A Molecular Dynamics Study of Polyethylene

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The Degree of Master of Technology

By

Deepa Maheshvare M.

भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Department of Chemical Engineering

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(Student Name)
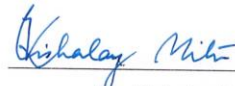
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This thesis entitled "A Molecular Dynamics Study of Polyethylene" by Deepa Maheshvare M., is approved for the degree of Master of Technology from IIT Hyderabad.

Dr. Debaprasad Shee
Examiner

Dr. Chandra Shekhar Sharma
Examiner

Dr. Kishalay Mitra
Co-Adviser

Dr. Saptarshi Majumdar
Adviser

Dr. Raja Banerjee
Chairman

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Deepa Maheshvare M.

Dedicated to

My parents and friends

Contents

Abstract

We have performed molecular dynamics simulation to demonstrate the conformational changes of a linear homopolymer chain, in the presence of solvent molecules. We examine the folding and unfolding of a single chain of polyethylene using implicit and explicit solvent models. In the implicit model, the solvent effect is incorporated by means of the truncated Lennard-Jones potential. The explicit solvent model was simulated by immersing the polymer chain in four different solvents. In addition to the random initial configuration, we have also probed the impact of a collapsed initial configuration to understand the physics involved in unfolding of a collapsed structure. These findings will have great significance in understanding the release of drug molecules loaded in polymers which can act as drug delivery vehicles. The structural changes are quantified by estimating the radius of gyration which gives a statistical measure of the size of the polymer chain. In the end, we establish a protocol to relate implicit and explicit solvent models.

Nomenclature

GB	Group based
LJ	Lennard-Jones
ILJ	Implicit Lennard-Jones
Solute	Polymer
δ	Hilderbrand solubility parameter($MPa^{0.5}$)
δ_1	Solubility parameter of solute
δ_2	Solubility parameter of solvent
vdw	van der Waal
R_g	Radius of gyration(Å)
R_{end}	End to end distance(Å)
PE	Polyethylene
CPE	Collapsed polyethylene
RPE	Random polyethylene
p-XY	p-Xylene
HX	Hexane
ET	Ethanol
H_2O	Water
N_b	Number of bonds
DP	Degree of polymerization/Number of monomers
R_0	Equilibrium distance(Å)
D_0	Equilibrium well depth(kcal/mol)
ps	Picoseconds
ns	Nanoseconds

S.D.	Standard deviation
E	Energy(kcal/mol)
Rc	Cutoff distance(Å)
<Rg>	Ensemble average of radius of gyration(Å)
T	Temperature(K)
P	Pressure(atm.)
X	Flory-Huggins interaction parameter/chi parameter
L	Simulation box length(Å)
R	Universal gas constant(kJ/kmol*K)
V_c	Volume of the simulation cell($Å^3$)
E_s	Energy of the molecule in vacuum(kcal/mol)
E_b	Energy of the molecule in bulk(kcal/mol)
E_{coh}	Cohesive energy density(kcal/mol)
ν	Exponent in scaling relation
v_m	Molar volume ($Å^3$/mol)
k_s	Adiabatic compressibility(Pa^{-1})
N_m	Number of molecules
ρ	Density(g/cc)
v_{seg}	Molar volume of the polymer segment($Å^3$/mol)
att	Attraction
rep	Repulsion
NVT	Canonical ensemble
NPT	Isothermal-Isobaric
CED	Cohesive energy density

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1. Introduction

The behavior of a polymer immersed in a solvent has been investigated by many researchers, using experimental [1] as well as atomistic [2]and coarse-grained molecular modeling techniques[3]. A number of publications report the coil-globule transition [4]of a single polyethylene chain quenched in different solvent qualities[5][6]. However, a majority of these studies provide evidence for the variation in the characteristic size and shape of a polyethylene chain immersed in large number of solvent molecules. Explicit treatment of solvent molecules is computationally expensive. Introducing scaled[7] and truncated implicit solvent models [8]mimic the solvent effect by tuning the interaction between the polymer segments. When compared with the explicit solvent model, the implicit solvent model is computationally less intensive. Therefore, establishing a relation between the implicit and explicit solvent models would be a more useful approach for determining the structural properties of a polymer immersed in a solvent.

In this work, we are motivated to conduct yet another molecular dynamics study of polyethylene to address the following:

1. To examine whether scaling laws hold for the implicit solvent model.

2. To determine the scaling exponents for different cutoff distances in the ILJ potential.

3. To find the scaling exponent of Rg using explicit solvent model and relate it with implicit solvent model.

4. To understand the role of different initial configurations, a) Extended coil configuration b) Collapsed configuration.

2. Selection of force field

The atomistic simulations were performed using the Materials Studio software version 6.0, developed by Accelrys. COMPASS and Dreiding are the most commonly employed force fields for studying polymer systems[9]. Validation studies show that the parameters of the Dreiding force field were optimized to fit the sublimation energies[10]. Whereas the parameterization and optimization of the

COMPASS force field were from the experimental and simulation data of cohesive energy density and density [11]As the constants were validated and obtained from the aforementioned liquid properties, we found that the COMPASS force field correctly predicts the value of Hilderbrand solubility parameter[12]. Therefore, we use COMPASS as the force field for computing the bonded and non-bonded interactions in all the simulations.

In COMPASS, the contribution of van der Waals term to the non-bonded potential is determined using the LJ 9-6 functional form, whereas Dreiding uses LJ 12-6 functional form. In addition, the COMPASS force field has diagonal and cross term contributions in the bonded potential. Group Based (GB) summation method is found to be accurate and computationally less expensive than Ewald and atom based summation methods. More importantly, GB works well for non-ionic systems. Therefore, GB method is applied for calculating the van der Waals' and electrostatic interactions.

3. Solvent Model

3.1. Implicit Solvent Model

The nature of the solvent determines how well a polymer interacts with the solvent molecules. We have employed the implicit Lennard-Jones potential[7] to understand the role of non-bonded interaction on the coil to globule transition of an isolated chain. The effect of the presence of explicit solvent molecules is induced by truncating[13] the attractive tail of the Lennard-Jones 9-6 potential.

$$E = D_0 \left[2 \left(\frac{R_0}{R} \right)^9 - 3 \left(\frac{R_0}{R} \right)^6 \right]$$

The effect of solvent quality is incorporated by means of the choice of the cutoff distance. The magnitude of the cutoff determines the characteristic size of the polymer. A single chain immersed in a good solvent at polymer infinite dilution may be represented by a repulsive chain simulated in the vacuum. At a cutoff value of $R=R_0$ (3.854 Å) [11], the distance at which the LJ 9-6 pair potential is minimum, the isolated chain behaves as a purely repulsive chain. We systematically increase the cut-off distance from purely repulsive to include the attractive tail. The

simulation was carried out with five different cutoffs, ranging from purely repulsive (3.854Å) to totally attractive (12.5 Å).

3.1.1. Simulation Methodology

The fully-extended initial configuration of a single chain of polyethylene with 64 monomers was constructed in the all-trans state, using the Polymer Builder tool. Geometry optimization was performed to obtain conformations with minimum energy. The energy minimization step was followed by the dynamic run using NVT ensemble, in the vacuum. The chain was equilibrated for 200ps.The properties were analyzed from the trajectory files generated from the 800ps production run. The LJ potential was truncated at the following cutoff distances, Rc: 3.854Å, 5 Å, 5.7 Å, 6.1 Å, 6.5 Å, 9 Å, 10.5 Å, 12.5 Å. At R_0=3.854Å, the molecule is unstable and the conformation of the chain keeps changing. When the attractive tail of LJ potential is included, the chain achieves a stable, collapsed configuration, which has minimum energy. The chain never unfolds. These observations are further validated from the time evolution of potential energy displayed in Fig. 3.1.
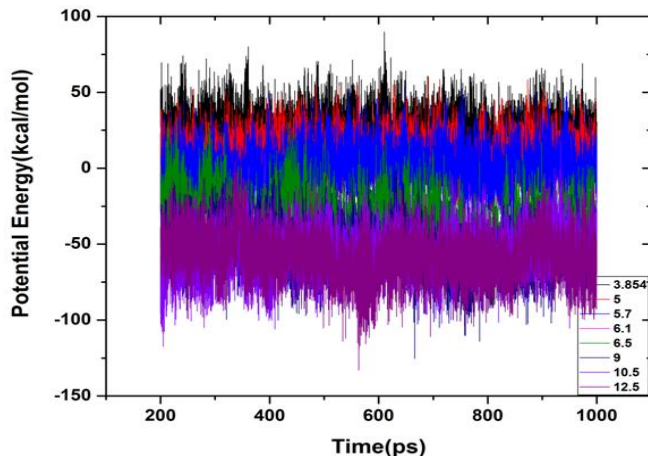
Figure 3.1: Potential Energy vs. Time

The extended coil configuration has high energy. Therefore, the chain folds and unfolds, continues to remain in the extended coil state. When the attractive tail is included, the range of interaction is more; the segments of the chain come closer. The time evolution of R_g at different cutoff distances is shown in Fig.3.2.The ensemble average <Rg> and standard deviation (S.D.) of radius of gyration

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calculated in the interval of 200ps-800ps are reported in Table 3.1.It is observed that the size of the chain decreases with increase in the cutoff distance. When R_c is large, attraction is promoted, the chain attains an energetically stable conformation. Hence, the standard deviation is less.
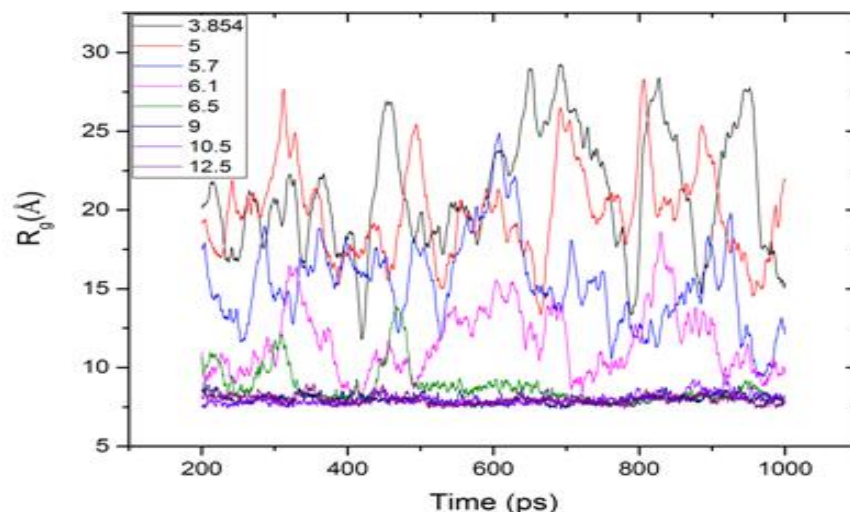
Figure 3.2: Radius of gyration vs. Time at different cutoff distances

Table 3.1: Variation of <Rg> and S.D. with change in Rc

Rc	3.854	5	5.7	6.1	6.5	9	10.5	12.5
<Rg> (Å)	21.19	19.87	15.36	11.58	8.77	7.99	7.99	7.97
S.D.	3.75	2.86	2.79	2.12	1.12	0.26	0.34	0.27
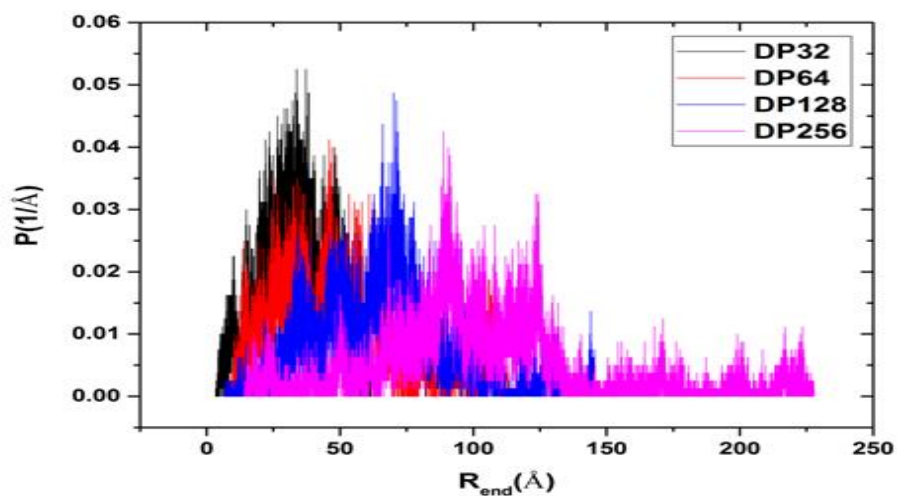
Figure 3.3: R_{end} vs. Time for different chain lengths at R_0=3.854Å

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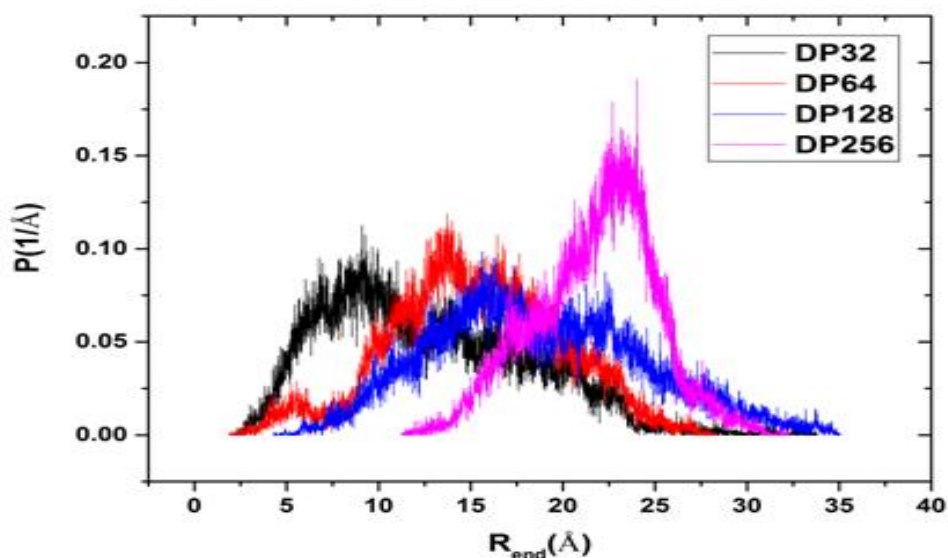
Figure 3.4: R_{end} vs. Time for different chain lengths at $R_0=12.5$Å

The figure displayed above shows the distribution of end to end distance of the polyethylene chain. In Fig.3.3, the non-bonded interaction is purely repulsive. In fig.3.4, the distribution is narrower; the non-bonded interaction has the attractive tail.

3.1.1.1. Observation

When the isolated polymer is subjected to a cut off of 12.5Å, the chain forms a stable collapsed configuration after a dynamic run of 150ps.A study conducted by Sundarajan's group[14] reveal the formation of unstable folds in a short chain which contains less than $30CH_2$ units, using the Dreiding force field. Although COMPASS force field was employed in our work, for a chain length of 32 monomers, we observe a collapsed structure. The results were consistent with the observations of previous study [15].

3.2. Explicit solvent model

The study presented here focuses on examining the structural evolution of a single polyethylene chain immersed in a solvent. The folding and unfolding behavior of a single chain of polyethylene, soaked in different solvent qualities, is elucidated. In particular, we concentrate on the solute-solvent interaction at infinite polymer dilution[1]. We also address the know-why and know-how associated in determining

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the choice of the explicit solvent condition, the role of the solvent, behavior of the solute at atmospheric pressure and 298 K.

3.2.1. Choice of solvent

3.2.1.1. Miscibility of polymer-solvent mixture

To study the conformational changes of the polymer chain quenched in solvents of different qualities, we identify the choice of good and poor solvent[16] from the value of solubility parameters. The Flory-Huggins binary interaction parameter X[17], calculated from the difference in solubility of the polymer-solvent pair, gives a measure of the extent of solvency[18]. We use the following relation, which was found to be more successful in predicting PE-solvent miscibility in the dilute limit, to estimate X.

$$X = v_{seg}\left(\frac{\delta_1 - \delta_2}{RT}\right)$$

Several other relations define the composition dependence of X parameter[19]. However, X is expected to be independent of composition for a non-polar solute in non-polar/moderately polar solvents.

3.2.1.1.1. Calculation of δ

3.2.1.1.1.1. Estimation of solubility parameter of polyethylene

It is essential to determine the minimum number of monomer units required to carry out the simulation. The chain length chosen must predict the right value of the liquid property that matches well with the experimental findings. At the same time, the smaller the chain length, the lesser is the computational effort required for property estimation. We address the following questions: What should be the chain length? How many molecules are required?

In an earlier study by Jawalker et al.[19], it was shown that the solubility of chitosan stabilized when the degree of polymerization was above 60. However, for polyethylene, we expect the solubility to level off at a much lower chain length. This is striking; because, the presence of polar groups in chitosan molecule can give rise to fluctuations in the value of δ at smaller chain lengths. The absence of functional

groups in polyethylene hints that the dependence of δ on chain length will be less pronounced. To validate this conclusion, we have determined the value of Hilderbrand solubility parameter at four different chain lengths, displayed in the figure [no.]. Furthermore, the standard deviation of CED calculated from δ is less than 5% of the ensemble average. The numerical values were in reasonable agreement with the experimental findings. The following relation[20] is used to estimate solubility.

$$\delta = \sqrt{\frac{E_{coh}}{V_C}} = \sqrt{\frac{E_v - E_b}{V_C}}$$

3.2.1.1.1.1.1. Calculation of δ with a single chain packed at liquid density

3.2.1.1.1.1.1.1. Simulation Methodology

The fully-extended initial configuration of a single chain of polyethylene with 96 monomers was constructed in the all-trans state, using the Polymer Builder tool. A single chain of polyethylene was loaded into a cubic periodic simulation cell at 1g/cc. Geometry optimization was followed by equilibration step. As the accurate value of density is not known, NPT ensemble was employed and the system was allowed to equilibrate for 1ns. The temperature and pressure were set to 298K and 1 atm., respectively.

When the cell is packed with a single chain at the liquid density, we observe that the presence of void volume in the cubic cell leads to artifacts. As a result, the predicted values do not agree with the experimental data. The general idea is to pack the simulation volume with a few thousands of atoms to overcome such artifacts.

3.2.1.1.1.1.2. Calculation of δ with multiple chains packed at liquid density

3.2.1.1.1.1.2. Simulation Methodology

The fully-extended initial configuration of a single chain of polyethylene with 32 monomers was constructed in the all-trans state, using the Polymer Builder tool. Amorphous structures were created by adding 10 chains of polyethylene into a cubic periodic simulation cell, at 1 g/cc. NPT ensemble was employed and the system was

allowed to equilibrate. All the simulations were performed at atmospheric pressure for a time span of 1ns.δ is an intensive property. Therefore, we expect the value to remain unaltered with the addition of more number of molecules into the simulation box. We observe that δ is the same for 10 chains and 30 chains. The data of solubility parameter calculated for 10 molecules, 30 molecules is reported in Table 3.2 for comparison. Therefore, we conclude that including more number of molecules in the cubic cell is not required.

To check for the dependence of δ on chain length, we have repeated the above steps at three different chain lengths. The results are in accordance with the findings of Goel et al. [21]. They have shown that there was no significant difference in the value of interfacial tension when the chain length of n-alkane was increased from C10 to C13.

Table 3.2: Variation of δ with increase in chain length of polyethylene

Chain length	$\delta(MPa^{1/2})$ 10 molecules(30 molecules)
32	15.95(15.78)
64	15.64
128	15.51

3.2.1.1.1.2. Estimation of solubility parameter of solvent

The condensed state of p-xylene, ethanol and hexane were built using the Amorphous Cell Construction task in Material Studio. The cubic cell was packed with 100 molecules at a density of 1g/cc. The temperature was maintained at 298 K. Geometry optimization was followed by NPT equilibration at 1atm pressure for 150ps.Table 3.3 presents the results of δ obtained from simulation. The δ of Nitrobenzene obtained from simulation is consistent with the value reported in a previous study[22].

Table 3.3: Values of δ for different solvent species

Solvent	δ from simulation(MPa$^{0.5}$) 100 molecules	δ from experimental data MPa$^{0.5}$) [ref]
Xylene	16.85	18.2
Hexane	14.48	14.9
Ethanol	25.23	26.2
Nitrobenzene	20.9	22

3.2.1.2. Calculation of Flory-Huggins chi parameter

Table 3.4: Values of chi parameter

Solute-Solvent	X
PE in Hexane	0.017
PE in Ethanol	1.19
PE in p- Xylene	0.019

3.2.2. Choice of solvent conditions

The question is "What should be the simulation temperature and pressure?" .We considered hexane [23]as the good solvent for two reasons. First, PE and hexane have similar solubilities. Second, n-alkanes with 1-4 carbon atoms exist in the gaseous state at 298K and atmospheric pressure as the boiling points are low. In a previous publication [2], Zifferer and Kornherr presented a quantitative study on determining the structural properties of polyethylene in hexane, starting with a randomly constructed amorphous initial configuration. We have made an attempt to explore the swelling of a collapsed polyethylene chain when added in a suitable solvent like hexane.

We also alter the solvent quality from good to poor and monitor the variation in Rg of the polymer chain. Ethanol has low solubility; dipole-dipole interactions are profound, it acts as a poor solvent. The conformational change of polyethylene in p-xylene [24]and water is also examined. Moreover, as the boiling point of hexane, p-xylene, water and ethanol are 68°C, 110°C, 100°C and 78°C respectively, the

solvents selected exist as the liquid at the simulation temperature. All the simulations were carried out at 298K and 1 atmospheric pressure.

3.2.3. Simulation

3.2.3.1. Artifact in Periodic Boundary Condition

When the dimension of the box is comparable to the characteristic size of the polymer, with the progress in time, the chain may move out of the cell and interact with its own image in the adjacent cell. This will probably result in a physically unrealistic behavior[25]. For example, if the size of the simulation cell is small, it is likely that a long chain polymer immersed in a solvent may swell as a consequence of its interaction with the periodic image. Apparently, this will not give an adequate picture of whether the swelling has occurred because of the solvent effect. Hence, the choice of the box length plays a crucial role in studying the response of the polymer in different solvent environments. In order to eliminate the finite size effect, in practice, box length L of size greater than 5Rg is recommended [26]. Therefore, to find L, it is essential to know the value of Rg beforehand.

We introduce a procedure to determine the extent to which a polymer can swell or collapse in the presence of a solvent. The idea is to mimic the good or poor solvent condition for an isolated chain using implicit Lennard-Jones. We do this by employing a smaller cut-off to exclude the attractive tail of the LJ potential. The approximate value of Rg is calculated from the simulation methodology described in section 3.1.1. The Rg thus calculated is used to compute L.

3.2.3.2. Pressure fluctuations in a system

The fluctuation in average pressure of a system is given by the equation

$$\sigma_p = \frac{\sqrt{\dfrac{RT}{v_m k_s}}}{\sqrt{N_m}}$$

When the number of molecules present in the simulation box volume is small, the fluctuation is pressure is large. The presence of fluctuations in the system will lead

to erroneous results. To avoid this, the system has to be packed with a sufficient number of solvent molecules in order to attain equilibrium.

3.2.3.3. Methodology

Two different initial conformations of the polyethylene chain were created a) random configuration b) collapsed configuration. A cubic cell of box length L=100Å was built. Solvent molecules were loaded into the box using the Amorphous Cell Packing task at a density of 0.155g/cc. A large number of solvent molecules are essential as the volume of the simulation cell is large. The randomly generated solute configuration was merged with the cell consisting of the solvent. The solute was positioned at the center of the cubic cell. By doing this, the finite-size effect could be eliminated. Thus, the amorphous structure was constructed. This step was followed by geometry optimization and a 500ns NPT equilibration run through the Forcite Module. The evolution of the polymer in solution was captured every 1ps.The equilibrium properties were evaluated from the trajectory files sampled in the production run. For the second initial configuration, the polymer in collapsed state was immersed in a box containing solvent molecules. The steps described above were repeated. The standard deviations of the total average energy, density and temperature are within 5% of the ensemble average.

4. Results and Discussion

4.1. Implicit solvent model
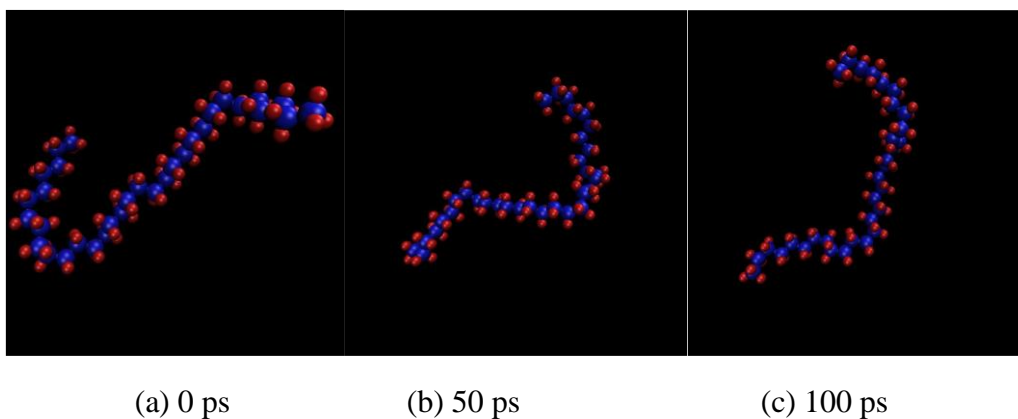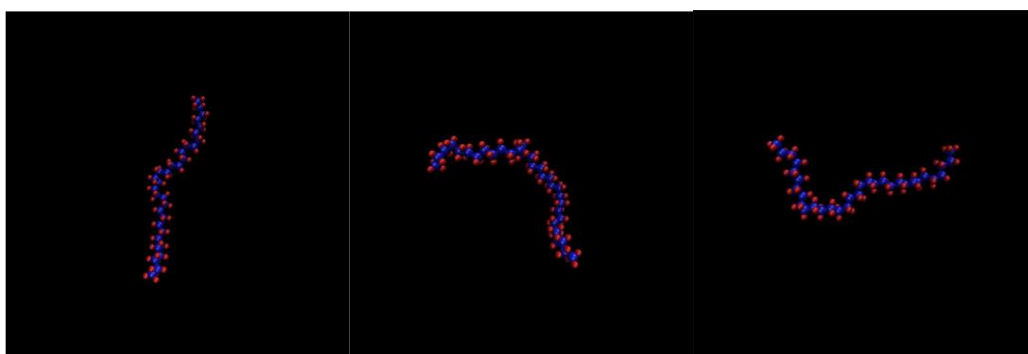
(a) 0 ps   (b) 50 ps   (c) 100 ps

(c) 200 ps   (d) 500 ps   (e) 1000 ps

Figure 4.1: Conformations of a polyethylene chain consisting of 16 monomers. Here, the non-bonded interaction is purely repulsive.

(a) 0 ps   (b) 50 ps   (c) 100 ps
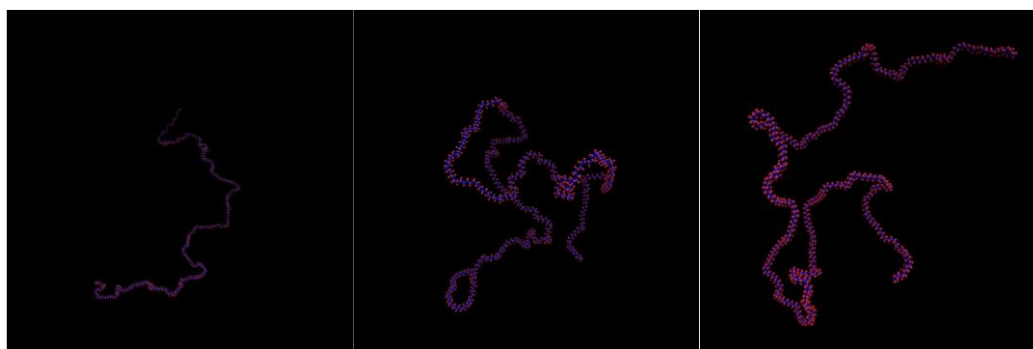
(c) 200 ps   (d) 500 ps   (e) 1000 ps

Figure 4.2: Conformations of a polyethylene chain consisting of 256 monomers. Here, the non-bonded interaction is purely repulsive.

(a) 0 ps	(b) 50 ps	(c) 100 ps
(c) 200 ps	(d) 500 ps	(e) 1000 ps

Figure 4.3: Conformations of a polyethylene chain consisting of 16 monomers. Here, the non-bonded interaction has the attractive tail.

(a) 0 ps	(b) 50 ps	(c) 100 ps

<div align="center">

(c) 200 ps   (d) 500 ps   (e) 1000 ps

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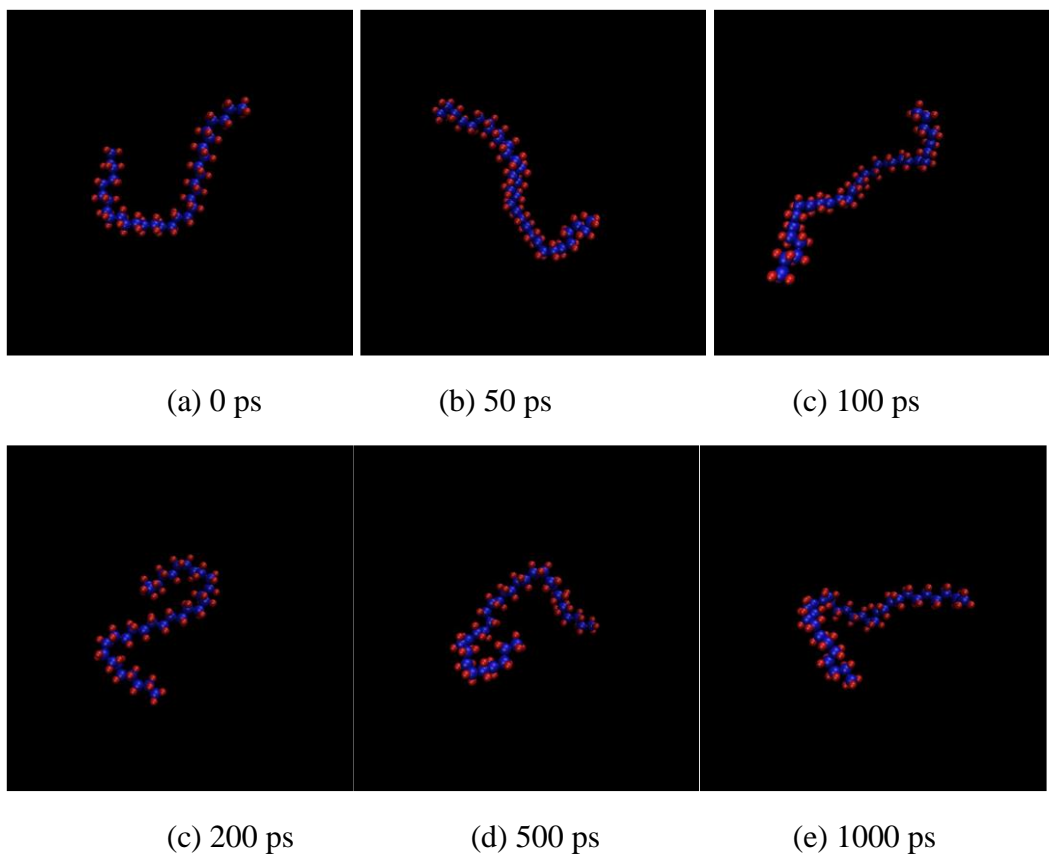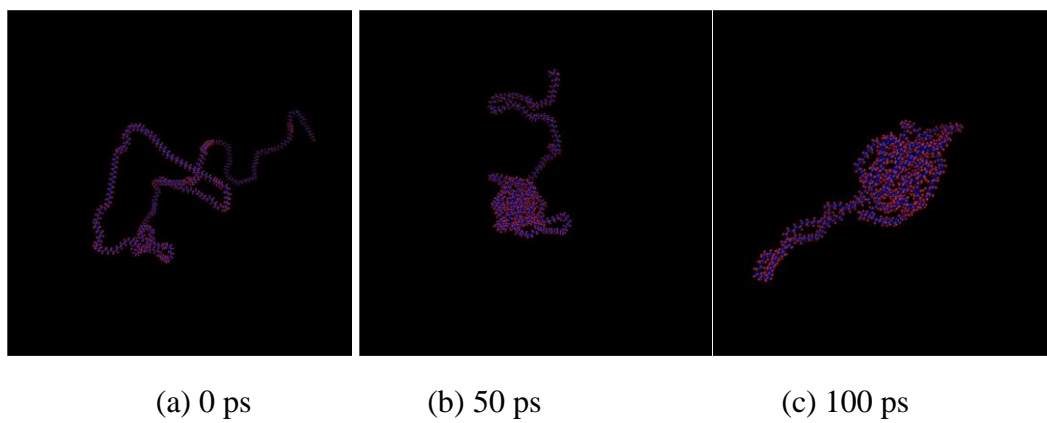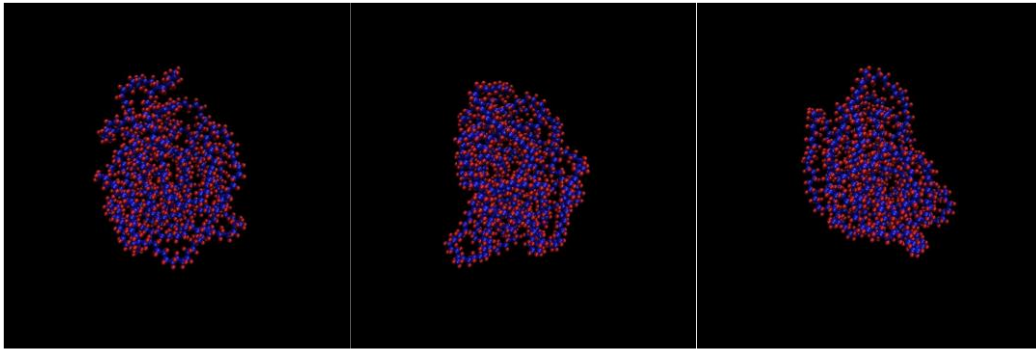**Figure 4.3:** Conformations of a polyethylene chain consisting of 256 monomers. Here, the non-bonded interaction has the attractive tail.

4.1.1. Validation using scaling law

The radius of gyration is given by the following relation,

$$Rg \sim N^{v}$$

Where, $v=0.33$ for collapsed conformation; $v=0.6$ for an excluded volume chain. The results of the simulation displayed in Fig. 4.1, are found to be in close agreement with the predictions by scaling law.

<div align="center">

Figure 4.5: ln(Rg) vs. ln(N)

</div>

4.2. Explicit solvent model

Ethanol and water are poor solvents for polyethylene. The collapsed chain swells when soaked in hexane molecules. Also, the rate of swelling of the polymer chain soaked in hexane is faster when compa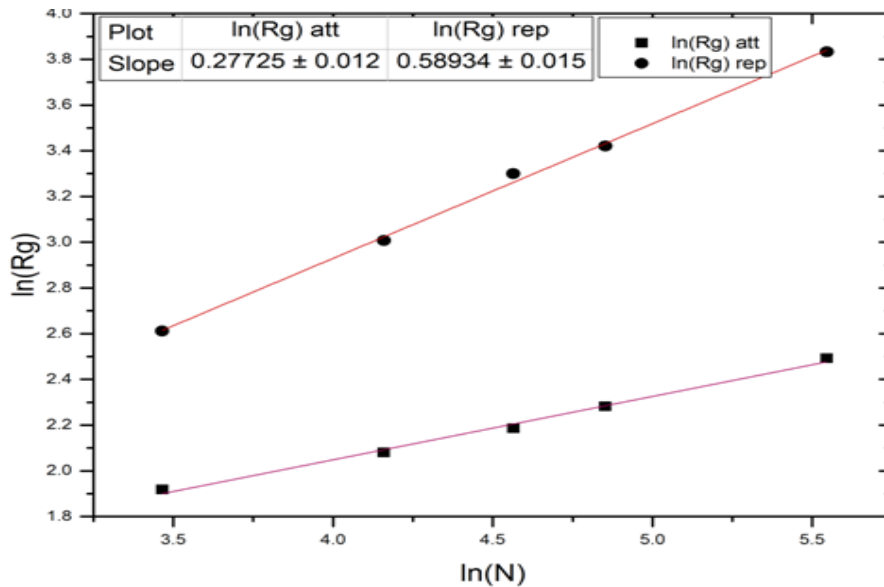red with the rate of swelling in the ethanol solvent. In water, the extended coil configuration folds to form a collapsed structure displayed in Fig.4.2.For PE in H_2O, the Rg of the final configuration is close to the value of Rg obtained using the implicit solvent model, for the case in which the non-bonded interaction has the attractive tail. Although the initial configurations are different, with the progress in time the Rg of the collapsed conformation and Rg of the random conformation reach the same value. This is shown for the case of PE in ET, the ensemble average calculated for every 500 ps is shown in Table4.1.
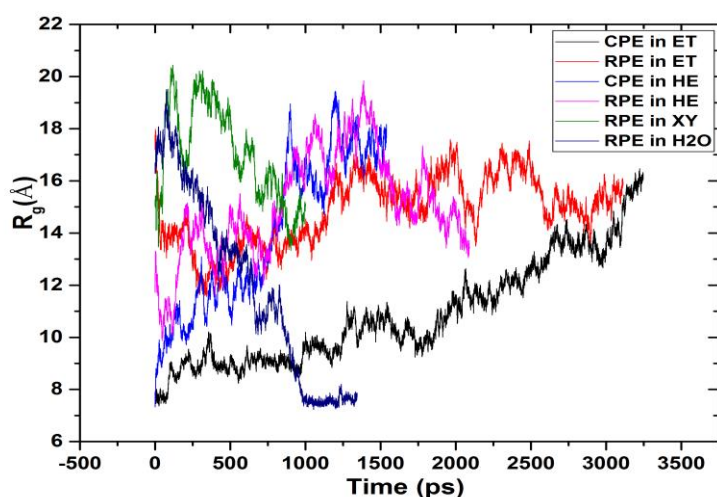
Figure 4.6: Rg vs. Time plotted at various solvent conditions

Table 4.1: The change in Rg of PE immersed in ethanol measured at different
time intervals for two different initial configurations

Time(ps)	1-500	501-1000	1001-1500	1501-2000	2001-2500	2501-3000	3001-3250
RPE- ET$<$Rg$>$(Å)	13.31	13.57	15.39	15.67	16.04	15.10	-
CPE-ET$<$Rg$>$(Å)	8.73	9.01	10.03	10.39	11.79	13.4	15.12

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5. Outcome

v=0.5 ideal chain v=0.6 excluded volume chain v=0.33 collapsed chain	Implicit ⟷	Explicit
	Rc [N=6] = [3.85,5,6.5,9,10.5,12.5]	Solvent [M=4] = [HX, H2O,p-XY , ET]

Implicit: Variables Truncation distance Rc_i = (3.84 to 12.5) Chain length (DP) DP32-DP256	Fix Rc_i, vary DP i=1….6 → Find v ← Fix S_j, vary DP j=1….4

Find v → ↓

Change Rc, vary N	Yes ⟵ ◇ v ILJ=Explicit ◇ No ⟶	Establish a correlation

Explicit: Variables Solvent S_j Chain length (DP) DP32-DP256 X_j=Chi parameter

v_1	Rc_1
v_i	Rc_i

if v_i(LHS) = v_j (RHS)

$Rc_i = X_j$

Validate with another chemical
species (e.g. polypropylene)

v_1	S_1
v_j	S_j

Step1: For a particular value of Rc_i, the number of monomers(DP) can be varied and Rg can be estimated for each chain length.

Step2: Using the relation $Rg \sim N^v$, v_i can be found

Step3: Step 1 and Step 2 can be repeated for i=[1,….,N] and for a fixed Rc_i the respective value of v_i can be calculated.

Step4: Similarly, For a particular value of S_j, the number of monomers(DP) can be varied and Rg can be estimated for each chain length.

Step5: Using the relation $Rg \sim N^v$, v_j can be found

Step6: Step 4 and Step 5 can be repeated for $j=[1,....,M]$ and for a fixed Rc_i the respective value of v_j can be calculated.

Step7: v_i 's obtained from Step 3 and v_j's obtained from Step 6 can be examined.

Step8: When v_i determined at a specific value cutoff distance Rc_i matches with the v_j estimated at a particular solvent condition, a correlation can be established between Rc_i as a function of (S_j/X_j)

The value of exponent of scaling relation will remain the same for all types of chemical species. The validity of the correlation obtained from the above steps could be tested for a different chemical species, for example: polypropylene. Using this procedure, explicit solvent model can be successfully mapped to the truncation distance of the implicit solvent model; it will save the enormous computational cost of explicit solvent models.

6. References

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