. Also the movement of the benzene and the water molecules was remarkably fast.

The next model, number five as mentioned in experiment, contained one benzene and 27 water molecules. This model showed a more realistic movement and a shorter distance between the molecules. It was also noticed that the benzene would move from its central position to a spot more on the edge of the box.

The final model we wanted to simulate, containing more than eight benzene molecules and 27 water molecules per benzene, appeared to be too large to execute on a laptop computer. The number of interactions increases so rapidly with each extra benzene, that the conformation search already took too much cpu time, and that the actual simulation would not have succeeded as well because of cpu and memory shortage. Instead we tested a model with eight benzene molecules and eight water

molecules per benzene. Upon running this model, it was noticed that there were water molecules in the cluster of benzene molecules.

### **Conclusion and discussion:**

The results of the simulations will be discussed on the representation value.

Our research aimed to investigate whether it was possible to simulate a phase separation between benzene and water, starting from a mixed state. And simultaneously, which interactions were necessary to create these different liquid phases.

The single benzene ring model was quite realistic because the vibrations were visible. Only the bigger than expected movement out of the plane is somewhat less realistic. The multiple benzene molecules model was also reliable because the noticed conformations were in agreement with what was expected according to the article from Coutinho et al<sup>11</sup> on liquid benzene.

The first benzene-water model might differ from the realistic visualization that the molecules are closely together, due the use of values from a 'four-point model' in a 'three-point model'. The greater distance might also be caused by absence of Lennard-Jones interactions between carbon atoms and hydrogen atoms of benzene and water or the lacking of L-J interactions between oxygen and hydrogen of water and benzene.

The fifth model was more reliable because benzene was able to interact with a water molecule from different directions at the same time so the movement was less severe and the equilibrium distance was less large. Besides, the coordination of the water molecules with respect to the benzene molecules was as expected from results of the study of the benzene-water complex by Shin Li & Valentino Cooper<sup>12</sup>. Nevertheless it would be more realistic to know how multiple benzene molecules would have effect on the movement of water molecules and vice versa because it is utterly unlikely that only three molecules can be easily isolated and studied.

The final model was as accurate as the previous ones, but not big enough for actual research. It is logical that generating more benzene molecules and also more water molecules provides a simulation closer to reality. For example, 125 benzene molecules would be a more accurate reproduction than the eight we had, but that would have required a total of 1,779,000 interactions. But to research that, extra computational power is necessary.

Reaching back to a research goal, our conclusion is that the model gave an acceptable representation but for actual results, further research is required. So it is possible to generate a good looking model of water and benzene molecules with ClassicalDynamics, but the accuracy has to be verified. That will be discussed next in the recommendations section.

### **Recommendations**

Suggestions for future research of the phase separation simulation between water and benzene will be discussed below.

The most important aim would be to verify how well the model corresponds with reality. Not by just looking at it, but by doing calculations with the simulation. As a first step, a Radial Distribution Function (RDF) should be created to measure the distance between different atoms at a variable time. The distance between atoms in benzene or water molecules could be calculated or the distance between atoms from different molecules. This will result in plots where the potential well is the ideal conformation of the two atoms or molecules like Coutinho et al<sup>11</sup>, Li et al<sup>12</sup> and Allesch, Lightstone, Galli et al<sup>13</sup>. Fergusons water model<sup>10</sup>, which we used for the water molecules, was also successfully tested by himself with a RDF.

Second, the model should be tested with more than one benzene molecule, for example with  $n^3$  number of molecules where  $n$  is larger than one and a real number. Due to a shortage of computational power (MS Windows Vista, 2.9GHz, and 4GB memory) it was unable for us to test the model with a 1M solution of benzene in water, which corresponds to one benzene molecule and 27 water molecules. For these calculations a grid of computers could be used for sufficient computational power.

Third, it should be considered whether or not Lennard-Jones(LJ) interaction between, hydrogen atoms of water and benzene, hydrogen atoms of benzene and oxygen atoms, carbon atoms and hydrogen atoms of water, would contribute a significant role in representing the real mixture.

Fourth, it should be taken into account that the energy of the LJ benzene-benzene interaction should be lower than the LJ benzene-water interaction or the equilibrium distance between the molecules. There should be no water molecules in the benzene phase otherwise it is not a correct visualization of the phase separation.

Finally, the influence of the interaction between hydrogen atoms of water molecules and oxygen atoms from other water molecules could also be considered.

1 © 2005, Dr. M.F. Somers, Theoretical Chemistry Department, Leiden University

2 Somers, Dr. M.F.. ClassicalDynamics Manual. <http://boinc.gorlaeus.net/download/Downloads/Classical.txt>. Laatste update 2005. Geraadpleegd 2009.

3 © 2005, Classical Builder is built for ClassicalDynamics by Erik Kerkvliet & Paul van Santen and licensed by Dr.M.F.Somers.

4 Hexane model made by students of the Leiden University, supervised by Dr. Mark F. Somers of the Theoretical Chemistry department of the Leiden Institute of Chemistry (LIC).

5 Bercés, A., Ziegler, T., The harmonic force field of benzene calculated by local density functional theory, Chemical Physical Letters 1993, Vol. 203, 595.

6 Kim, J.H., Lee, S.H., Molecular Dynamics Simulation Studies of Benzene, Toluene and p-Xylene in a Canonical Ensemble, MD Simulation of Benzene and its Derivatives, Bull. Kor. Chem. Soc. 2002, Vol.23, No.3 441

7 Friedrich, A., Lustig, R., Thermodynamics of fluid benzene from molecular dynamics simulations, Journal of Molecular Liquids 2002, vol. 98-99, p. 241-259.

8 Raschke, T.M., Levitt, M., Detailed Hydration Maps of Benzene and Cyclohexane Reveal Distinct Water Structures, J. Phys. Chem. B 2004, 108, 13492-13500

9 Flexible Water Model extended by Dr. Mark F. Somers of the Theoretical Chemistry department of the Leiden Institute of Chemistry (LIC) from Fergusons model.

10 Parameterization and evaluation of an flexible water model, Ferguson, J. Comput. Chem. 1995, Vol.16, 501.

11 Coutinho, K., Canuto, S., Zerner, M.C., Calculation of the Absorption Spectrum of Benzene in Condensed Phase, A study of the Solvent Effects, International Journal of Quantum Chemistry 1997, Vol.65, 885-891.

12 Li, S., Cooper, V.R., Thonhauser, T., Puzder, A. and Langreth, D.C., A Density Functional Theory Study of the Benzene-Water Complex, J. Phys. Chem. A 2008, Vol. 112, 9031-9036.

13 Allesch, M., Lightstone, F.C., Schwelger, E., Galli, G., First principles and classical molecular dynamics simulations of solvated benzene, J. Chem. Phys. 2008, Vol. 128, 14501.