Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 11 (4) 177-185: Winter 2015
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Modifications of Internal Molecular Structures of Asphalt Components Due to Physical Aging

Iffat R. Arisa*

Lecturer, University of Asia Pacific, Dhaka-1205, Bangladesh

Received December 2014; Accepted December 2014

ABSTRACT

The internal structure of a molecule can be presented in terms of intra-molecular (i.e., inter atomic) and inter-molecular energies such as van der Waals, bond and bending, torsion, and inversion energy. In this study, changes in molecular energies of individual asphalt components are evaluated as a function of physical aging factors. The factors for physical aging such as temperature and pressure are considered in a molecular dynamics simulation framework. The simulations are carried out by varying temperatures within the range from -35 ºC to 75 ºC and pressures within the range from 0.95 atm to 1.1 atm. The outputs of the simulations give a clear idea about the internal structure of molecules in liquid state. Simulation results show that physical aging process causes increase in bond stretching, angle bending, and torsion energy. Application of high temperatures results in high stretching of asphalt atoms. At high temperature intermolecular van der Waals repulsion increases. Pressure variation has negligible effects on intra and inter-molecular energy changes. From inversion energy values, the geometry of the molecules is found.

Keywords: Molecular dynamics simulation; Physical aging; Asphaltene; Resin; Naphthene aromatics; saturates; van der Waals; Bond stretching; Angle bending; Torsion; Inversion.

INTRODUCTION

Asphalt consists of four components such as asphaltene, resin, naphthene aromatic, and saturate. Asphaltene provides viscous nature and colloidal behavior to asphalt [1]. Asphaltene molecules are surrounded by resin molecules. Indeed, resin disperses asphaltenes and thereby imparts ductility to asphalt [1,2]. Asphaltene has a large number of condensed aromatic polycyclic rings and heteroatoms compared to those in resins. Carbon-to-hydrogen ratio in asphaltene is higher than the ratio in resin. Naphthene aromatic has uncondensed non polar aromatic ring structure, which provides plasticity to asphaltene and resin components of asphalt [3]. Saturates are non polar chain hydrocarbon molecules. It has high hydrogen-to-carbon ratio and it provides fluidity to the overall asphalt compound molecule [4]. There exists evidence that the internal molecular structures of the asphalt components change due to heat, temperature, pressure, and oxidation; and

---

*Corresponding author: iffatrafiq.001@gmail.com

the results are bond formation and breakage, evaporation of volatiles, polymerization (combining of like molecules), separation of oily constituents, resins, or asphaltenes from asphalt binder by selective porous aggregates, etc [5-7].

These changes involve both physical and chemical modifications which are termed as aging. Aging has dramatic effects on asphalt structure and properties such as bonding patterns, adhesion, cohesion, viscoelasticity. According to Anderson and Marasteanu (1999) [8], physical aging is a reversible process. In this process, amorphous materials are quenched from melting temperature to beneath the glass transition temperature. It results in the change of bond length, shape, and orientations of the atoms. To this day, physical aging of asphalt has been studied mainly through the laboratory measurements of rheology of aged and unaged binder [3]. In this study, the asphalt components are considered separately and the changes or modifications of internal molecular structures are measured in terms of energy, and temperature, pressure are employed as physical aging factors.

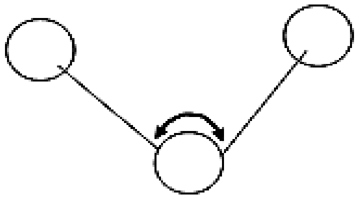
The main objectives of this research are:

- To evaluate the modifications of molecular structures of the model asphalt component molecules as a function of temperature and pressure.
- To determine the change in molecular interaction, i.e., van der Waals force of asphalt components as a result of physical aging using molecular dynamics (MD) simulations.

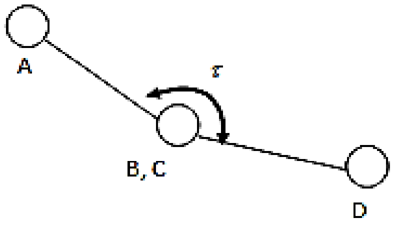
Internal molecular structure

The internal molecular structure consists of two components, e.g., bonded and non-bonded interactions. These terms are defined by a force field. Usually bonded terms (i.e., covalent bond) describe bond stretching, angle bending, and proper dihedral potentials. Improper torsional potential may also be added here. The non-bonded terms include both the electrostatic and van der Waals interactions.

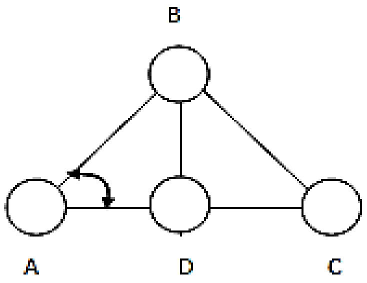
(a) Bond stretching



(b) Angle bending



(c) τ in torsional rotations



(d) out of plane bending

Fig. 1. Bonded interactions.

In bond stretching, bond between two atoms are compressed or elongated (Figure 1a). The angle bending interaction arises from the angle developed by three atoms which are connected by two bonds (Figure 1b). Harmonic oscillations are used to model both bond and angle bending potentials. Another option to describe covalent bond at higher stretching is Morse potential, which is realistic but expensive [9]. Torsional term describes the change in energy due to bond rotation (Figure 1c) as well as the out-of-plane bending interactions (Figure 1d). Generally, these are modeled using Fourier series [9].

In the non-bonded terms, many more interactions such as dispersion, repulsion and induction are considered. These interactions can be limited to pairwise energies.

MODEL STRUCTURES USED IN SIMULATION

Asphaltene

The asphaltene molecule employed in this study (Figure 2a) consists of a small aromatic ring core, long aliphatic side chain branches, and a heteroatom sulfur [10]. The molecular formula of this model is $C_{72}H_{99}S$. Sulfur atom is connected with carbon-hydrogen ring structure.

Resin

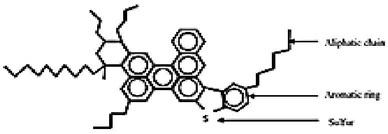
The source of the molecular structure of resin used here is Venezuelan crude oil [11]. As shown in Figure 2b, the molecule has several heteroatoms – nitrogen, oxygen, and sulfur. These heteroatoms are connected with cyclic and aromatic rings. Both saturated and unsaturated rings are found in this molecule. It also contains small alkane chain structures. Its molecular formula is $C_{59}H_{85}S_1N_1O_1$.

Naphthene Aromatic

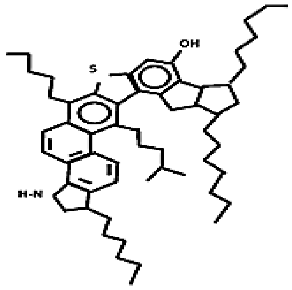
Figure 2c shows 1,7-dimethylnaphthalene. It can be used as a simple structure to represent naphthene aromatic component of asphalt [12]. The molecular formula of this model is $C_{12}H_{12}$.

Saturates

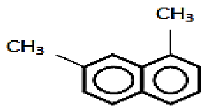
As a representative of saturate molecule, n-docosane is used in MD simulations [12]. It is a long hydrocarbon chain without polar or aromatic ring components (Figure 2d). The molecular formula of this molecule can be written as n-$C_{22}H_{46}$.



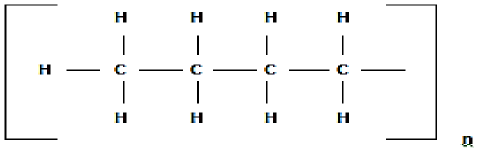
(a) Asphaltene (Groenzing and Mullins 2000)



(b) Resin (Murgich et al., 1996)



(c) Naphthene aromatic



(d) Saturates (Zhang and Greenfield, 2007)

Fig. 2. Molecular structures of asphalt components.

Simulation matrix

MD simulation matrix is presented in Table 1. It includes three input parameters: molecules of asphalt components, pressure, and temperature. Pressure is varied from 0.95 atm to 1.1 atm. Different temperature conditions are considered within the range from -35 ºC to 75 ºC varying 10 ºC from each other. Simulation outputs are quantified in terms of interaction energies, such as, bond stretching, angle bending, torsion, inversion, intra-molecular and inter-molecular van der Waals energy. Four molecules of asphaltene are taken for the simulation. Each molecule has 172 atoms; the total number of atoms considered here is 688. For resin, five molecules are used, each having 147 atoms, and so the total of 735 atoms has been used. Twenty molecules of naphthene aromatic are simulated, each having 24 atoms with a total of 480 atoms. Ten saturate molecules totaling 680 atoms are considered, whereas each saturate molecule contains 68.

Description of md simulation

In this research, the LAMMPS software is used for MD simulations, along with Dreiding force field [13]. Dreiding force field uses simple energy expressions, and contains very generic atomic force field types (Mayo et al., 1990). In this study, the all-atom model version of the force field is used, without any charges. All simulations are executed in a cubic box under periodic boundary conditions.

At first, an energy minimization is carried out for 250 ps (picosecond, 10^{-12} s) to attain a lower energy or equilibrium condition. In order to minimize energy, a velocity rescaling method in a constant volume and temperature is used. Here, a time step of 0.5 fs (femtosecond, 10^{-15} s) is selected through trials. After minimization, molecular dynamics (MD) simulations at specific temperature and pressure are used for 500 ps throughout the study. In MD, the natural ensemble is canonical where the system volume, number of particles and energy remain constant. Here, the specific temperature and pressure are obtained by Berendsen approach [14-16]. Since the non-bonded (i.e., van der Waals) forces range to infinite length and simulation boxes are finite, a spherical cutoff to such interaction is often applied during MD simulations (Allen and Tildesley, 1994). In this work, a cutoff distance of 7.5 Å (angstrom) is applied with standard long range corrections to correct for the introduction of the cutoffs.

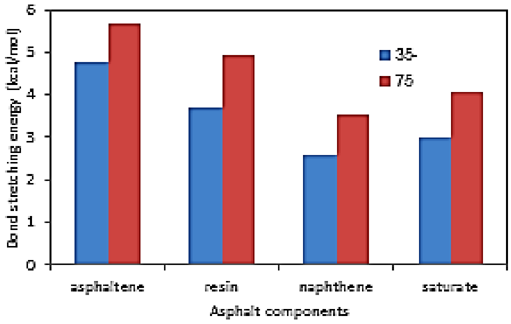
RESULTS AND DISCUSSIONS

Bond Stretching Energy

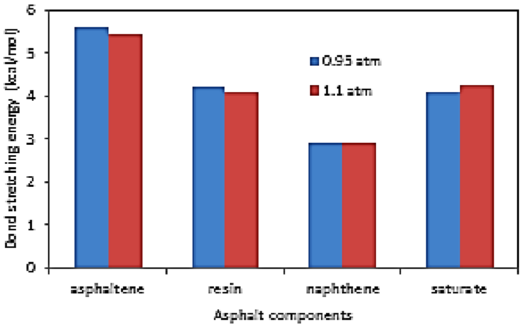
Figure 3 displays the change in bond stretching energies of asphalt components with temperatures and pressures. Asphaltene molecule has higher bond stretching energy than other asphalt components as asphaltene has a large molecular structure. The more the chain molecules joined with polar condensed aromatic rings, the more the energy required to deviate from their equilibrium values. On the other hand, naphthene aromatic has the lowest bond stretching energy because it consists of lowest number of bonds and it does not have long chain structure. Larger distortion of bond lengths occurs in chained molecular structure. That’s why larger stretching of bond is observed in aliphatic chains of saturates, asphaltene and resin. With increasing temperature, bond stretching energy increases (Figure 3a). Atomic motion increases with increase in temperature. As a result, the atoms are more stressed at high temperature. Again bond stretching energy shows almost stable and unaltered values with small change in pressure (Figure 3b).

Angle bending energy

The angle bending properties of asphalt components have been investigated using molecular dynamics simulations which are shown in Figure 4. The naphthene aromatic shows the smallest change in energy compared to that of the other components. As naphthene aromatic molecule has the smallest structure, it has few bonds and angles. So, the energy required to distort the angles is also relatively small. Figure 4(a) displays the influences of temperature in the angle bending energy of the molecular components. At low temperature, the atoms are relaxed. When the temperature of the system increases, the atoms are more stressed.



(a) due to temperature

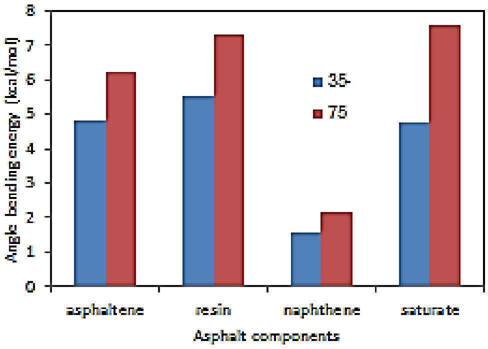


(b) due to pressure

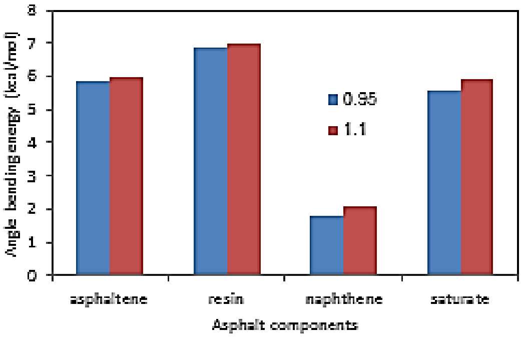
Fig. 3. Change in bond stretching energy of asphalt components.

For this reason, there is an increase in bending energy. Saturate molecules don't have fused rings. So the distortion of the angle in the chain structure of saturate is higher.

The pressure of the system in MD simulation is varied from 0.95 atm to 1.1 atm. The atoms are slightly stressed within this small range. So the simulation results show a small increase in the angle bending energy of the molecules (Figure 4b).



(a) due to temperature

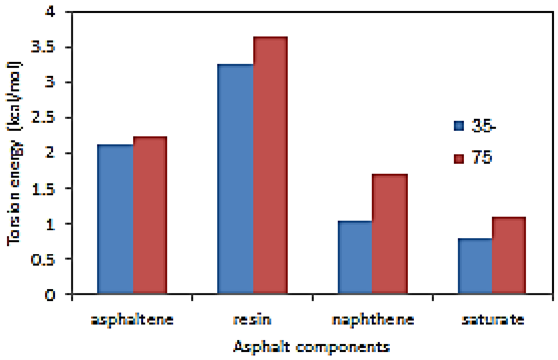


(b) dua to pressure

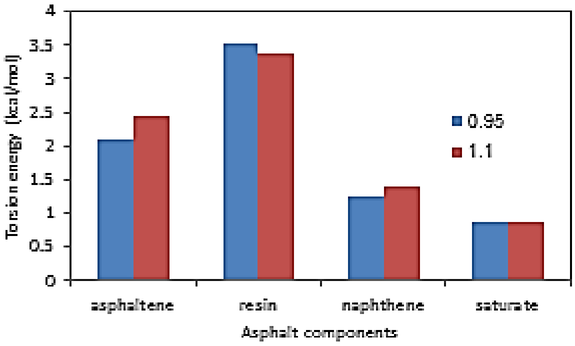
Fig. 4. Change in angle bending energy of asphalt components.

Torsional energy

From Figure 5, it is clear that resin shows the highest torsional energy. This is because resin molecules have sp^2 atoms (carbon and sulfur), resonant atoms (oxygen, nitrogen atoms), and aromatic atoms. These atoms have high rotational barrier. On the contrary, asphaltenes consist of sp^3 and sp^2 atoms, aromatic atoms, but resonant atoms are not present there. That's why asphaltenes have less rotational barrier as well as less torsion energy than resins. Lowest torsion energy is observed in naphthene aromatics and saturates structures. Naphthene aromatic has only aromatic atoms and saturate has sp^3 and sp^2 atoms, their rotational barrier are low. In fact, torsion energy depends on hybridization; it doesn't depend on the particular atoms involved.



(a) due to temperature



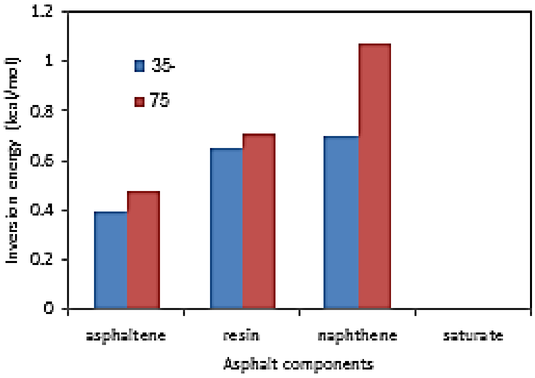
(b) due to pressure

Fig. 5. Change in torsion energy of asphalt components.

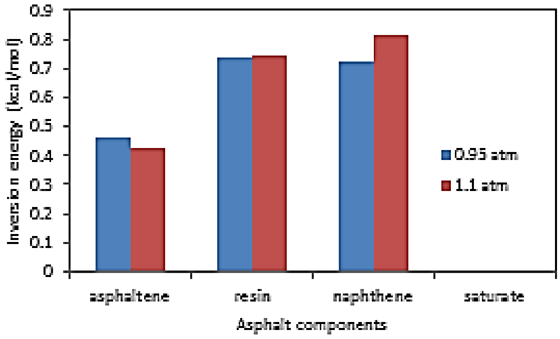
Figure 5(a) shows an increase in torsional energy due to increase in temperature. When temperature is increased, molecules gain thermal energy and their molecular motion increases. Therefore, the movement of atoms relative to each other also increases. For this reason, increase in bond rotational energy is observed. Figure 5(b) shows that the change in pressure doesn't have any effect on torsion energy of the asphalt components.

Inversion energy

Figure 6 displays that inversion energy is more in resin than in asphaltene. Resin has less fused (i.e., bond connected) rings. This indicates that it is difficult to force any three bonds of resin molecules into one plane. Although asphaltenes have ring segment, a large number of those are fused rings that combine to form rigid structure and therefore, out of plane fluctuation is less in asphaltene than resin. The presence of fused rings and the rigidity of the combined ring segment give asphaltene a planar (flat) structure. Similarly, naphthene aromatic has very small inversion energy as it consists of two rigid fused rings. For saturates, there is zero inversion energy since these molecules have no ring segments.



(a) due to temperature



(b) due to pressure

Fig. 6. Change in inversion energy of asphalt components.

Figure 6(a) shows that increase in temperature increases inversion energy of the system. Thus at high temperature the fluctuation of the atoms are high. Again at the same temperature, a small structure exhibits higher out of-plane motions (fluctuation) than a large structure. For this reason, naphthene aromatic shows the highest increase in inversion energy due to increase in temperature. Figure 6(b) presents variation in inversion energy of all the components due to variation in pressure. Change in pressure is low, so the change in out-of-plane bending motion of the molecule is also very small.

Van der Waals Energy

Table 2 presents the changes of van der Waals energy due to physical aging. The intra-molecular van der Waals energy is attractive (long range) and the inter-molecular van der Waals energy is repulsive (short range). In case of intra-molecular van der Waals interactions, energy varies with inter atomic separation. At close range, this interaction repels.

Simulation results prove that there is a positive change in attractive intra-molecular van der Waals energy of asphaltene and saturate due to increase in temperature. This is an indication of increasing attraction among the atoms of a molecule, and thus increasing the separation among atoms with temperature. Resin and asphaltene show a slight decrease in the intra-molecular attraction, which proves that their atoms come closer.

Again, the repulsive van der Waals energy among the molecules increases as a result of increase in temperature. So the heat formation of the system is higher. Here asphaltene shows the least increase in repulsion because of its molecular rigidity. Saturate shows the highest increase in repulsion.

Table 1. Simulation matrix

Components	Pressures	Temperatures	Outputs
Asphaltenes (4 molecules, 688 atoms, 172 atoms per molecule)	0.95, 1, 1.05, and 1.1 atmosphere	-35 ºC to 75 ºC, varying @ 10 ºC	Different interaction energies, such as, bond stretching, angle bending, torsion, inversion, intramolecular and intermolecular van der Waals.
Resins (5 molecules, 735 atoms, 147 atoms per molecule)			
Naphthene aromatics (20 molecules, 480 atoms, 24 atoms per molecule)			
Saturates (10 molecules, 680 atoms, 68 atoms per molecule)			

Table 2. Percentage Changes in Van der Waals energy due to Physical aging

Change in Energy	Intramolecular vdW (%) (attractive)		Intermolecular vdW (%) (repulsive)	
Increase in temperature	100 (-25 ºC to 75 ºC)	0	100 (-25 ºC to 75 ºC)	0
Increase in pressure	0	0.15 (0.95 atm to 1.1 atm)	0	0.15 (0.95 atm to 1.1 atm)
Asphaltene	10	0.04	10	-0.32
Resin	-1.65	-1.39	19	-0.63
Naphthene	-0.7	-8.7	18	3.3
Saturate	4.3	-0.3	27	3.5

It can be noted here that asphalt component atoms are not assigned any charges in the simulations. Thus electrostatic interaction is not a part of the simulation outputs. Again, hydrogen bonding is not considered in this study for physical aging. Only van der Waals interactions are considered herein with the assumption that asphalt component molecules are held together by van der Waals force.

CONCLUSIONS

Following conclusions can be drawn from this research:

- Temperature is the major factor for physical aging. At high temperature, bond, bending, and torsional energy of the molecules increase. So, the increase in temperature is more likely to cause asphalt molecules stressed.
- Inversion energy values from the simulation prove that saturates are non-planar but other components such as asphaltene and resin possess planar structures.
- In case of long range attractive intra-molecular van der Waals interactions, asphaltene shows the maximum increase in intra-molecular energy at high temperature.
- Short range repulsive inter-molecular van der Waals interactions of asphalt components increases due to increasing temperatures. Physical aging causes the highest increase of inter-molecular energy in saturates.

REFERENCES

[1]. Rostler, F. S., and White, R. M. (1959). “Influence of Chemical Composition of Asphalts on Performance, Particularly Durability”, *American Society for Testing Materials*, Volume 277, pp. 64-88.

[2]. Corbett, L. C. (1970). “Relationships between Composition and Physical Properties of Asphalts”, Proc., Association of Asphalt Paving Technologists, Vol. 39, pp. 481-491.

[3]. Petrsen, J. C. (2009). “A Review of the Fundamentals of Asphalt Oxidation”, *Transportation Research Circular*, E-C140.

[4]. Brown, E. R., Kandhal, P. S., Roberts, F. L., Kim, Y. R., Lee, D., and Kennedy, T. W. (2009). Hot Mix Asphalt Materials, Mixture design, and Construction, NAPA Research and Education Foundation, Maryland.

[5]. Collop, A.C. and Airey, G.D. (2007) “Effects of Pressure and Aging in SATS Test.”, ASCE Journal of

Transportation Engineering, Vol. 133, No. 11, pp. 618-624.

[6]. Basu, A., Marasteanu, M. O. and Hesp, S. M. (2003). "Time-temperature superposition and physical hardening effects in low-temperature asphalt binder grading." Transportation Research Record. J. Transport. Res. Board, Vol. 1829, pp. 1–7.

[7]. Robertson, R. E., (2007). Transportation Research Circular Number 499, "Chemical Properties of Asphalts and Their Effects on Pavement Performance." Transportation Research Board, National Research Council.

[8]. Anderson, D. A., and Marasteanu, M. O. (1999). "Physical Hardening of Asphalt Binders Relative to their Glass Transition Temperatures", Transportation Research Record: Journal of the Transportation Research Board, Vol. 1661, pp. 27-34.

[9]. Leach, A. R. (2001). Molecular Modelling: Principles and Applications, 2nd Edition, Prentice Hall, England.

[10]. Groenzing, H. G., and Mullins, O. C. (2000). "Molecular size and Structure of Asphaltenes from Various Sources", Energy & Fuels, Vol. 14, pp. 677-684.

[11]. Murgich, J., Rodriguez, J., and Aray, Y. (1996). "Molecular Recognition and Molecular Mechanics of Micelles of Some Model Asphaltenes and Resins", Energy & Fuels, Vol. 10, pp. 68-76.

[12]. Zhang, L., and Greenfield, M. L. (2007). "Analyzing Properties of Model Asphalts Using Molecular Simulation", Energy & Fuel, Vol. 21, pp. 1712-1716.

[13]. LAMMPS, (2001). LAMMPS home page http://lammps.sandia.gov/index.html

[14]. Berendsen, H. J. C., Postma, J. P. M., van Gunsteren, W. F., DiNola, A., and Haak, J. R. (1984). "Molecular Dynamics with coupling to an external bath", J. Chem. Phys., Vol. 81, pp. 3684-3690.

[15]. Allen, M. P., and Tildesley, D. J. (1994). Computer Simulation of Liquids, Oxford University Press: New York.

[16]. Mayo, S. L., Olafson, B. D., and Goddard, W. A. (1990). "DREIDING: A Generic Force Field for Molecular Simulations", Journal of Physical Chemistry, Vol. 94, pp. 8897-8909.