Atomistic Modeling and Simulation of the Mechanical Properties of sPMMA – Graphene Nanocomposites

by

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Abstract

Polymer nanocomposites are materials in which nanoscopic organic or inorganic particles, typically 10-100 Å in at least one dimension are dispersed in a polymer matrix in order to dramatically improve the performance properties of the polymer. Polymer nanocomposites represent a new alternative to conventionally filled polymers. Because of their nanometer sizes, filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers. These include increased elastic modulus and strength, outstanding barrier properties and improved electrical and heat resistance. However, the cost of nanoparticles, their availability and the challenges that remain to achieve good dispersion pose significant obstacles to these goals.

In the present work, we examine the effects that are caused to the dynamical, structural and mechanical properties from the presence of graphene sheets (as nanoparticle) in a polymer matrix compared to the bulk material. By applying classic Molecular Dynamics (MD) method we simulate real polymeric and polymer nanocomposite systems and after validating our results with available experimental data, we finally estimate the elastic constants for various systems.

Firstly, detailed atomistic MD simulations are executed to systems which are only consisted by pure polymer and specifically syndiotactic poly(methyl methacrylate) (s-PMMA)\(^1\). After a procedure for equilibrating the system, which will be discussed in detail in Chapter 4, we submit several well relaxed and completely independent conformations to mechanical tests in order to extract the elastic properties of the pure polymer.

In the second part, we disperse graphene sheets of different chemical structure of the same weight fractions in the polymer matrix, creating so the graphene/s-PMMA nanocomposite (GPNC), and by following the same procedure which mentioned above, we extract the elastic constants of the nanocomposites as well.

Finally a comparison of the dynamical, structural and mechanical properties between the bulk and GPNC systems showed us whether or not improvement of these properties exists.
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Chapter 1

Introduction

1.1 Nanotechnology and Nanoparticles

The prefix “nano” is becoming increasingly common in the scientific literature. “Nano” is now a popular label for much of modern science, and many “nano-” appear now in dictionaries, including: nanometer, nanosecond, nanoscale, nanoscience, nanotechnology, nanostructure, nanotube etc.

The nanometer is a metric unit of length, and denotes one billionth of a meter ($10^{-9}$ m). Popularly, “nano” is also used as an adjective to describe objects, systems, or phenomena with characteristics arising from nanometer-scale structure. Despite many exceptions, most of the exciting properties of “nano” begin to be apparent in systems smaller than approximately 100 nm.

Nanotechnology can be defined as the design, synthesis, and application of materials and devices whose size and shape have been engineered at the nanoscale. It exploits several unique chemical, physical, electrical, and mechanical properties that emerge when matter is structured at the nanoscale.

Nanostructured materials did not first come into existence with the recent emergence of the field of nanotechnology. Many existing materials are structured on the micro- and nanometer scales, and many industrial processes that have been used for decades (e.g. polymer and steel manufacturing) exploit nanoscale phenomena. The natural world is replete with examples of systems with nanoscale structures, such as proteins, cells, bacteria, viruses etc.

Recent advances in synthesis and characterization tools, however, have fueled a boom in the study and industrial use of nano-structured materials. While the atomic and molecular building blocks (~0.2 nm) of matter are considered as
nanomaterials, examples such as bulk crystals with lattice spacing on the order of nanometers but with macroscopic dimensions overall, are commonly excluded.

Nanoparticles are particles with at least one dimension smaller than 1 micron and potentially as small as the atomic and molecular length scales (~0.2 nm). Nanoparticles can have amorphous or crystalline form and their surfaces can act as carriers for liquid droplets or gases. To some degree, nanoparticulate matter should be considered as a distinct state of matter (in addition to the solid, liquid, gaseous, and plasma states) due to its distinct properties (large surface area and quantum size effects). Examples of materials in crystalline nanoparticle form are fullerenes, graphene and carbon nanotubes, while traditional crystalline solid forms are graphite and diamond.

### 1.2 Graphene and its structure

In recent years, graphene, a one-atom-thick planar sheet of sp2-bonded carbon atoms densely packed in a honeycomb crystal lattice (Figure 1.1), has attracted the attention of many scientists all over the world. As about its chemical structure, the 2s orbital interacts with the 2pₓ and 2pᵧ orbitals from where 3 σ bonds are formed, which are the strongest covalent bond that can exist. This is the source of the excellent mechanical properties of graphene. The rest 2pₓ orbital is uniformly distributed between the two carbon atoms creating a π bond (Figure 1.2). The pₓ electrons have very weak interaction with the nuclei, which leads to graphene’s enormous electrical properties.

**Figure 1.1:** A typical graphene sheet.  
**Figure 1.2:** The created bonds between two carbon atoms.
Graphene is the basic building block for graphitic materials of all other dimensionalities (Figure 1.3). It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes, or stacked into 3D graphite.

![Graphene](image.png)

**Figure 1.3:** Graphene, the building block of all graphitic forms.²

It has attracted appreciable attention as a next generation material to many applications due to its exceptional properties including among others, extremely high mechanical strength, high electrical and thermal conductivity, optical transmittance, and super hydrophobicity at nanometer scale. The first graphene was extracted from graphite using a technique called micromechanical cleavage.³ This approach allowed the easy production of high-quality graphene crystallites and further led to enormous experimental activities.

Since its discovery, the research community has shown a lot of interest in this novel material owing to its unique properties. As shown in Figure 1.4, the number of publications on graphene has dramatically increased in the recent years.
1.3 Production methods of graphene

After a long and tenacious series of unsuccessful attempts to produce single sheet graphene, the publication of a simple method was presented by Geim’s group in 2004, called also as the “scotch tape method”. By repeatedly cleaving a graphite crystal with an adhesive tape to its limit, and then by transferring the thinned down graphite onto an oxidized silicon wafer with the appropriate color, the authors finally produced the 2D carbon lattice. This discovery marked the onset of experimental physics on graphene, which then made it relevant to test methods in order to produce single sheet graphene. In general, the production methods can be classified in two categories:

- Bottom up methods
- Top down methods

The two types of methods are reviewed in the next paragraphs of this Chapter.

1.3.1 Bottom up methods for graphene production

In bottom-up processes, graphene is synthesized by a variety of methods, such as:
1.3 Production methods of graphene

1. Epitaxial growth on metal Carbides\textsuperscript{4,5,6,7,8,9}
2. Chemical vapor deposition (CVD)\textsuperscript{10,11,12,13}
3. Arc discharge\textsuperscript{14}
4. Unzipping carbon nanotubes (CNT’s)\textsuperscript{15,16}

CVD and epitaxial growth on SiC are the most common and widely used but they often produce tiny amounts of large-size, defect-free graphene sheets. They may be more attractive than the mechanical cleavage method\textsuperscript{2} for production of graphene sheets for fundamental studies and electronic applications, but are not a suitable source for producing polymer nanocomposites that require a large amount of graphene sheets preferably with a modified surface structure. The nature, average size, and thickness of graphene sheets produced by different bottom-up methods as well as the advantages and disadvantages of each method are summarized in Table 1.1.

<table>
<thead>
<tr>
<th>Method</th>
<th>Typical dimension</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epitaxial growth on metal Carbides</td>
<td>Few layers</td>
<td>Up to cm</td>
<td>Very large area of pure graphene</td>
</tr>
<tr>
<td>CVD</td>
<td>Single, bi-, few layers</td>
<td>Up to cm</td>
<td>Large size and high quality</td>
</tr>
<tr>
<td>Arc discharge</td>
<td>Single, bi-, few layers</td>
<td>From few nm to few μm</td>
<td>Very high production rate</td>
</tr>
<tr>
<td>Unzipping carbon nanotubes</td>
<td>Multi layers</td>
<td>Few μm</td>
<td>Size controlled by the selection of CNT’s</td>
</tr>
</tbody>
</table>
1.3 Production methods of graphene

Up to now, the most effective CVD method seems to be the one that has been reported by Li et al.\textsuperscript{10} Using as substrate thick Cu foils at high temperature (approximately 1000 °C) and low pressure (~500mTorr), and by introducing gas methane (CH\textsubscript{4}(g)) as raw material, they fabricate single graphene sheets at 95%, with only 3-4% bilayers and lower than 1% trilayers.

Rollings et al.\textsuperscript{3} reported the synthesis and characterization of graphite thin films produced by thermal decomposition of the (0001) face of a 6H-SiC wafer, demonstrating the successful growth of single crystalline films down to approximately one graphene layer. At high temperature (1250 °C) and ultrahigh vacuum conditions (8\times10^{-8} Torr) they succeeded in producing atomically-thin graphite films of thicknesses down to 1-2 graphene layers.

1.3.2 Top-down methods for graphene production

In the top-down approach, we start with a bulk material and then break it into smaller pieces using mechanical, chemical or other forms of energy. A schematic representation of the building of nanostructures with bottom-up and top-down approaches (and the differences between them) is given at Figure 1.5.
1.3 Production methods of graphene

In top-down processes, graphene is synthesized by several ways such as:

1. Micromechanical exfoliation of graphite\(^2\)
2. Direct sonication of graphite\(^18,19\)
3. Chemical reduction of organically treated Graphite Oxide (GO)\(^20,21\)
4. Thermal exfoliation/reduction of GO\(^22,23\)

As mentioned above, the micromechanical exfoliation of graphite as a method to produce single sheets of graphene is the one that caused the outburst in this research field in 2004.\(^2\) In top-down processes, graphene or modified graphene sheets are produced by separation/exfoliation of graphite or graphite derivatives, such as graphite oxide (GO). In general, these methods are suitable for large scale production required for polymer composite applications. Starting from graphite or its derivatives offers significant advantages over the bottom-up methods for fabricating graphene based polymer nanocomposites. Table 1.3.2 shows a block diagram which summarizes the different routes for the production of graphene or modified graphene starting from graphite or GO.

**Figure 1.5:** Schematic representation of the building up of nanostructures.


1.4 Properties of graphene

The rapid adoption of graphene as a material of interest lies principally in the diverse and unusual set of properties (mechanical, electrical, thermal, optical etc.) that monolayer, few-layer graphene and graphene oxide exhibit. These properties happen to be matching the shortcomings of other materials (such as carbon nanotubes, graphite etc.) that have been studied and used for quite some time. The ultimate goal of the research efforts of many groups in the field nowadays is to exploit these extraordinary properties in nanotechnology applications so as to fabricate materials with improved mechanical,
1.4 Properties of graphene

electrical, thermal etc. performance. In what follows, we will give a brief account of the basic mechanical, electrical, and thermal properties of graphene.

1.4.1 Mechanical properties

Graphite, diamond, and carbon nanotubes have their own record in terms of mechanical strength, hardness, or Young’s modulus. Graphene is no exception although its mechanical behavior has been much less investigated than its electronic and optical properties. The reported stiffness of the order of 300 - 400 N/m (with a breaking strength of about 42 N/m) represents the intrinsic strength of a defect-free sheet. Estimates of the Young’s modulus are on the order of 0.5-1.0 TPa which is very close to the accepted value for bulk graphite. Interestingly, and despite their defects, suspended graphene oxide sheets retain almost intact mechanical performances with a Young’s modulus of 0.25 TPa. These values, combined with the relative low cost of thin graphite and the ease of blending graphene oxide into matrices, render these materials ideal candidates for mechanical reinforcement, the study of which is the main goal of the present Master’s thesis.

1.4.2 Electrical properties

Graphene has been shown to have an electrical resistivity at room temperature of about $1\mu\Omega\cdot \text{cm}$. This is about 35% less than the resistivity of silver, the lowest resistivity material known at room temperature.

In semiconductors (such as graphene), a different measure (mobility) is used to quantify how fast electrons move. Mobility can also be expressed as the conductivity of a material per electronic charge carrier, and so high mobility is also advantageous for chemical or bio-chemical sensing applications in which a charge signal from (for instance, a molecule adsorbed on the device) is translated into an electrical signal by changing the conductivity of the device. The limit to mobility of electrons in graphene is set by the thermal vibration of the atoms, and is about $200.000 \text{cm}^2/V\cdot \text{s}$ at room temperature,
1.4 Properties of graphene

compared to about 77.000 cm²/V·s in indium antimonide (the highest known inorganic semiconductor), and to about 100.000 cm²/V·s in carbon nanotubes.

Chen et al.\textsuperscript{33, 34} showed that although the room temperature limit of mobility in graphene is as high as 200.000 cm²/V·s, in present-day samples the actual mobility is lower (around 10.000 cm²/V·s) leaving significant room for improvement. Because graphene is only one atom thick, current samples must sit on a substrate, in this case silicon dioxide. Trapped electrical charges in the silicon dioxide (a sort of atomic-scale dirt) can interact with electrons in graphene, thereby causing a reduction in mobility.

Graphene is therefore a very promising material for chemical and bio-chemical sensing applications. Its low resistivity and extremely thin nature render it a very promising material for applications also in thin, mechanically tough, electrically conducting, and transparent films which are needed in a variety of electronics applications (from touch screens to photovoltaic cells).

1.4.3 Thermal properties

Apart from its excellent mechanical and electrical properties, graphene exhibits amazing performance as a thermal conductor. Balandin et al.\textsuperscript{35} reported values of thermal conductivity for a single-layer graphene at room temperature in the range of 4.84x10³ W/m·K to 5.30x10³ W/m·K. This extremely high value of thermal conductivity suggests that graphene can outperform carbon nanotubes in heat conduction, as this value is larger than conventionally accepted experimental values reported for individually suspended CNTs, corresponding to the upper bound of the highest values reported for single-wall CNT bundles.\textsuperscript{36,37,38}

However, contact with a substrate could affect the thermal transport properties of graphene. Seol et al.\textsuperscript{39} showed experimentally that the value of the thermal conductivity for a monolayer graphene exfoliated on a silicon dioxide support is still as high as about 600 W/m·K near room temperature, exceeding those of metals such as copper. It is lower, though, than that of suspended graphene because of phonons leaking across the graphene-
support interface and strong interface-scattering of flexural modes, which make a large contribution to thermal conductivity in suspended graphene according to a theoretical calculation.

The superb thermal conduction properties of graphene are beneficial for many electronic applications proposed today, establishing graphene as an excellent material for thermal management.

1.5 Graphene as a nanoparticle

Due to its remarkable physical properties, graphene has attracted the attention of a growing number of scientists from several disciplines. In what follows, we will concentrate only at the utilization of graphene as nanofiller in graphene-based polymer nanocomposites (PNC’s), focusing mainly on the available preparation methods and their properties.

1.5.1 Production of graphene/based polymer nanocomposites

In recent years, a variety of processing routes have been reported for dispersing graphene sheets into polymer matrices. Many of these procedures are similar to those used for other nanocomposite systems (CNT’s/polymer nanocomposites) although some of these techniques have been applied uniquely to graphene-based composites.

A crucial step in the production of polymer nanocomposites is the dispersion of the nanofillers. A well dispersed state ensures a maximized reinforced surface area, which will affect the neighboring polymer chains and, consequently, the properties of the whole matrix. Efforts have therefore focused on achieving a homogeneous and well-dispersed system by developing either covalent or non-covalent functionalization of the filler surface.

Most graphene/polymer composites have been developed using mainly one of the following three strategies:
1) solvent processing  
2) in situ polymerization  
3) melt processing

Each strategy offers advantages and disadvantages in the procedure of production of PNC’s, and these are discussed below.

### 1.5.1.1 Solvent processing

After a procedure of producing graphene sheets (applying mainly the methods of chemical or thermal reduction of graphite oxide, as mentioned above), the steps making up the solving-blending process can be summarized in the followings:

1) Dispersion of graphene sheets in suitable solvent assisting it by, for example, ultrasonication  
2) Addition of the polymer in the blend of solvent/graphene  
3) Removal of the solvent by evaporation or distillation

Several composites have been synthesized using this strategy both in aqueous solvent (such as nafion\(^{41}\) and polystyrene (PS)\(^{42}\)) or in organic solvents (such as PS\(^{27}\), polyurethane (PU),\(^{43}\) poly(methyl methacrylate) (PMMA),\(^{44,45}\) and poly(styrene-b-isoprene-b-styrene) (SIS) block copolymer\(^{46}\)).

Due to the simplicity of the procedure, it is expected that graphene/polymer composites will continue to be developed using this methodology. However, a word of caution is in place here, as it has been reported that common organic solvents are strongly adsorbed on graphene sheets in a permanent way. Barroso-Bujans et al.\(^{47}\) found that all tested solvents penetrated and modified the graphene layers to the degree that (even after careful removal and drying procedures) traces of the solvents were found to have remained adsorbed on the materials.

### 1.5.1.2 In situ polymerization


In this strategy, the graphene sheets are mixed with the targeted monomers or pre-polymers (sometimes in the presence of a solvent) and then the polymerization reaction proceeds by adjusting parameters such as temperature and time. Examples of in situ polymerization include PU, PS, PMMA, and polydimethylsiloxane (PDMS) foams.

Research on in situ polymerized nanocomposites should not only analyze the effect of nanofillers in the polymer matrix morphology and final properties, but also in the polymerization reaction. A study on this subject has revealed a decrease in the rate of the polymerization reaction by the addition of thermally exfoliated graphene and a change in the dynamic evolution of the reaction as compared to the effect of CNT. Changes in the molecular weight of thermoplastic polyurethane (TPU) due to the presence of graphene sheets have also been reported.

The advantages of this strategy are double: first, it provides a strong interaction between graphene and the polymer matrix, and second, it enables an outstanding and homogeneous dispersion. However, it is usually accompanied by a viscosity increase that hinders manipulation and loading fraction.

1.5.1.3 Melt processing

Melt processing is much more commercially attractive than the other two methods, as both solvent processing and in situ polymerization are less versatile and environmentally friendly. This strategy involves the direct inclusion of the graphene sheets into the melted polymer using a twin-screw extruder and adjusting parameters such as screw speed, temperature and time. Most of the reported examples have been developed by mixing isolated graphene with the following polymers: PU, isotactic polypropylene (iPP), poly(styrene-co-acrylonitrile) (SAN), polyamide 6 (PA6), and polycarbonate (PC).

The drawbacks of this procedure are the low bulk density of the thermally exfoliated graphene that makes extruder feeding a troublesome task, and the lower degree of
dispersion compared to solvent blending.\textsuperscript{43} This reduced degree of dispersion often results in poorer mechanical, electrical, and thermal properties.

1.5.2 Properties of graphene/based polymer nanocomposites

Due to the recent development of graphene and graphene-based polymer nanocomposites, the literature on this subject is still in its early stages but rapidly developing. Thus, several interesting studies have already been reported illustrating the properties of the new nanocomposites and many interesting applications. In many cases, surprising improvements in mechanical, electrical and thermal properties of these materials are achieved at very low concentrations of suspended graphene sheets in the polymer matrix.

1.5.2.1 Mechanical Properties

The higher mechanical properties of graphene sheets have attracted increasing attention worldwide. The mechanical properties of PNC’s depend on the dispersion of isolated graphene layers within the polymer matrix and the degree of interfacial bonding established between the nanofiller and the matrix. Although pure graphene is not compatible with polymer matrices and tends to aggregate (layer by layer stacking) due to van der Waals interactions, graphene oxide (GO), which contains hydroxyl and epoxy groups on the sheet and carbonyl and carboxyl groups at the edges, interacts more strongly with polymers. GO is more soluble in water and polar solvents, and its surface is relatively easy to modify via the insertion of amines, esters, aromatics and isocyanate functionalities that stabilize dispersions, thus facilitating composite processing.

However, pure GO is an insulator and not an optimum filler for fabricating electrically conducting composites. Therefore, an alternative strategy consists of the surface modification of GO for obtaining a good dispersion at a molecular level, and a subsequent reduction to recover, at least partially, the electrical and thermal conductivity via restoring the graphitic network of the sp\textsuperscript{2} hybridized carbon.\textsuperscript{55}
1.5 Graphene as a nanoparticle

Although PNC’s show enhanced stress-strain behavior when compared to conventional composites, we are still far from the values predicted theoretically. For example, one of the maximum increases in Young’s modulus found in the literature is reported by Lee: \(^{56}\) 200% increase in Young’s modulus for thermoplastic polyurethanes modified with 5% of graphene. As mentioned in a recent review, \(^{57}\) improvements of Young’s modulus and tensile strength are reported to range between 15-90% and 60-100% respectively.

The effect of nanofiller on the matrix mechanical properties needs to be more deeply studied since several matrix processes such as phase separation or crystallization may be altered. For example, a significant increment in modulus accompanied by the creation of a polymer crystalline layer on the surface of the nanofiller has been reported for polycaprolactone reinforced with GO nanosheets. \(^{58}\) In contrast, Xu et al. \(^{59}\) grafted nylon 6 on graphene sheets and observed that the crystallization of chains was depressed. When using graphite nanoplatelets, incomplete exfoliation or restacking of the sheets reduces the mechanical properties of the material. Furthermore, once dispersed, the graphene sheets can adopt distorted structures that reduce the value of the modulus, as they do not have a tendency to stretch under tensile stress.

The production method of graphene-based polymer nanocomposite has also an effect in the mechanical performance of the final material. Via in situ polymerization, the result is composites with good mechanical properties and low percolation thresholds (between 0.3 and 1.6% vol). For example, Nutt and co-workers \(^{49}\) reported an improvement of 70% in the tensile strength, and of 57% in the Young’s modulus for polystyrene composites in which the graphene sheets were grafted with polystyrene chains by atomic transfer radical polymerization (ATRP).

A solvent processing method was used to prepare poly(ethyleneco-vinyl acetate) reinforced with expanded graphite and a 100% increase in modulus was observed with a 4% loading. \(^{60}\) It has also been used to prepare poly(methylmethacrylate) composites with functionalized graphene sheets (FGS) obtained by thermal expansion of completely oxidized graphite oxide. Here, increments in the Young’s modulus and ultimate strengths of 80% and 20%, respectively, were reported at 1% w/w loading. \(^{44}\) This result demonstrated the ability of FGS to interact with polar polymers to create a percolated
Graphene as a nanoparticle

Interphase in which the properties of the host polymer matrix are substantially altered. In Table 1.3, we summarize the mechanical properties of Graphene/Polymer nanocomposites.

Table 1.3: Mechanical Properties of Graphene/Polymer nanocomposites.\(^\text{17}\)

<table>
<thead>
<tr>
<th>polymer(^*)</th>
<th>reinforcements</th>
<th>processing</th>
<th>(E_{\text{matrix}}) (MPa)</th>
<th>graphene concentration (wt %)</th>
<th>modulus increase (%)</th>
<th>tensile strength increase (%)</th>
<th>ultimate strain increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>GO</td>
<td>solvent</td>
<td>2100</td>
<td>2.5</td>
<td>128</td>
<td>76</td>
<td>−70</td>
</tr>
<tr>
<td>PVA</td>
<td>GO</td>
<td>in situ</td>
<td>2130</td>
<td>(0.69)(^\text{a})</td>
<td>43</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PMMA</td>
<td>GO</td>
<td>polymerization</td>
<td>520⁰</td>
<td>(1.7)</td>
<td>34⁰</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PCL</td>
<td>GO</td>
<td>solvent</td>
<td>340</td>
<td>(2.4)</td>
<td>108</td>
<td>36</td>
<td>−90</td>
</tr>
<tr>
<td>PCL</td>
<td>GO</td>
<td>in situ</td>
<td>260</td>
<td>(0.46)</td>
<td>59</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>epoxy TRG</td>
<td>in situ</td>
<td>polymerization</td>
<td>2830</td>
<td>(0.05)</td>
<td>31</td>
<td>40</td>
<td>N/A</td>
</tr>
<tr>
<td>PEN</td>
<td>TRG</td>
<td>melt</td>
<td>2350</td>
<td>2.4</td>
<td>57</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PC</td>
<td>TRG</td>
<td>melt</td>
<td>2860</td>
<td>1.3</td>
<td>55</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PMMA</td>
<td>TRG</td>
<td>solvent</td>
<td>2100</td>
<td>(0.005, 0.5)</td>
<td>33, 80</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PVDF</td>
<td>TRG</td>
<td>solvent</td>
<td>1250</td>
<td>(3.1)</td>
<td>92</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>SAN</td>
<td>TRG</td>
<td>solvent + melt</td>
<td>2350</td>
<td>(2.3)</td>
<td>34</td>
<td>N/A</td>
<td>−58</td>
</tr>
<tr>
<td>PC</td>
<td>TRG</td>
<td>solvent</td>
<td>1480</td>
<td>(2.5)</td>
<td>52</td>
<td>N/A</td>
<td>−98</td>
</tr>
<tr>
<td>PP</td>
<td>990</td>
<td></td>
<td></td>
<td>(1.5)</td>
<td>43</td>
<td>N/A</td>
<td>−99</td>
</tr>
<tr>
<td>PA6</td>
<td>1650</td>
<td></td>
<td></td>
<td>(2.4)</td>
<td>32</td>
<td>N/A</td>
<td>−94</td>
</tr>
<tr>
<td>natural rubber</td>
<td>TRG</td>
<td>solvent/melt</td>
<td>1.3</td>
<td>(1.2)</td>
<td>750</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PDMS</td>
<td></td>
<td>in situ</td>
<td>0.6</td>
<td>(2.2)</td>
<td>1100</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>styrene—butadiene rubber</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>N/A</td>
</tr>
<tr>
<td>TPU</td>
<td>TRG</td>
<td>solvent</td>
<td>458</td>
<td>(1.2)</td>
<td>43</td>
<td>−23</td>
<td>−15</td>
</tr>
<tr>
<td>silicone foam</td>
<td>TRG</td>
<td>in situ</td>
<td>250⁰</td>
<td>(0.12)</td>
<td>200⁰</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PVA</td>
<td>acid functionalized TRG</td>
<td>polymerization</td>
<td>660</td>
<td>(0.4)</td>
<td>35</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PMMA</td>
<td>amine treated, acid functionalized TRG</td>
<td></td>
<td>2120</td>
<td>(0.3)</td>
<td>70</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TPU</td>
<td>TRG</td>
<td>melt</td>
<td>6.1−7.1</td>
<td>1.6</td>
<td>250</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PS</td>
<td>iGO</td>
<td>solvent</td>
<td>1450</td>
<td>(0.4)</td>
<td>57</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TPU</td>
<td>chemically reduced GO</td>
<td></td>
<td>9.8</td>
<td>(0.3)</td>
<td>120</td>
<td>75</td>
<td>N/A</td>
</tr>
<tr>
<td>TPU</td>
<td>GO</td>
<td>solvent</td>
<td>6</td>
<td>(2.4)</td>
<td>900</td>
<td>−19</td>
<td>−60</td>
</tr>
<tr>
<td>PAN</td>
<td>exfoliation of alkali intercalated graphite</td>
<td>electrospinning, solvent</td>
<td>2450</td>
<td>(2.1)</td>
<td>100</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

1.5.2.2 Electrical Properties

One of the most promising aspects of graphene-based materials is their potential for use in device and other electronics applications, owing to their high electrical conductivity. Graphene, as a highly conductive material, when used as filler may increase the bulk conductivity of an otherwise insulating polymer, such as poly(styrene)\(^\text{27}\) and poly(ethylene terephthalate),\(^\text{61}\) by several orders of magnitude.
1.5 Graphene as a nanoparticle

In order for a nanocomposite with an insulating matrix to be electrically conductive, the concentration of the conducting filler must be above the electrical percolation threshold where a conductive network of filler particles is formed. As shown in Figure 1.6, once the electrical percolation has been achieved, the increase in conductivity as a function of filler loading can be modeled by a simple power-law expression of the form:

$$\sigma_c = \sigma_f \left( \varphi - \varphi_c \right)^t$$

where $\varphi$ is the filler volume fraction, $\varphi_c$ the percolation threshold, $\sigma_f$ the filler conductivity, $\sigma_c$ the composite conductivity, and $t$ a scaling exponent.

![Figure 1.6: Conductivity of Polystyrene composites filled with graphene sheets.](image)

Production of electrically conductive polyolefin,$^{53}$ vinyl$^{62}$ and acrylic polymers,$^{63}$ polyester,$^{64}$ polyurethane,$^{43}$ and epoxy$^{65}$ with graphene has been reported. These materials can be used, for example, for electromagnetic shielding,$^{65}$ antistatic coating, and conductive paints. Table 1.4 shows the wide range of electrically conductive polymer/graphene composites, their production methods, and minimum filler volume fraction for electrical conduction.
1.5  *Graphene as a nanoparticle*

The lowest electrical percolation threshold was 0.1 vol % reported by Stankovich et al.\textsuperscript{27} for PS solvent blended with isocyanate-treated GO (iGO), followed by solution-phase reduction with dimethylhydrazine.

Table 1.4: Electrical Properties of several Graphene/Polymer nanocomposites.\textsuperscript{66}

<table>
<thead>
<tr>
<th>Matrix Polymer</th>
<th>Lowest percolation threshold (wt %)</th>
<th>Maximum conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>1.0</td>
<td>0.05 (19 wt%)</td>
</tr>
<tr>
<td>Nylon – 6</td>
<td>0.5</td>
<td>0.00084 (1.8 wt%)</td>
</tr>
<tr>
<td>Poly(aniline)</td>
<td>0.7</td>
<td>522 (1.8 wt%)</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>0.3</td>
<td>0.5 (4.8 wt%)</td>
</tr>
<tr>
<td>Poly(ethylene)</td>
<td>0.2</td>
<td>0.1 (1.3 wt%)</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>1.0</td>
<td>0.02 (6.5 wt%)</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>0.7</td>
<td>1 (10 wt%)</td>
</tr>
<tr>
<td>Poly(propylene)</td>
<td>0.7</td>
<td>0.005 (10 wt%)</td>
</tr>
<tr>
<td>Poly(styrene)</td>
<td>0.2</td>
<td>0.15 (2 wt%)</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>0.5</td>
<td>0.1 (7.5 wt%)</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>1.4</td>
<td>0.06 (14.8 wt%)</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>2.0</td>
<td>0.0003 (4 wt%)</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>0.6</td>
<td>N/A</td>
</tr>
</tbody>
</table>
In the last few decades, molecular simulations have emerged as a very useful and important tool to connect the predictions of theoretical models with experimental results, also to explain many of the microscopic mechanisms behind the measured properties. The prediction of materials’ properties from their chemical composition is crucial for the improvement of products at industrial level. The capability to compute the values of very important physicochemical properties from the molecular structure before the material is actually synthesized, especially for materials with a complex polymeric structure, has great value at the design level. Molecular simulations play a key role in the study of these materials, as they constitute a very effective way not only for the computation of their macroscopic physical and chemical properties, but also for elucidating the atomistic mechanisms that determine these properties, thereby providing a link between the micro and macro levels.

There are three main technics of molecular simulations:

1) Molecular Mechanics (MM)
2) Molecular Dynamics (MD)
3) Monte Carlo (MC)

In the method of Molecular Mechanics, the properties of the system are calculated by considering first a collection of static microstructures. These microstructures are created by starting from an initial configuration where the particles are randomly arranged in the simulation box. They are typically characterized by exceedingly large values of the potential energy because of the presence of atom-atom overlaps, thus the energy should be quickly minimized for these overlaps to be removed. The microstructures that are
created from such a potential energy minimization correspond therefore to local minima of the potential energy, and are often used as initial configurations for Molecular Dynamics and Monte Carlo simulations.

The Molecular Dynamics method is based on the solution of Newton’s equations of motion. These equations are numerically integrated and the result of the integration yields the positions and velocities of each particle or atom in the system in the course of time. In this way it is possible to study the time evolution of the simulated model system. And after system equilibration (at the prescribed temperature or pressure conditions), one can extract all the dynamical and structural properties of the system.

In the Monte Carlo method, thermodynamic average values are calculated via stochastic sampling of a very large number of configurations of the microscopic system. Monte Carlo techniques can efficiently exceed large energy barriers, thus allowing for the fast relaxation of the simulated system. But because the system is not allowed to evolve naturally in time, this technique cannot offer any information about the dynamical behavior of the system.

In this chapter, we will give a theoretical reference to molecular simulations, especially to the Molecular Dynamics method which is the method mostly used in this thesis. First, we will introduce some basic concepts from the field of statistical mechanics with an emphasis on the use of statistical ensembles, then we will discuss important technical aspects of the molecular simulations (such as the atomistic model, the periodic boundary conditions, etc.), then we will focus on the formulation of Molecular Dynamics methods in several ensembles, and finally we will discuss some modern trends in the field in the last years to improve the efficiency of the method (by resorting, e.g., to parallel programming).

2.1 Introduction to Statistical Mechanics

Statistical Mechanics introduces a very general and strict formalism for the calculation of macroscopic properties of a system, given a Hamiltonian. Analytical solutions for this
formalism are in many cases impossible, due to the complexity of the systems of interest. Only in very simple cases these can be obtained (e.g. ideal gas) which rarely are of research interest. Because systems of practical interest are very complicated, in order to get an analytical solution, great simplifications must be done.

In this effort, molecular simulations constitute a great alternative approach, since they afford accurate numerical results that are only subjected to numeric errors. So, they can be considered as the numerical solution of the full statistical-mechanics problem, without introducing any simplifications. The comparison then between the predictions of a simplified theory and the results of an accurate simulation is not only very useful in order to opine whether or not the simplifications that are introduced in models are realistic, but also to modify the existing approximations to get a more accurate model. Furthermore, the results of the simulations can be compared directly with the corresponding experimental ones, certifying the accuracy of the molecular model used, leading to corrections if necessary. If the comparison between simulation and experiment is favorable, then simulation can explain the experimental observation as it provides direct access to the mechanisms governing molecular interactions in the material.

It is obvious therefore that the role of simulations is twofold: a) their results can be compared not only with theoretical predictions but also with experiment data, and b) they are the link between experimental (macroscopic) observation and microscopic causes that lead to a specific experimental behavior.
Because of this link, molecular simulations are commonly known as “numerical experiments”. By using information about the geometry of the molecules and the interactions between their atoms, taking into account the macroscopic restrictions of the employed statistical ensemble, molecular simulations can predict both the static and the dynamical properties of the model system, thus clarifying the microscopic mechanisms that govern material behavior.

But applying molecular simulations on real systems faces two major challenges: first, the interactions between the atomistic units of the simulated system must be known, and second these kinds of simulations are inherently time-consuming. The first problem is overcome by resorting to quantum-mechanical calculations which help derive classical potential functions that can accurately describe the interatomic interactions. For the
second one, it is necessary to develop hierarchical modeling approaches which can help simulate large systems over significantly long time scales.

### 2.2 Statistical Ensembles

In classical statistical mechanics, the state of a system is fully described by the vector \( \mathbf{q} \equiv (q_{11}, q_{12}, q_{13}, q_{21}, q_{22}, q_{23}, \ldots, q_{N1}, q_{N2}, q_{N3}) \equiv (q_1, q_2, \ldots, q_N) \) of generalized coordinates and the vector \( \mathbf{p} \equiv (p_{11}, p_{12}, p_{13}, p_{21}, p_{22}, p_{23}, \ldots, p_{N1}, p_{N2}, p_{N3}) \equiv (p_1, p_2, \ldots, p_N) \) of generalized momenta, for the \( N \) atomistic units making up the system. The \( 3N \)-dimension ensemble of generalized coordinates \( \mathbf{q} \) is defined as the configuration space while the \( 3N \)-dimension ensemble of generalized momenta \( \mathbf{p} \) is defined as the momentum space. The \( 6N \)-dimension vector \( \mathbf{X} \equiv (\mathbf{p}, \mathbf{q}) \equiv (q_1, q_2, \ldots, q_N; p_1, p_2, \ldots, p_N) \) is defined as the phase space and can be denoted as \( \Gamma \); each point in \( \Gamma \) corresponds to one and only one microscopic state.

We assume that the system is isolated and it evolves in time under the influence of the interactions between the particles that compose it. As the time \( t \) passes, the phase point that represents one system realization is mowing through the phase space sketching a trajectory. This trajectory is a line whose points correspond to system snapshots at specific time instances. A very important function in the description of the system is the Hamiltonian \( H(\mathbf{X}, t) \equiv H(\mathbf{p}, \mathbf{q}, t) \) which equals the sum of the potential (\( U \)) and of the kinetic (\( K \)) energies of the system. If the Hamiltonian does not depend explicitly on time (its time dependence comes only from the dependence of \( \mathbf{q} \) and \( \mathbf{p} \) on \( t \)), then it is constant of motion.

The thermodynamic state of a system is usually defined by an ensemble of macroscopic parameters such as the number of particles \( N \), the temperature \( T \), and the pressure \( P \). When a system is defined by a set of macroscopic constraints that are imposed on it, it is not correct to refer to a microstate but to an ensemble of microstates each one of which is compatible with the constraints considered external to the system. The number of these microstates defines a statistical ensemble. Geometrically, a statistical ensemble
2.2 Statistical Ensembles

corresponds to an amount of elements of phase space that are distributed in a specific way.

This distribution is characterized by the probability density $\rho(X, t)$ which is determined by the macroscopic restrictions imposed on the system. The definition of probability density is given by:

$$\rho(X,t) d^{6N} X = \rho(p, q, t) d^{3N} q d^{3N} p$$ (2.1)

which expresses the probability a point of phase space $X$ that belongs to the control volume to be found between $X$ and $X + dX$. The probability density obeys the normalization condition as shown below:

$$\int_{\Gamma} \rho(X,t) d^{6N} X \equiv \int_{\Gamma} \rho(p, q, t) d^{3N} q d^{3N} p = 1$$ (2.2)

As the time evolves, the number of points that constitute the ensemble is moving in phase space. If the system is isolated, then it will reach an equilibration state. The probability density of the ensemble of such a system will evolve to an equilibrium probability density $\rho^{eq}(X)$ which is equally distributed in the phase space of the system.

Let us consider a system of $N$ particles and $X$ a specific point in phase space. The value of any variable $A$ of the system will clearly be a function of phase space, i.e., $A = A(X)$. If the system is isolated, then the trajectory evolves to a hyper surface $\Sigma$ of constant energy and of dimension $6N - 1$. The average value of this arbitrary variable in phase space is defined as:

$$\langle A \rangle_\Sigma = \frac{1}{\Omega_\Sigma} \int_\Sigma A(X) d^{6N-1} X$$ (2.3)

where $\Omega$ is the total volume of this (constant energy) hyper surface. The average value of variable $A$ with respect to time is defined as:
2.2 Statistical Ensembles

\[ \langle A \rangle_t = \lim_{t \to \infty} \frac{1}{t} \int_{t_0}^{t} A(X(t)) dt \]  

(2.4)

If the system satisfies the ergodicity condition, then the average value of \( A \) with respect to phase space will be equal to the average value of \( A \) with respect to time \( t \), i.e., \( \langle A \rangle_\Sigma = \langle A \rangle_t \). From that, the average value can be calculated either by following the trajectory of the isolated system as \( t \) evolves, or by sampling all the possible microstates that the system can take at a specific time instance.

Given a phase space function, the ensemble average with respect to the ensemble probability density \( \rho(X,t) \) is defined as:

\[ \langle A \rangle_{\rho(X,t)} = \int_{t} A(X) \rho(X,t) d^6X \]  

(2.5)

In the following we will discuss the basic concepts of statistical mechanics (referred to above) in conjunction with three widely used statistical ensembles: the NVE, the NVT and the NPT ones.

2.2.1 Microcanonical statistical ensemble (NVE)

The microcanonical statistical ensemble describes an isolated system with a given number of particles \( N \), a constant volume \( V \), and a constant energy \( E \). In the quantum mechanical description, the probability density at equilibrium is uniform among all discrete microscopic states \( i \) with energy between \( E - \delta E \) and \( E \). Mathematically this is expressed as:

\[ \rho_{NVE}^{i} = \begin{cases} \frac{1}{W(N,V,E)}, & \text{if } E - \delta E < E_i < E \\ 0, & \text{otherwise} \end{cases} \]  

(2.6)

where \( W(N,V,E) \) denotes the number of microscopic states (solutions of Schrodinger equation) with energy between \( E - \delta E \) and \( E \).
In the classical description, the probability density in equilibrium is uniform on the E-hypersurface. Mathematically this is expressed as:

\[ \rho^{\text{NVE}}(N,V,E) = \begin{cases} 
\frac{1}{\Sigma(N,V,E)}, & \text{if } E - \delta E < H(X) < E \\
0, & \text{otherwise}
\end{cases} \]  

(2.7)

where \( \Sigma(N,V,E) \) is a “shell” of thickness \( \delta E \) around the E-hypersurface. The link that reconciles quantum and classical descriptions is:

\[
W(N,V,E) = \frac{1}{h^{3N}N!} \Sigma(N,V,E)
\]

(2.8)

The connection of statistical mechanics and macroscopic thermodynamics is given by the famous Boltzmann’s equation for the entropy of an isolated system:

\[
S(N,V,E) = k_B \ln W(N,V,E)
\]

(2.9)

where \( k_B \) is the Boltzmann constant. Entropy is the fundamental quantity of the microcanonical statistical ensemble. By knowing \( S \) as a function of the set \( (N,V,E) \), all thermodynamic properties of the system can be calculated by applying known equations of classical thermodynamics.

### 2.2.2 Canonical statistical ensemble (NVT)

The canonical statistical ensemble describes a system with a given number of particles \( N \), a constant volume \( V \), and a constant temperature \( T \). This is considered to be achieved by assuming that the system \( \Sigma \) at equilibrium interacts with a much bigger system called “heat bath” \( B \) which offers the necessary amount of energy in order for the temperature of the sub-system \( \Sigma \) to be kept constant. The full \( \Sigma + B \) system is isolated and its energy is constant, so it can be described as an NVE statistical ensemble.

In the quantum mechanical description, the probability distribution at equilibrium is given by:
\[ \rho_{i}^{NVT} = \frac{\exp \left( -\frac{E_i}{k_B T} \right)}{\sum_i \exp \left( -\frac{E_i}{k_B T} \right)} = \frac{\exp \left( -\frac{E_i}{k_B T} \right)}{Q(N,V,T)} \] (2.10)

where \( Q(N,V,T) \) is the canonical partition function, equal to \( \sum_i \exp \left( -\frac{E_i}{k_B T} \right) \). The classical description of the equilibrium probability density is given by:

\[ \rho^{NPT}(p,q,V) = \frac{1}{h^{3N} N! Q(N,P,T) V_0} \exp \left( -\frac{H(p,q)}{k_B T} \right) \] (2.11)

where the canonical partition function is defined as:

\[ Q(N,V,T) = \frac{1}{h^{3N} N!} \int \exp \left( -\frac{H(p,q)}{k_B T} \right) d^3 p d^3 q \] (2.12)

The connection with macroscopic thermodynamics is made through the definition of the fundamental equation in the Helmholtz free energy representation, namely:

\[ A(N,V,T) = -k_B T Q(N,V,T) \] (2.13)

Exactly like in the microcanonical statistical ensemble, knowledge of the Helmholtz free energy \( A \) as a function of the set \((N,V,T)\) allows one to calculated the rest of the thermodynamic properties of the system.

2.2.3 Isothermal-isobaric statistical ensemble (NPT)

The isothermal-isobaric statistical ensemble describes a system with a given number of particles \( N \), a constant pressure \( P \) and a constant temperature \( T \). It is the most common ensemble used in molecular simulations, because it reproduces the behavior of a material in real conditions of pressure and temperature. The classical description of the equilibrium probability density in this ensemble is given by:
\[ \rho^{\text{NPT}}(p,q,V) = \frac{1}{h^{3N}N!} \frac{1}{\Delta(N,P,T)} \exp\left(-\frac{H(p,q) + PV}{k_B T}\right) \]  

(2.14)

where the partition function \( \Delta(N,P,T) \) is defined as:

\[ \Delta(N,P,T) = \frac{1}{h^{3N}N!} \int dV \int d\gamma \exp\left(-\frac{H(p,q) + PV}{k_B T}\right) d^{3N}p d^{3N}q \]  

(2.15)

The partition functions of the NPT and NVT statistical ensembles are connected through:

\[ \Delta(N,P,T) = \frac{1}{V_0} \int Q(N,V,T) \exp\left(-\frac{PV}{k_B T}\right) dV \]  

(2.16)

where \( V_0 \) is a reference volume (e.g., the average value of the volume of the system). The connection with macroscopic thermodynamics is made through:

\[ G(N,P,T) = -k_B T \Delta(N,P,T) \]  

(2.17)

which defines the fundamental equation in the Gibbs free energy representation. Then, any other thermodynamic property of the system can be extracted by knowledge of this function.

### 2.3 Atomistic models

As referred to above, the complexity of materials that are of technological interest (such as polymers) causes insurmountable difficulties in solving the corresponding full statistico-mechanical problem analytically. Molecular simulations overcome these difficulties by solving the corresponding problem numerically, given a mathematical model for the molecular geometry and the description of the inter-atomic interactions.

In the case of polymeric materials, there are two types of models that can be adopted: Explicit atom (EA) models (see Figure 2.2(a)) where every atom is considered independently, and united atom (UA) models (see Figure 2.2(b)) where the contribution
of hydrogen atoms can be neglected by considering a relatively larger, spherically interacting particle that encloses both the contributions of the hydrogen atoms and of the atom (e.g., the carbon or the fluorine atom) to which these hydrogens are bonded. The basic advantage of the first class of models is that they can describe the structure of the real system in detail and very-very accurately; with the second class of models, the material properties in some cases are not simulated accurately enough. The basic disadvantage of the EA models is that rather small sizes can be considered in the simulation, because for the same number of molecules considered, they involves practically twice as many particles as the UA models. This explains why simulations that use an EA model are considerably more time-consuming than the corresponding ones that use an UA model.

![Figure 2.2: Representation of the two types of models for the same molecule, here butane: (a) Explicit atom model, (b) United atom model.](image)

Given the type of model adopted, what remains to be defined next are the interactions between the particles of the system. The quantification of these interactions is very crucial because the resulting function of the potential energy is the one that will be used to solve the equations of motion. Generally, the interactions between atomistic particles can be categorized in two main classes: bonded interactions and non-bonded interactions.

The bonded interactions, in turn, are distinguished in three basic types:

- Bond stretching
- Bond bending
- Bond torsional
The non-bonded interactions, on the other hand, are distinguished in two main types:

- Inter- and intra-molecular van der Waals interactions
- Inter- and intra-molecular Coulombic interactions

All these types of interaction are described in some detail below.

- **Bond stretching interactions**: Commonly, they are described by an oscillatory potential that refers to the fluctuation of the distance between two consecutive atoms that are bonded around a reference distance $r_0$:

  $$U_{\text{str}}(r) = \frac{1}{2} k_{\text{str}} (r - r_0)^2$$  \hspace{1cm} (2.18)

  Here $k_{\text{str}}$ is the constant of the spring and $r$ the distance between the two bonded atoms.

- **Bond bending interactions**: Just like the stretching ones, these are usually described by an oscillatory potential. It governs how the angle between three bonded atoms fluctuate around a reference angle $\theta_0$:

  $$U_{\text{bend}}(\theta) = \frac{1}{2} k_{\text{bend}} (\theta - \theta_0)^2$$  \hspace{1cm} (2.19)

  Here $k_{\text{bend}}$ is the constant of the spring and $\theta$ the angle formed by the three atoms.

- **Bond torsional interactions**: They are connected with the variation of the energy due to rotation of the third bond between four consecutive atoms along the chain with respect to the previous two bonds through a dihedral angle $\varphi$. There are
several types of torsional potential that have been proposed in the literature. The most commonly used is:

\[
U_{\text{tors}}(\varphi) = \sum_{i} C_{i} \cos^{i}(\varphi)
\]  

(2.20)

where \( k \) is the maximum number of terms of the summation, and \( C_{i} \) the multiplier of each power term for each cosine in the summation.

- **Lennard–Jones potential**: This potential refers to the interactions that are developed between atoms along the same macromolecular chain that are separated by three bonds and more, or between atoms belonging to different chains. A typical expression is:

\[
U^{ij}_{LJ}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^a - \left( \frac{\sigma_{ij}}{r} \right)^b \right]
\]  

(2.21)

where \( \varepsilon_{ij} \) denotes the well depth (it is a measure of how strongly the two atoms attract each other) and \( \sigma_{ij} \) is distance at which the Lennard-Jones potential between the two particles becomes zero. \( \sigma_{ij} \) gives a measure of how close two nonbonded atoms can get and is thus referred as the van der Waals radius. Both parameters are strongly dependent on the type of atoms involved in the interaction. If these are different, one can use the following approximate expressions:

\[
\sigma_{ij} = \frac{\sigma_{i} + \sigma_{j}}{2}
\]

\[
\varepsilon_{ij} = \sqrt{\varepsilon_{i} \varepsilon_{j}}
\]  

(2.22)

- **Electrostatic potential**: By assuming that the charged portions of atoms are described approximately as point charges, the electrostatic (or Coulomb) potential is an effective pair potential that quantifies the interaction between these point
Periodic Boundary Conditions (PBC’s)

The goal of molecular simulations is to provide information about the physical properties of a macroscopic system. A difficulty to overcome in these calculations is that they are computationally time consuming, limiting in most cases the size of the simulated system to only a few thousands of particles. This number is clearly far from the thermodynamic limit; for such small systems it cannot be safely assumed that the choice of the boundary conditions has a negligible effect on the properties of the system.

In order to simulate bulk phases it is essential to choose boundary conditions that mimic practically an infinite sample of the material. This is usually achieved by employing the

\[ U_{el}(r_{ij}) = -\frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}} \]  

(2.23)

where \( \varepsilon_0 \) is the dielectric constant in vacuum with value \( 8.85418782 \times 10^{-12} \text{ F/m} \), and \( q_i \) and \( q_j \) the charges of atoms \( i \) and \( j \), respectively.

Due to their very long range nature, Coulombic interactions cannot be limited only between the atoms that are contained in the simulation box. Normally, the strength of these interactions decline and become negligible at distances larger than three or four times the simulation box. Because of this, many methods have been proposed for the calculation of Coulombic interactions.

The most accurate method is *Ewald summation*, but it is very demanding in CPU time since it scales as \( N^2 \) where \( N \) is the number of atoms in the system. Methods that use a cut-off reduce considerably the required CPU time for the calculation of the Coulombic potential, at the expense however of accuracy. Typical methods of this type are the *spherical truncation* \(^68\) and the *Particle-Particle Particle-Mesh Ewald* (PPPM) \(^69,70\) methods.
so called periodic boundary conditions. The volume containing the \(N\) particles is treated as the primitive cell of an infinite periodic lattice of identical cells, as shown in Figure 2.3. A given particle from the primitive cell interacts with all other particles in this infinitely periodic system, i.e., with all other particles in the same periodic cell and all particles (including its own periodic image) in all other cells. Also, as a molecule leaves the central box, one of its images will enter through the opposite face. There are no walls at the boundary of the central box, and no surface molecules.

![Figure 2.3: A two dimensional periodic system. Molecules can enter and leave each box across each of the four edges. In a three-dimensional example, molecules would be free to cross any of the six cube faces.](image)

An example of how PBCs act is given in Figure 2.3. In this figure, as particle 1 moves through a boundary, its closest image in one of the “ghost” cells (1A, 1B, 1C, etc.) moves
2.4 Periodic Boundary Conditions (PBC’s)

in across the corresponding boundary. Thus, the primitive cell loses particle 1 as it exits through cell C but gains its image from cell G. So, the entire number density of particles in the primitive cell is conserved.

In molecular simulations, it is crucial to calculate the potential energy of the simulated system as accurate as possible, and as fast as possible. But, it is almost impossible to simulate systems that are of experimental sizes, since they consist practically of an infinitive number of molecules. To overcome this, the concept of Minimum Image Convention (MIC) is introduced.

Consider molecule 1 which belongs to the primitive cell, as shown in Figure 2.4, but think of it as being at the center of a cell with the same shape and size. This molecule interacts with all molecules that lie within a region that is within the closest periodic images of the other \(N-1\) molecules. In the MIC, then, the total number of interactions for the calculation of the potential energy is still \(N (N-1)/2\). This happens because in the primitive cell there are \((N-1)\) interactions for each molecule, but we divide this number by 2 in order not to double count interactions.

Figure 2.4: The minimum image convention in a two-dimensional system.\(^{67}\)
This number will be very large for cases the simulated system is on the order of thousands of particles. The largest contribution to the intermolecular potential energy comes from neighbors close to the molecule of interest, and for short-range forces we normally apply a spherical cut-off. The dashed circle in Figure 2.4 represents this cut-off, and in this case molecules 2 and 4E contribute to the force on particle 1, while the rest of the particles do not contribute.

2.5 The Molecular Dynamics method

Molecular Dynamics simulations are in many respects similar to real experiments. When a real experiment is carried out a sample of the material is prepared which is connected with the measuring instruments (thermometers, manometers, viscometers etc.) and the desired property is measured. The value of a specific property is computed as the average of many measurements in order for the statistical noise to be as low as possible.

Exactly the same approach is followed in a Molecular Dynamics simulation. A model system of \( N \) particles is selected and Newton’s equations of motion are integrated (numerically), until the average properties of the system no longer change with time. After equilibration, several measurements are made using the trajectory (containing complete information about the atomic positions and velocities in the system). The basic structure of a typical Molecular Dynamics algorithm is resented in Figure 2.5.
2.5 The Molecular Dynamics method

Figure 2.5: A typical flow chart of the basic steps of a Molecular Dynamics simulation.

2.5.1 Equations of motion

At the heart of a Molecular Dynamics simulation is the solution of the equations of motion, which defines the trajectory of the system in phase space. Suppose that the studied system consists of $N$ particles (or atomistic units) and its total potential energy is
described by a function $U$. Then, the equations of motion for this system can be described by three different formalisms: the Langrangian, the Hamiltonian and the Newtonian formalism. We briefly discuss all three of them below.

### 2.5.1.1 The Langrangian formalism

In the Langrangian formalism, the key function is the Langrangian $L$ of the system defined as the difference between the kinetic energy $K$ and the potential energy of the system $U$ of the system:

$$L = L(q,\dot{q},t) = K - U \quad (2.24)$$

The vector of generalized coordinates $q$ of the atomic positions is governed by eq. (2.24) and the vector of generalized momenta $p$ by eq. (2.25):

$$\frac{\partial L}{\partial \dot{q}_k} = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_k} \right) \quad (2.25)$$

$$p_k = \frac{\partial L}{\partial \dot{q}_k} \quad (2.26)$$

### 2.5.1.2 The Hamiltonian formalism

The Hamiltonian $H$ is defined from the Langrangian $L$ through:

$$H(q,p,t) = \sum_k \dot{q}_k p_k - L(q,\dot{q},t) \quad (2.27)$$

The vector of generalized coordinates $q$ of atomic positions and the vector of generalized momenta $p$ obey then the following equations:

$$\dot{q}_k = \frac{\partial H}{\partial p_k} \quad (2.28)$$
2.5  The Molecular Dynamics method

\[ \dot{p}_k = -\frac{\partial H}{\partial q_k} \quad (2.29) \]

If the Hamiltonian of the system is not directly dependent on time, then it also represents the total energy of the system.

2.5.1.3  The Newtonian formalism

In this formalism, the Cartesian coordinates \( r_i \) of the particles are introduced, whose time dynamics is described by Newton’s law, namely:

\[ m\ddot{r}_i = F_i \quad (2.30) \]

with \( F_i \) being the force that acts on particle \( i \). The above equation leads to a system of \( 3N \) 2\(^{nd}\) order differential equations which is easily transformed into 2 sets of \( 3N \) 1\(^{st}\) order differential equations of the form:

\[ \dot{r}_i = v_i = \frac{p_i}{m_i} \quad (2.31) \]

\[ \dot{p}_i = -\nabla_{r_i} U \equiv -\frac{\partial U}{\partial r_i} = F_i \quad (2.32) \]

The solution of these two sets of equations provides the time evolution of the system.

2.5.2  Integration of the equations of motion

In a Molecular Dynamics simulation, solving (=integrating) the differential equations of motion can be achieved with many algorithms. A good algorithm for must meet the following requirements:

- should not require an expensively large number of force evaluations per time step
- should permit the use of a large time step
• should be fast
• to satisfy the energy conservation law
• should require low memory

There are many algorithms that have been proposed to satisfy the above criteria, the most widespread being the *Gear predictor-corrector* and the *Verlet* algorithms. Both of them are presented in good detail in the next paragraphs.

### 2.5.2.1 Gear predictor–corrector algorithms

These algorithms are developed as follows: Let us assume that we know the positions, velocities and higher order derivatives of the atomic positions at time instance \( t \). Then, we can get estimates of all these variables (positions, velocities and higher order derivatives) at a time instance \( t + dt \) by expanding them into a Taylor series with respect to \( t \), as follows:

\[
\begin{align*}
\mathbf{r}^p(t + dt) &= \mathbf{r}(t) + \mathbf{v}(t)dt + \ddot{\mathbf{r}}(t)\frac{dt^2}{2} + \dddot{\mathbf{r}}(t)\frac{dt^3}{6} + \dddot{\dddot{\mathbf{r}}}(t)\frac{dt^4}{24} + \ldots \quad (2.33) \\
\mathbf{v}^p(t + dt) &= \mathbf{v}(t) + \dot{\mathbf{r}}(t)dt + \ddot{\dot{\mathbf{r}}}(t)\frac{dt^2}{2} + \dddot{\dot{\dot{\mathbf{r}}}}(t)\frac{dt^3}{6} + \ldots \quad (2.34) \\
\dot{\mathbf{r}}^p(t + dt) &= \dot{\mathbf{r}}(t) + \ddot{\mathbf{r}}(t)dt + \dddot{\mathbf{r}}(t)\frac{dt^2}{2} + \ldots \quad (2.35) \\
\mathbf{r}^p(t + dt) &= \mathbf{r}(t) + \dot{\mathbf{r}}(t)dt + \ddot{\mathbf{r}}(t)dt + \ldots \quad (2.36)
\end{align*}
\]

The superscript on the left hand side of each of the above equations has been used to denote that all these variables are just predictions of the corresponding variables. By employing these equations as such, the computed values will not give the exact trajectory for each particle, since we have not made use of the equations of motion. To this, the predicted values are replaced by the corrected values, as follows:
2.5 The Molecular Dynamics method

\[ \mathbf{r}^{(t+dt)} = \mathbf{r}^{(t)} + \mathbf{v}^{(t)} dt + \mathbf{a}^{(t)} \frac{dt^2}{2} + \mathbf{b}^{(t)} \frac{dt^3}{6} + \ldots \]  
(2.37)

\[ \mathbf{v}^{(t+dt)} = \mathbf{v}^{(t)} + \mathbf{a}^{(t)} dt + \mathbf{b}^{(t)} \frac{dt^2}{2} + \mathbf{c}^{(t)} \frac{dt^3}{6} + \ldots \]  
(2.38)

\[ \mathbf{a}^{(t+dt)} = \mathbf{a}^{(t)} + \mathbf{b}^{(t)} dt + \mathbf{c}^{(t)} \frac{dt^2}{2} + \mathbf{d}^{(t)} \frac{dt^3}{6} + \ldots \]  
(2.39)

\[ \mathbf{b}^{(t+dt)} = \mathbf{b}^{(t)} + \mathbf{c}^{(t)} dt + \mathbf{d}^{(t)} \frac{dt^2}{2} + \mathbf{e}^{(t)} \frac{dt^3}{6} + \ldots \]  
(2.40)

In the above equations, \( \Delta \mathbf{x} \) is defined as:

\[ \Delta \mathbf{x} = \mathbf{a}^{(t)} \left( \mathbf{r}^{(t+dt)} \right) - \mathbf{b}^{(t)} \left( t + dt \right) \]  
(2.41)

and gives the deviation of the predicted value of the vector of atomic accelerations from the exact value calculated by applying the equations of motion. \( c_i \), on the other hand, are numerical constants that immunize the stability and the accuracy of the algorithm.

2.5.2.2 Verlet algorithms

The Verlet algorithms are simple, accurate and, as we will see below, time reversible, which explains why they are widely used in MD simulations. The initial form of the Verlet equations is obtained by utilizing a Taylor expansion at times \( t - dt \) and \( t + dt \):

\[ \mathbf{r}(t + dt) = \mathbf{r}(t) + \mathbf{v}(t) dt + \mathbf{a}(t) \frac{dt^2}{2} + \mathbf{b}(t) \frac{dt^3}{6} + \ldots \]  
(2.42)

\[ \mathbf{r}(t - dt) = \mathbf{r}(t) - \mathbf{v}(t) dt + \mathbf{a}(t) \frac{dt^2}{2} - \mathbf{b}(t) \frac{dt^3}{6} + \ldots \]  
(2.43)

Summing the two equations gives:

\[ \mathbf{r}(t + dt) = 2\mathbf{r}(t) - \mathbf{r}(t - dt) + \mathbf{a}(t) \frac{dt^2}{2} + \ldots \]  
(2.44)

with \( \mathbf{a}(t) \) calculated from the forces at the current positions. The calculation of the velocities is obtained by subtracting eq. (2.43) from eq. (2.42):
2.5  The Molecular Dynamics method

\[ v(t + dt) = \frac{r(t + dt) - r(t - dt)}{2dt} \]  \hspace{1cm} (2.45)

This is the coordinate version of the Verlet algorithm which has several drawbacks, since the velocities are not among the variables used in integrating the equations of motion. Thus, the following two modifications of the Verlet scheme are of wide use. The first is the leap-frog algorithm where positions and velocities are calculated at different times, as follows:

\[ r(t + dt) = r(t) + v\left( t + \frac{dt}{2} \right) \]  \hspace{1cm} (2.46)

\[ v\left( t + \frac{dt}{2} \right) = v\left( t - \frac{dt}{2} \right) + \ddot{r}(t) dt \]  \hspace{1cm} (2.47)

An estimate of the velocity at time \( t \) (needed in the calculation of the Hamiltonian) is obtained as the average of its values at times \( t + dt/2 \) and \( t - dt/2 \), i.e.:

\[ v(t) = \frac{1}{2} \left( v\left( t + \frac{dt}{2} \right) - v\left( t - \frac{dt}{2} \right) \right) \]  \hspace{1cm} (2.48)

The second modification is the velocity-Verlet algorithm where positions and velocities are calculated at the same (and not different) times, as follows:

\[ r(t + dt) = r(t) + v(t) dt + \ddot{r}(t) \frac{dt^2}{2} \]  \hspace{1cm} (2.49)

\[ v(t + dt) = v(t) + \left( \ddot{r}(t) + \dddot{r}(t + dt) \right) \frac{dt}{2} \]  \hspace{1cm} (2.50)

The corresponding accelerations are calculated from the forces at the current moment by applying Newton’s law. Figure 2.6 provides a schematic illustration of the Verlet algorithm and its modifications.
2.5 The Molecular Dynamics method

Figure 2.6: Various forms of the Verlet algorithm: (a) Verlet’s original method. (b) The leap–frog method. (c) The velocity–Verlet method.

If we were to compare the two families of integration algorithms, we would note that the Gear algorithms offer more accuracy than the Verlet ones, especially at small times. The biggest advantage of the latter though is that they are time reversible, implying that they satisfy the energy conservation law even at large simulation times. This is the reason why the Verlet algorithms are preferred to Gear ones in most Molecular Dynamics simulations. In the present thesis, the velocity-Verlet method will be employed for the integration of the equations of motion for the systems of interest (polymers and polymer nanocomposites).

2.5.3 Molecular Dynamics simulations in different ensembles

An MD simulation must be carried out at pre-specific values of a carefully chosen set of external or macroscopic variables, such as the temperature and the pressure. The most widely used statistical ensembles are the NVT and NPT ones, which are those that will be analyzed in the following sections.

2.5.3.1 MD in the NVT statistical ensemble
2.5 The Molecular Dynamics method

In terms of Statistical Mechanics, the temperature $T$ is defined as the average value of the instantaneous temperature $T_{\text{ins}}$ defined as:

$$T_{\text{ins}} = \frac{2K}{(3N - n_c)k_B} = \frac{1}{(3N - n_c)k_B} \sum_{i=1}^{N} \left| \frac{\mathbf{p}_i}{m_i} \right|^2$$  \hspace{1cm} (2.51)

where $N$ is the total number of particles in the system, $\mathbf{p}_i$ and $m_i$ the momentum and mass of each particle, respectively, and $n_c$ the number of external system constraints. These refer not only to geometry (such as rigid bonds/angles) but also to constraints imposed directly to the system (zero total momenta etc.)

That the number of particles and the volume of the system remains constant in the NVT simulation means that during the execution of the corresponding algorithm neither insertion or deletion of particles is allowed nor fluctuations of the cell dimensions. To keep the temperature constant, then, many methods have been proposed, the most widely used being those based on the use of the Berendsen\textsuperscript{71} and Nosé-Hoover\textsuperscript{72,73} thermostats.

In the Nosé – Hoover thermostat, which is the one also used in the present study, the temperature is kept constant by imposing an extra degree of freedom, the variable $s$. In this new degree of freedom coordinates (a position and a momentum) are assigned, thus also a kinetic and a potential energy. The variable $s$ plays the role of a “heat bath” which keeps the temperature of the system constant in a specific, pre-defined value. The kinetic and potential energy terms connected with $s$ are:

$$U_s = gk_B T \ln s$$  \hspace{1cm} (2.52)

$$K_s = \frac{Q}{2} \left( \frac{s}{\dot{s}} \right)^2 = \frac{\mathbf{p}_s^2}{2Q}$$  \hspace{1cm} (2.53)

with $g$ denoting the total number of degrees of freedom of the system, and $Q$ and $\mathbf{p}_s$ the mass and momentum of the variable $s$.

The total Hamiltonian of the system, which is a conserved quantity in case no external forces are applied, is expressed as:
2.5 The Molecular Dynamics method

\[ H = \sum_{i=1}^{N} \frac{p_i^2}{m_i} + U(r^N) + gk_bT \ln s + \frac{p_s^2}{2Q} \]  

(2.54)

The first two terms in this equation correspond to the total energy of the system particles while the last two are associated with the presence of the thermostat.

The resulting equations of motion take then the following final form:

\[ \dot{r}_i = \frac{p_i}{m_i} \]  

(2.55)

\[ \dot{p}_i = -\frac{\partial V}{\partial r_i} - \frac{s}{s} p_i \]  

(2.56)

\[ \dot{s} = p_s \frac{s}{Q} \]  

(2.57)

\[ \dot{p}_s = \frac{\left( \sum_{i=1}^{N} \frac{p_i^2}{m_i} - gk_bT \right)}{Q} \]  

(2.58)

2.5.3.2 MD in the NPT statistical ensemble

In terms of Statistical Mechanics considerations, the pressure \( P \) is defined as the average value of the instantaneous pressure \( p_{ins} \) defined according to the Virial theorem as:

\[ p_{ins} = \rho k_B T + \frac{1}{3V} \sum_{i=1}^{N} \sum_{j=1}^{N} (r_i - r_j) F_{ij} \]  

(2.59)

where \( \rho \) denotes the number density of the particles. For keeping the pressure of the system constant during an NPT simulation, many methods have been proposed, such as the Andersen\textsuperscript{74} and the Parinello-Rahman\textsuperscript{75,76} ones. The Nosé-Hoover thermostat and the Andersen barostat have been combined by Hoover\textsuperscript{77} in a way which describes a system in the NPT ensemble. The NPT ensemble is generated by allowing the volume to fluctuate such that the average internal pressure of the system \( P \) is equal to an externally applied
pressure $P_{\text{ext}}$. The volume is thus introduced as a dynamical variable $\varepsilon$ in the equations of motion, which now take the form:

$$\dot{r}_i = \frac{p_i}{m_i} + \frac{p_\varepsilon}{W} r_i$$

(2.60)

$$\dot{p}_i = -\frac{\partial V}{\partial r_i} - \dot{s} \dot{r}_i - \frac{p_\varepsilon}{W} p_i$$

(2.61)

$$\dot{s} = \frac{p_s}{Q}$$

(2.62)

$$\dot{p}_s = \frac{\left( \sum_{i=1}^{N} \frac{p_i^2}{m_i} - (g+1)k_B T + \frac{p_\varepsilon^2}{W} \right)}{Q}$$

(2.63)

$$\dot{V} = \frac{dV}{W} p_\varepsilon$$

(2.64)

$$\dot{p}_\varepsilon = dV \left( P_{\text{int}} - P_{\text{ext}} \right) - \frac{p_s}{Q} p_\varepsilon$$

(2.65)

where $W$ and $p_\varepsilon$ are the mass and momentum of the variable $\varepsilon$, respectively, and $P_{\text{int}}$ denotes the instantaneous internal pressure of the system defined as:

$$P_{\text{int}} = \frac{1}{dV} \left[ \sum_{i=1}^{N} \frac{p_i^2}{m_i} + \sum_{i=1}^{N} r_i \cdot F_i - dV \frac{\partial U^{pot}}{\partial V} \right]$$

(2.66)

The total Hamiltonian of the system in the NPT ensemble is expressed then by:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{m_i} + U(r^N) + gk_B T \ln s + \frac{p_s^2}{2Q} + \frac{p_\varepsilon^2}{2W} + P_{\text{ext}} V$$

(2.67)

### 2.5.4 Multiple Time Step algorithms
Multiple Time Step (MTS) integration algorithms have been developed in order to reduce the computational time needed for the calculation of the forces on each particle. A widely used multiple time step algorithm is the reversible Reference System Propagator Algorithm or rRESPA.\textsuperscript{78,79} This is based on the following idea: the interactions that take place in the system in the course of the MD simulation can be split in two types depending on their characteristic time scales: fast \((F_f)\), such as the bonded interactions, which change frequently with time, and slow \((F_s)\), such as the non-bonded ones, which change less often. Based on such a splitting, rRESPA enables one to integrate and calculate the non-bonded forces (the most time-consuming step in an MD simulation) less often than the fast ones, and this renders the MD algorithm considerably faster.

For the description of the equations of motion, Tuckerman et al.\textsuperscript{56} and Martyna et al.\textsuperscript{57} used the Louiville operator \(L\), and developed an MD algorithm that is time reversible. The Louiville operator \(L\) is defined as:

\[
iL = \sum_{i=1}^{N} \left[ \dot{r}_{i} \frac{\partial}{\partial r_{i}} + F_{i} \frac{\partial}{\partial p_{i}} \right]
\]

and can be separated in two terms:

\[
iL = iL_1 + iL_2 = \sum_{i=1}^{N} \left[ F_{i} \frac{\partial}{\partial p_{i}} \right] + \sum_{i=1}^{N} \left[ \dot{r}_{i} \frac{\partial}{\partial r_{i}} \right]
\]

If we apply the idea that the forces can be categorized in fast and slow as mentioned above, then eq. (2.68) becomes:

\[
iL = iL_1 + iL_2 + iL_3 = \sum_{i=1}^{N} \left[ F_{i}^{f} \frac{\partial}{\partial p_{i}} \right] + \sum_{i=1}^{N} \left[ \dot{r}_{i} \frac{\partial}{\partial r_{i}} \right] + \sum_{i=1}^{N} \left[ F_{i}^{s} \frac{\partial}{\partial p_{i}} \right]
\]

The studied system then evolves in phase space as dictated by the evolution operator:

\[
\Gamma(t) = \exp(iLt)\Gamma(0)
\]

which, by using Trotter’s theorem:
The Molecular Dynamics method

\[
\exp^{(A+B+\Gamma)} = \left( e^{\frac{A}{2}P} e^{(B+\Gamma)/P} e^{\frac{A}{2}P} \right)^P = \left( e^{\frac{A}{2}P} \left( e^{B/2P^2} e^{\Gamma/P^2} e^{B/2P^2} \right)^P e^{\frac{A}{2}P} \right)^P
\]  

(2.72)

allows us to re-write eq. (2.70) in the form:

\[
\exp(iL\Delta t) = \exp\left( iL_3 \frac{\Delta t}{2} \right) \exp\left( iL_1 \frac{dt}{2} \right) \exp\left( iL_2 dt \right) \exp\left( iL_1 \frac{dt}{2} \right) \exp\left( iL_3 \frac{\Delta t}{2} \right)
\]  

(2.73)

2.5.5 Parallel MD algorithms

The goal of a parallel algorithm is in general twofold: a) to decrease the computational time of a simulation, and b) to address problems with realistic size systems that could not be simulated by just one processor.

As we have mentioned several times so far in this thesis, the most time-consuming part in a Molecular Dynamics simulation is the calculation of the forces acting on the particles. An ideal algorithm would be then one that could equally distribute the number of force calculations over all available processors. In addition, it would be desirable if each processor could work independently and communicate rarely with the other processors. Based on these two criteria, the basic parallel algorithms that are used for the calculation of forces in MD simulations can be classified in three main categories:

- Atom decomposition algorithm
- Force decomposition algorithm
- Domain decomposition algorithm

The distribution of the system atoms on the available processors is done differently in each of these three algorithms. For this reason, the information exchanged among the processors is dissimilar, which affects the efficiency of the corresponding parallel code.

In the following, we will provide a brief description only of the domain decomposition algorithm, because this is the one that is used in the commercial computational package LAMMPS (the MD simulation engine used in the present study).
In the domain decomposition method, the simulation cell is split in smaller cells, depending on the available processors, as shown in Figure 2.7. Each processor involves only one cell with length \( L_z = L / P \), where \( L \) is the total length of the simulation cell and \( P \) the number of available processors.

![Figure 2.7: Decomposition and distribution of atomistic units into P available processors using the Domain Decomposition method.](image)

As the simulation time passes, the atoms in a given cell are refreshed and distributed among the processors as they are moving in space. To compute the forces on each particle, each processor has to know the positions of atoms only in the neighboring cells. By that way, the time needed for the communication among processors in drastically reduced. The integration steps of the equations of motion in a parallel MD algorithm can then be summarized as follows:

a) Calculate the bonded and non-bonded forces on all atoms in a specific cell.

b) The processors that calculate the atomic forces in the neighboring cells exchange information and eventually all these forces are summed up to estimate the total force acting on each particle.

c) Calculate the new atomic positions, when the force calculation has been finished.
2.5 The Molecular Dynamics method

d) Communicate this information between the processors of neighbor cells and refresh the neighbor lists.

e) Assign atoms that have been moved outside a specific simulation cell to the appropriate processor with respect to the boundary conditions.

2.5.6 The LAMMPS simulation software

In this section, a description of the LAMMPS code is given, because this is the code employed in the present study for the execution of all MD simulation. The basic features and advantages of this code can be summarized as follows:

- LAMMPS is a classical molecular dynamics code, and an acronym for Large-scale Atomic/Molecular Massively Parallel Simulator.
- In the most general sense, LAMMPS integrates Newton's equations of motion for collections of atoms, molecules, or macroscopic particles that interact via short- or long-range forces with a variety of initial and/or boundary conditions.
- It contains many potential functions in its libraries both for soft (biomolecules, polymers) and solid-state (metals, semiconductors) materials, as well as for coarse-grained or mesoscopic systems. The Coulombic interactions are addressed by many different methods such as the Ewald and the particle-particle, particle-mesh Ewald methods.
- Sophisticated force fields, such as AMBER and CHARMM, have also been introduced allowing the user to simulate complicated molecules (proteins and DNA).
- The integration of the equations of motion can be done either with the velocity Verlet or the rRESPA algorithm.
- Molecular Dynamics simulations in the NVT and NPT statistical ensembles are routinely carried out in LAMMPS. The temperature is kept constant either with the Berendsen or the Nosé-Hoover thermostats and the pressure is kept constant with the Nosé-Hoover barostat.
2.6 Minimization of the potential energy

- The biggest advantage of LAMMPS though is that it is optimized in order to work as efficiently as possible on parallel machines. LAMMPS uses spatial-decomposition techniques to partition the simulation domain into small 3d sub-domains, each one of which is assigned to a different processor. Processors communicate by using the message passing method via the MPI libraries.

2.6 Minimization of the potential energy

From a mathematical point of view, the problem of the potential energy minimization belongs to the general category of optimization problems. The main goal of the optimization problems is to choose appropriate values for the variables \( x_1, x_2, x_3, \ldots, x_N \) so as to optimize (minimize or maximize) a scalar function \( f(x_1, x_2, x_3, \ldots, x_N) \). In molecular simulation problems, this function is the potential energy of the system \( U(r^N) \); its optimization corresponds to the minimization of its value. So, the target is to find the optimal values of the particle positions in the system so that the total potential energy reaches a minimum.

In general, the conditions that have to be satisfied for the minimization of the potential energy lead to a highly coupled system of non-linear equations which can be solved in general with several numerical methods. The corresponding algorithms are called energy minimization algorithms.

The optimization codes are distinguished in two main categories: iterative methods and descent methods. The iterative methods initially begin from a specific point \( x_0 \) and construct a sequence of points \( \{x_i\}_{i=0}^{\infty} \) with respect to the following rule: every new point in the sequence is resulting from the previous points via a depiction \( A : \mathbb{R}^n \rightarrow \mathbb{R}^n \) so that \( x_{i+1} = A(x_i) \). The depiction \( A \) characterizes the algorithm and differs from every other algorithm of this category. The basic principle of the descent methods is that every new point \( x_{i+1} \) of the sequence reduces the value of a continuing function \( \varphi(x_{i+1}) \), where \( \varphi \)
characterize the under study problem (the total potential energy of the system for example), compared to the value of this function at the previous point, i.e. $z(x_{i+1}) < z(x_i)$.

In the problem of energy minimization the descent methods are mostly employed. Steepest descent (SD), Conjugate Gradient (CG), and Hessian Free-Truncated Newton (HFTN) are typical examples of methods that are widely used for this purpose. In the current study, the HFTN method was employed because of its higher accuracy, which is absolutely necessary in our study. The Hessian (second derivatives) of the energy is not formed directly but approximated in each conjugate search direction by a finite difference directional derivative. When close to an energy minimum, the algorithm behaves like Newton’s method, exhibiting a quadratic convergence rate to high accuracy.
As referred to above, the main goal of the present study is to develop and apply atomistic-level simulation methodologies to predict the structural and mechanical properties of polymer nano-composite materials (PNCs) enhanced with graphene sheets.

Our effort is based on the method first proposed by Theodorou and Suter\(^8^5\). In this method, a thermodynamic analysis shows that entropic contributions to the elastic response to deformation of polymeric glasses can be neglected. A statistical mechanical analysis further indicated that vibrational contributions of the hard degrees of freedom are not significant, so that estimates of the elastic constants can be obtained from changes in the total potential energy of static microscopic structures subjected to simple deformations in place of the internal energy. In the following, an in depth analysis on the thermodynamic and statistic mechanical considerations underlying the method is presented followed by a summary of the assumptions of the method and a practical guide with every step will be given.

3.1 Thermodynamic Considerations

A polymeric material is regarded as a collection of atoms whose positions are denoted by \( \mathbf{r}_0 = (r_{0,1}, r_{0,2}, r_{0,3}) \) vector in the reference (undeformed) state and

by \( \mathbf{r} = (r_1, r_2, r_3) \) in a deformed state. For solid polymers, deformations are applied by assuming a change in the shape of the model system. So \( \mathbf{a}, \mathbf{b} \) and \( \mathbf{c} \) denote the vectors defining the dynamic cell, where from them, the tensor of the state of the system \( \mathbf{h} = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\} \) is defined whose value in the undeformed state is \( \mathbf{h}_0 \). The vector \( \mathbf{s} \) with
components $s_i = r_i - r_{0,i}$ is the displacement vector. The material strain tensor $\varepsilon$ is defined by:

$$
\varepsilon_{LM} = \frac{1}{2} \left( \sum_{i=1}^{3} \frac{\partial r_i}{\partial r_{0,L}} \frac{\partial r_i}{\partial r_{0,M}} - \delta_{LM} \right) = \frac{1}{2} \left( \frac{\partial s_L}{\partial r_{0,M}} + \frac{\partial s_M}{\partial r_{0,L}} \right) + \frac{1}{2} \left( \sum_{i=1}^{3} \frac{\partial s_i}{\partial r_{0,M}} \frac{\partial s_i}{\partial r_{0,L}} \right)
$$

(3.1)

We are only concerned with very small deformations, so second order terms in the derivatives of the displacement with respect to the position can be neglected in defining $\varepsilon$, and material and spatial strain will be considered identical.

The material stress tensor is denoted by $\tau$. The element $\tau_{LM}$ is taken equal to the force per unit area acting on an element of surface perpendicular to axis $L$ and along the direction $M$. If $d\mathbf{F}$ is the surface force on an element of surface $dS$, where the exterior unit normal is $\mathbf{n}$, we write in matrix notation:

$$
d\mathbf{F} = \tau^T \mathbf{n} dS
$$

(3.2)

The tensors $\varepsilon$ and $\tau$ are symmetric thus it can also be represented, in Voigt notation, as vectors of six components. The two notations will be used interchangeable by making use of the following correspondence:

$$
\begin{align*}
\varepsilon_1 &= \varepsilon_{11} \\
\varepsilon_2 &= \varepsilon_{22} \\
\varepsilon_3 &= \varepsilon_{33} \\
\varepsilon_4 &= 2\varepsilon_{23} \\
\varepsilon_5 &= 2\varepsilon_{31} \\
\varepsilon_6 &= \varepsilon_{12}
\end{align*}
$$

(3.3)

$$
\begin{align*}
\tau_1 &= \tau_{11} \\
\tau_2 &= \tau_{22} \\
\tau_3 &= \tau_{33} \\
\tau_4 &= \tau_{23} \\
\tau_5 &= \tau_{31} \\
\tau_6 &= \tau_{12}
\end{align*}
$$

The fundamental thermodynamic equation for an elastic system in terms of the stress and strain tensors, at constant chemical composition, assumes the form:
3.1 Thermodynamic Considerations

\[ dU = TdS + V_0 \sum_{LM} \tau_{LM} d\varepsilon_{LM} = TdS + V_0 \sum_{i} \tau_i d\varepsilon_i \]  
\[ (3.4) \]

In the Helmholtz free energy representation \( (A = U - TS) \), the corresponding fundamental thermodynamic expression in differential form is:

\[ dA = -SdT + V_0 \sum_{LM} \tau_{LM} d\varepsilon_{LM} = -SdT + V_0 \sum_{i} \tau_i d\varepsilon_i \]  
\[ (3.5) \]

This allows one to define the 4th order tensor of isothermal elastic coefficients \( C_{LMNK} \) determining the relationship between strain and tension tensors:

\[ C_{LMNK} = \frac{\partial \tau_{LM}}{\partial \varepsilon_{NK}} = \frac{1}{V_0} \frac{\partial^2 A}{\partial \varepsilon_{LM}\varepsilon_{NK}} \Bigg|_{\tau_{LM},\varepsilon_{NK}} \]  
\[ (3.6) \]

As a result of the Voigt symmetry relationships, the above equation can be condensed into a symmetric 6x6 matrix \( C \). For an isotropic material, such as an amorphous glassy polymer, the matrix \( C \) takes the form:

\[
C = \begin{bmatrix}
2\mu + \lambda & \lambda & \lambda & 0 & 0 & 0 \\
\lambda & 2\mu + \lambda & \lambda & 0 & 0 & 0 \\
\lambda & \lambda & 2\mu + \lambda & 0 & 0 & 0 \\
0 & 0 & 0 & \mu & 0 & 0 \\
0 & 0 & 0 & 0 & \mu & 0 \\
0 & 0 & 0 & 0 & 0 & \mu
\end{bmatrix}
\]  
\[ (3.7) \]

where \( \mu \) and \( \lambda \) are the Lamé constants. The tensile (Young’s Modulus) \( E \), the shear modulus \( G \), the bulk modulus \( B \), and the Poisson ratio \( v \) are related to \( \mu \) and \( \lambda \) by the above equations:

\[ E = \mu \frac{3\lambda + 2\mu}{\lambda + \mu} \]  
\[ (3.8) \]

\[ G = \mu \]  
\[ (3.9) \]
3.1 Thermodynamic Considerations

\[ B = \lambda + \frac{2}{3} \mu \]  
(3.10)

\[ v = \frac{\lambda}{2(\lambda + \mu)} \]  
(3.11)

The strain dependence of the entropy at constant temperature is given by the Grüneisen tensor \( \gamma \) :

\[ \gamma_{LM} = \frac{1}{\rho_0 c_v V_0} \left. \frac{\partial S}{\partial \varepsilon_{LM}} \right|_{T, \tau_{(LM)}} = -\frac{1}{\rho_0 c_v} \left. \frac{\partial \tau_{LM}}{\partial T} \right|_{\varepsilon} \]  
(3.12)

where \( c_v \) is the heat capacity per unit mass of material at constant strain.

Consider now an elastic solid which is subjected to an arbitrary isothermal small deformation. Expanding the internal energy \( U \) of the system into a Taylor expansion series around the undeformed state up to second order, and using the definitions introduced above, it is obtained:

\[
U = A + TS = U_0 + V_0 \sum_{LM} \left[ \tau_{LM} + \rho_0 c_v T \gamma_{LM} \right] \varepsilon_{LM} + \frac{1}{2} V_0 \sum_{LM} \sum_{NK} \left[ C_{LMNK} - T \frac{\partial C_{LMNK}}{\partial T} \right] \varepsilon_{LM} \varepsilon_{NK}
\]  
(3.13)

The first terms in the brackets are due to the strain derivatives of the Helmholtz energy while the second terms originate in the corresponding derivatives of entropy. The quantity

\[
\frac{1}{3} \text{Tr} \left( \boldsymbol{\tau} + \rho_0 c_v T \gamma \right) = -P + \frac{a_T T}{k_T} = \left. \frac{\partial U}{\partial V} \right|_T
\]  
(3.14)

is sometimes termed “internal pressure”. By analogy we call the tensor

\[ \boldsymbol{\sigma} = \boldsymbol{\tau} + \rho_0 c_v T \gamma \]  
(3.15)

the “internal stress tensor”.

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We can now focus on the second order term of eq. (3.13) in order to assess the relative importance of the contributions of internal energy and entropy to the elastic coefficients:

\[
V_0 C_{LMNK} = \frac{\partial^2 A}{\partial \epsilon_{LM} \epsilon_{NK}} - T \frac{\partial^2 S}{\partial \epsilon_{LM} \epsilon_{NK}}
= \frac{\partial^2 U}{\partial \epsilon_{LM} \epsilon_{NK}} - T \frac{\partial^2 \ln C_{LMNK}}{\partial \ln T}
\]
\[
(3.16)
\]

Entropic effects are relatively unimportant if the dimensionless ratio

\[
\left| \frac{1}{C_{LMNK}} \left( T \frac{\partial C_{LMNK}}{\partial T} \right) \right| = \left| \frac{\partial \ln C_{LMNK}}{\partial \ln T} \right| \ll 1
\]
\[
(3.17)
\]

Since the temperature derivatives of the elastic coefficients at constant strain rate are not usually available experimentally, the attention will be restricted to an isotropic solid under the condition that the undeformed state is characterized by an isotropic stress distribution. Then, the previous criterion can be transformed to

\[
\left| \frac{1}{C_{LMNK}} \left[ T \frac{\partial C_{LMNK}}{\partial T} + \frac{a_p T}{k_T} \frac{\partial C_{LMNK}}{\partial P} \right] \right| \ll 1
\]
\[
(3.18)
\]

For uniform hydrostatic compression the relevant elastic constant is

\[
B = C_{11} + C_{22} + C_{33} + 2C_{23} + 2C_{31} + 2C_{12}
\]
\[
(3.19)
\]

implying that the relevant criterion to consider in order to assess the importance of the entropic effects in the elasticity of amorphous polymers is

\[
\left| \frac{1}{B} \left[ T \frac{\partial B}{\partial T} + \frac{a_p TB}{\partial P} \frac{\partial B}{\partial P} \right] \right| \ll 1
\]
\[
(3.20)
\]

or
3.2 Statistical Mechanical Considerations

\[
\left| \frac{T \partial k_T}{k_T \partial T} \right| + \frac{a_T T}{k_T^2 \partial P} \frac{\partial k_T}{\partial T} \ll 1 \quad (3.21)
\]

For pure shear, on the other hand, e.g. perpendicular to z axis in the direction of x, the relevant elastic constant is

\[
G = \mu = C_{3131} = C_{55} \quad (3.22)
\]

implying that the relevant criterion to consider in order to assess the importance of the entropic effects in the elasticity of amorphous polymers is

\[
\left| \frac{T \partial G}{G \partial T} \right| + \frac{a_T T}{k_T} \frac{\partial G}{\partial P} \ll 1 \quad (3.23)
\]

For typical glassy polymers (e.g. PMMA) at room temperature, experimental data\textsuperscript{87} suggest that

\[
\left| \frac{T \partial k_T}{k_T \partial T} \right| + \frac{a_T T}{k_T^2 \partial P} \frac{\partial k_T}{\partial T} = 0.071 \ll 1 \quad (3.24)
\]

\[
\left| \frac{T \partial G}{G \partial T} \right| + \frac{a_T T}{k_T} \frac{\partial G}{\partial P} = 0.14 \ll 1 \quad (3.25)
\]

Thus, the above criteria are usually satisfied for an amorphous polymer below its glass transition temperature. The thermodynamic analysis has shown that the internal energy contribution to the elastic response to deformation is much more significant than the entropic contribution. This means that the estimation of the derivatives of the Helmholtz energy can be achieved by using the corresponding derivatives of the internal energy (as the derivatives of the entropy can be neglected).
From a statistical thermodynamics point of view, the Helmholtz energy $A$ and internal energy $U$ are simply related to the partition function $Q$ within the framework of the canonical ensemble by

\[
A = -\frac{1}{\beta} \ln Q \tag{3.26}
\]

\[
U = -\frac{\partial \ln Q}{\partial \beta} \tag{3.27}
\]

where $Q$ is the partition function in the canonical ensemble and $\beta$ is equal to $\frac{1}{k_B T}$.

In the quasi–harmonic approximation, $Q$ is equal to\(^88\):

\[
Q = \left(\frac{1}{2\pi \beta \hbar^2}\right)^{N/2} V^{\frac{1}{2}} \left(\sum_{k=1}^{N} m_k\right)^{\frac{1}{2}} \int \left[ \prod_{i=1}^{N} \left( \frac{\exp\left(\frac{-\beta \hbar \omega_i}{2}\right)}{1 - \exp(\beta \hbar \omega_i)} \right) \right] \left[ \frac{1}{\det G} \right]^{\frac{N}{2}} \exp\left(-\beta U^{\text{pot}}(\psi, \phi)\right) d\psi d\phi \tag{3.28}
\]

By substituting the expression of $Q$ in quasi–harmonic approximation in eqs. (3.26) and (3.27), these take the form

\[
A = U^{\text{pot}}_{\text{min}} + \frac{1}{2\beta} \ln \left( \frac{\det(G_{\text{min}} H_{\text{min}})}{V^2} \right) - \frac{1}{\beta} \ln \left[ \left( \sum_{k=1}^{N} m_k \right)^{3/2} \left( \frac{1}{\beta \hbar} \right)^{\left(\frac{N-3}{2}\right)} \right] + A^{\text{vib}} \tag{3.29}
\]

\[
U = U^{\text{pot}}_{\text{min}} + \left( N_s - \frac{3}{2} \right) \frac{1}{\beta} - U^{\text{vib}} \tag{3.30}
\]

where:
3.2 Statistical Mechanical Considerations

\[
A^{\text{vib}} = -\frac{1}{\beta} \ln Q^{\text{vib}} \quad (3.31)
\]

\[
U^{\text{vib}} = -\frac{\partial \ln Q^{\text{vib}}}{\partial \beta} \quad (3.32)
\]

Eqs. (3.28) and (3.29), which are actually the quasi-harmonic approximation applied to glassy amorphous polymers, break up the elastic constant into three terms:

1) The first term consists of a potential energy contribution. It expresses the dependence of the energy of the minimum, to which the system is confined, to changes in the spatial extent and shape of the system.

2) The second term incorporates a configurational entropy contribution. It depends on the curvature \((H_{\text{min}})\) of the potential energy hypersurface around the minimum and can be used to assess the importance of entropy effects on the classical constants. Above we have deduced that these effects are not significant, and this term will be neglected in the following. This corresponds to the strict harmonic approximation for the soft degrees of freedom.

3) The third term gives the volume dependence and strain dependence of the vibrational frequencies associated with the hard degrees of freedom.

Theodorou and Suter\(^85\) have analyzed quantitatively the significance of the terms arising from the configurational entropy and vibrational terms in eqs. (3.28) and (3.29), and have concluded that the error committed if one neglects them is on the order of 6%. As a result, one can estimate derivatives of the Helmholtz free energy using only the corresponding derivatives of the internal energy. This justifies the use of the total potential energy of the static structure in place of the internal energy. That is, one can use: 
3.3 Modeling of Deformation

Underlying, we can now summarize the assumptions that the modeling of elastic deformation in a polymer glass in the frame of the quasi-harmonic approximation:

a) The simulated material is regarded as an isotropic material.

b) The model is assumed to be static, i.e., it does not incorporate thermal motion; temperature enters only indirectly through specification of the density in the undeformed state.

c) Entropic contributions to the elastic coefficients are neglected; only potential energy effects are considered.

d) The glassy polymer is pictured in configuration space as an ensemble of mutually inaccessible states of microscopic liquid disorder under conditions that ensure detailed mechanical equilibrium.

e) Estimates of the macroscopic properties are obtained by arithmetic averaging of the undeformed microstructure and all deformed structures obtained from it satisfy the requirements of detailed mechanical equilibrium.

f) The analysis is limited to very small degrees of deformation (as a rule of thumb, polymer glasses are linearly elastic up to deformations of approximately 1%). This implies that we concentrate solely on the elastic response to deformation; viscoelastic phenomena associated with relaxation or flow are thus neglected.

\[
\frac{\partial U}{\partial \xi} \bigg|_{T} = \frac{\partial U_{\text{pot}}}{\partial \xi} \bigg|_{T} 
\]

(3.33)

for the estimation of internal pressure and stress, and

\[
\frac{\partial^2 A}{\partial \xi^2} \bigg|_{T} = \frac{\partial^2 U_{\text{pot}}}{\partial \xi^2} \bigg|_{T} 
\]

(3.34)

for the estimation of elastic coefficients.
Chain slippage is thus avoided, implying that each deformed microstate will be structurally similar to the undeformed microstate from which it is derived.

Overall, the method that Theodorou and Suter first developed for simulating the deformation of a glassy polymer consists of the following steps:

1) Start with an undeformed structure in detailed mechanical equilibrium. The continuation geometry in the undeformed state is cubic, i.e., the continuation vectors are mutually perpendicular and equal in magnitude. The starting structure is a member of the ensemble of minimum energy structures described earlier and satisfies the condition:

\[
U^{\text{pot}}(\mathbf{r}^0_x, \mathbf{r}^0_y, \mathbf{r}^0_z, L^0_x, L^0_y, L^0_z) = \min
\]

(3.35)

where the superscript 0 denotes undeformed conditions. Also \(L^0_x, L^0_y, L^0_z\) are the lengths of the simulation box in the 3 directions in the undeformed state, so that the continuation vectors are simply defined as \(L^0_x e^0_x, L^0_y e^0_y\) and \(L^0_z e^0_z\), where \(e^0_x, e^0_y\) and \(e^0_z\) are the corresponding unit vectors along x, y and z before deformation.

2) Choose the type of deformation to be imposed. Choose a small degree of deformation \(\varepsilon\) such that \(|\varepsilon| \ll 1\).

3) Modify the locations of the cube origin \(\mathbf{0}\) and the continuation vectors so that they correspond to the chosen deformation. For the simple deformations studied here, initial system quantities are transformed to give the deformed system quantities as follows:

For uniform hydrostatic compression:

\[
\mathbf{0} = \mathbf{0}^0 + \frac{1-(1-\varepsilon)^{\frac{1}{3}}}{2} \left\{ L^0_x e^0_x + L^0_y e^0_y + L^0_z e^0_z \right\}
\]

(3.36)
3.3  Modeling of Deformation

\[ L_x e_x = (1 - \varepsilon)^{3/2} L_x^0 e_x^0 \]

\[ L_y e_y = (1 - \varepsilon)^{3/2} L_y^0 e_y^0 \]

\[ L_z e_z = (1 - \varepsilon)^{3/2} L_z^0 e_z^0 \]

For pure uniaxial tension (along x – direction):

\[ 0 = 0_0 - \frac{1}{2} \varepsilon L_x^0 e_x^0 \]

\[ L_x e_x = (1 + \varepsilon) L_x^0 e_x^0 \] \hspace{1cm} (3.37)

\[ L_y e_y = L_y^0 e_y^0 \]

\[ L_z e_z = L_z^0 e_z^0 \]

4)  Re-minimize the total potential energy with respect to the microscopic degrees of freedom, keeping the continuation vectors equal to their deformed values:

\[ U^{pot}(r, \psi, \phi, L_x, L_y, L_z) = \min \] \hspace{1cm} (3.38)

The resulting structure will again satisfy the conditions of detailed mechanical equilibrium, but under the continuation geometry dictated by the mode and degree of deformation chosen in step 2; it is a deformed model structure.

5)  Repeat the procedure with different initial (minimum energy) structures and obtain a set of deformed model structures to get estimates of the mechanical properties of the simulated polymer by analyzing the results for the potential energy function in the two types of deformation experiments considered above according to the following expressions:

For uniform hydrostatic compression:
3.3 Modeling of Deformation

\[ U = U_{\text{pot}}^{\text{min,0}} - V_0 \frac{1}{3} \text{Tr} (\boldsymbol{\tau} + \rho_0 c_e T \gamma_0) \varepsilon \]

\[ + \frac{1}{2} V_0 \left[ C_{1111} + C_{1122} + C_{1133} + C_{2211} + C_{2222} + C_{2233} + C_{3311} + C_{3322} + C_{3333} \right] \varepsilon^2 = \]

\[ U_{\text{pot}}^{\text{min,0}} - V_0 \left( -P + \frac{a_p T}{k_T} \right)_0 \varepsilon + \frac{1}{2} V_0 B \varepsilon^2 = \] (3.39)

\[ U_{\text{pot}}^{\text{min,0}} - V_0 \left( -P + \frac{a_p T}{k_T} \right)_0 \varepsilon + \frac{1}{2} V_0 (6\mu + 9\lambda) \varepsilon^2 \]

thus

\[ \frac{\partial U_{\text{pot}}^{\text{min,0}}}{\partial \varepsilon} = V_0 \left( -P + \frac{a_p T}{k_T} \right)_0 \] (3.40)

\[ \frac{\partial^2 U_{\text{pot}}^{\text{min,0}}}{\partial \varepsilon^2} \equiv V_0 B \]

For pure uniaxial tension (along x – direction):

\[ U = U_{\text{pot}}^{\text{min,0}} + V_0 \left( \tau_{11} + \rho_0 c_e T \gamma_{11} \right)_0 \varepsilon + \frac{1}{2} V_0 C_{1111} \varepsilon^2 = \]

\[ U_{\text{pot}}^{\text{min,0}} + V_0 \left( \tau_{11} + \rho_0 c_e T \gamma_{11} \right)_0 \varepsilon + \frac{1}{2} V_0 C_{11} \varepsilon^2 = \] (3.41)

\[ U_{\text{pot}}^{\text{min,0}} + V_0 \left( \tau_{11} + \rho_0 c_e T \gamma_{11} \right)_0 \varepsilon + \frac{1}{2} V_0 (2\mu + \lambda) \varepsilon^2 \]

thus

\[ \frac{\partial U_{\text{pot}}^{\text{min,0}}}{\partial \varepsilon} = V_0 \left( \tau_{11} + \rho_0 c_e T \gamma_{11} \right)_0 \] (3.42)

\[ \frac{\partial^2 U_{\text{pot}}^{\text{min,0}}}{\partial \varepsilon^2} \equiv V_0 C_{11} \]
According to the above expressions, the first derivatives of the potential energy lead in
the case of uniform hydrostatic compression to the internal pressure \( P - \frac{a_p T}{k_T} \), and in
the case of tension to the internal stress tensor \( \sigma_0 \) (all first derivative information pertains
to the undeformed state only). From the second derivatives, on the other hand, we see that
we obtain the bulk modulus \( B \) in the case of compression, and the diagonal elements of
the 6x6 matrix of isothermal elastic coefficients \( C \) in the case of tension.
As it was mentioned in the introduction, the main goal of the present study is the estimation of the elastic constants of glassy polymer materials in their pure form, and reinforced with graphene sheets. At the beginning, a brief account of the simulated systems and of the force-field will be given. The simulation conditions and the procedure followed to obtain the properties of interest will be presented in detail, and finally results that refer to the structural, dynamic and mechanical properties of all simulated systems will be presented.

4.1 Systems studied

The polymer matrix was the syndiotactic poly(methyl methacrylate) (s-PMMA) with molecular formula \((C_5O_2H_9)_n\). A typical monomer of methyl–methacrylate, which is the building block of PMMA, is given in Figure 4.1(a). It contains five carbon atoms, two oxygen atoms and nine hydrogen atoms. The syndiotacticy of the polymer means that the substituents atoms (e.g. carbon atoms 4 and 7 with all their connecting oxygens and hydrogens) have alternate positions along the chain. A typically considered s-PMMA chain was made up of fifteen monomers as shown in Figure 4.1(b).
4.1 Systems studied

Figure 4.1(a): A typical methyl methacrylate monomer

Figure 4.1(b): A s-PMMA chain consisted by fifteen monomers

For the construction of the s-PMMA/graphene systems, two types of graphene were used: *pure graphene* sheets and *functionalized graphene* sheets: pure graphenes consist only of carbons in the main body of the sheet, and hydrogens as terminal atoms (Fig. 4.2(a)). Functionalized graphene sheets contain oxygens and OH’s (depending on case) as functional groups (Fig. 4.2(b)) randomly distributed on the surface of the graphene sheet and are called also *graphene oxide*.

Figure 4.2: The two types of graphene sheets used in the present study: (a) pure and (b) graphene oxide
Details of the systems simulated in the present study are given Table 4.1. From them, the elastic constants were extracted only for the first three. The rest, after some very interesting observations (as it will be analyzed in the following paragraphs) we made, it was concluded that they were not meeting the requirements that the method described in Chapter 3 imposes, thus they were excluded from the procedure followed for the estimation of the elastic constants.

**Table 4.1: Details about the simulated systems**

<table>
<thead>
<tr>
<th>System number</th>
<th>Composition</th>
<th>Number of polymer chains</th>
<th>Number of monomers in each polymer chain</th>
<th>Number of graphene sheets</th>
<th>Atoms per graphene sheet</th>
<th>Percentage on graphene sheets</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure s-PMMA</td>
<td>27</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Graphene/s-PMMA</td>
<td>27</td>
<td>15</td>
<td>3</td>
<td>88</td>
<td>5.85</td>
</tr>
<tr>
<td>3</td>
<td>f.Graphene/s-PMMA</td>
<td>27</td>
<td>15</td>
<td>3</td>
<td>101</td>
<td>6.54</td>
</tr>
<tr>
<td>4</td>
<td>Graphene/s-PMMA</td>
<td>200</td>
<td>15</td>
<td>3</td>
<td>250</td>
<td>2.49</td>
</tr>
<tr>
<td>5</td>
<td>f.Graphene/s-PMMA</td>
<td>200</td>
<td>15</td>
<td>3</td>
<td>286</td>
<td>2.78</td>
</tr>
</tbody>
</table>

For the two systems that contain functionalized graphene sheets, an elemental analysis for one sheet is provided in Table 4.2.

**Table 4.2: Elemental analysis of functionalized graphene sheets for systems No 3 and 5**

<table>
<thead>
<tr>
<th>System number</th>
<th>Carbon Atoms</th>
<th>Hydrogen Atoms</th>
<th>Oxygen Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>66</td>
<td>27 (22 terminal atoms and 5 in hydroxilic groups)</td>
<td>8 (5 in hydroxilic groups and 3 as epoxy)</td>
</tr>
</tbody>
</table>
4.1 Systems studied

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>210</td>
<td></td>
<td></td>
<td>(40 as terminal atoms and 18 in hydroxilic groups)</td>
<td>only in hydroxilic groups</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>58</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Typical atomistic configurations from the five simulated system are given below.
4.2  Applied Force field

To increase the predictive capability of our computational methodology, all simulations were carried out with the very accurate, explicit-atom DREIDING\textsuperscript{89} force field. The expression for each type of interaction and the values for every parameter incorporated in such an expression are given below:

1) The van der Waals interactions are described by a Lennard – Jones potential as described in eq. (2.21):

\[
U_{LJ}^{ij}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{\alpha} - \left( \frac{\sigma_{ij}}{r} \right)^{\beta} \right]
\]

with parameter values as given below.

<table>
<thead>
<tr>
<th>Lennard – Jones parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atom type</strong></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>C in CH\textsubscript{3} connected to main chain (C3)</td>
</tr>
<tr>
<td>C in CH\textsubscript{2} group (C2)</td>
</tr>
<tr>
<td>C in the main chain (C)</td>
</tr>
<tr>
<td>C connect to O by double bond (CD)</td>
</tr>
<tr>
<td>O connected to C by double bond (OD)</td>
</tr>
</tbody>
</table>
4.2 Applied Force field

<table>
<thead>
<tr>
<th>O in ester group (O)</th>
<th>3.033154</th>
<th>0.0957</th>
</tr>
</thead>
<tbody>
<tr>
<td>C in CH₃ group connected to ester O (CO)</td>
<td>3.47299</td>
<td>0.0951</td>
</tr>
<tr>
<td>H in alkane CH₃ or CH₂ groups (H)</td>
<td>2.846421</td>
<td>0.0001</td>
</tr>
<tr>
<td>H in ester OCH₃ group (HO)</td>
<td>2.4200</td>
<td>0.0152</td>
</tr>
</tbody>
</table>

2) The **Coulombic** interactions are described by an expression as defined in eq. (2.23):

\[
U_{el}(r_{ij}) = -\frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}}
\]

with parameter values as given below.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(q) (e.c.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3</td>
<td>-0.135</td>
</tr>
<tr>
<td>C2</td>
<td>-0.09</td>
</tr>
<tr>
<td>C</td>
<td>0.000</td>
</tr>
<tr>
<td>CD</td>
<td>0.510</td>
</tr>
<tr>
<td>OD</td>
<td>-0.430</td>
</tr>
<tr>
<td>O</td>
<td>-0.330</td>
</tr>
<tr>
<td>CO</td>
<td>-0.135</td>
</tr>
<tr>
<td>H</td>
<td>0.045</td>
</tr>
<tr>
<td>HO</td>
<td>0.045</td>
</tr>
</tbody>
</table>

3) The **bond stretching** interaction is described by an oscillatory potential as defined in eq. (2.18):
\[ U_{\text{str}}(r) = \frac{1}{2} k_{\text{str}} (r - r_0)^2 \]

with parameter values as given below.

**Table 4.5: Parameters of the bond stretching potential**

<table>
<thead>
<tr>
<th>Bonds</th>
<th>( k_{\text{str}} ) (kcal/mol/Å²)</th>
<th>( r_0 ) (Å)</th>
<th>Bonds</th>
<th>( k_{\text{str}} ) (kcal/mol/Å²)</th>
<th>( r_0 ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3-C</td>
<td>350</td>
<td>1.53</td>
<td>CD-O</td>
<td>350</td>
<td>1.32</td>
</tr>
<tr>
<td>C2-C</td>
<td>350</td>
<td>1.53</td>
<td>CO-O</td>
<td>350</td>
<td>1.42</td>
</tr>
<tr>
<td>CD-C</td>
<td>350</td>
<td>1.43</td>
<td>CT-HT&amp;</td>
<td>350</td>
<td>1.09</td>
</tr>
<tr>
<td>CD-OD</td>
<td>700</td>
<td>1.22</td>
<td>CO-HO</td>
<td>350</td>
<td>1.09</td>
</tr>
</tbody>
</table>

\& CT includes C3 and C2; HT includes H and HO

4) The bond bending interaction is described by an oscillatory expression as defined in eq. (2.19):

\[ U_{\text{bend}}(\theta) = \frac{1}{2} k_{\text{bend}} (\theta - \theta_0)^2 \]

with parameter values as given below.

**Table 4.6: Parameters of the bond bending potential**

<table>
<thead>
<tr>
<th>Bends</th>
<th>( k_{\text{bend}} ) (kcal/mole/rad²)</th>
<th>( \theta_0 ) (degrees)</th>
<th>Bends</th>
<th>( k_{\text{bend}} ) (kcal/mole/rad²)</th>
<th>( \theta_0 ) (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C2-C</td>
<td>50</td>
<td>109.47</td>
<td>CD-O-CO</td>
<td>50</td>
<td>104.51</td>
</tr>
<tr>
<td>CT-C-CT</td>
<td>50</td>
<td>109.47</td>
<td>H-CT-C</td>
<td>50</td>
<td>109.47</td>
</tr>
<tr>
<td>CT-C-CD</td>
<td>50</td>
<td>109.47</td>
<td>H-CT-H</td>
<td>50</td>
<td>109.47</td>
</tr>
<tr>
<td>C-CD-O</td>
<td>50</td>
<td>120</td>
<td>HO-CO-HO</td>
<td>50</td>
<td>109.47</td>
</tr>
</tbody>
</table>
4.2 Applied Force field

5) The proper dihedral interaction is described by an expression of cosines as follows:

\[ U_{\text{dihedral}}(\phi) = k_{\text{dihedral}} \left[ 1 + \cos(n\phi - d) \right] \]

with parameter values as given below.

<table>
<thead>
<tr>
<th>Proper Dihedral Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torsions</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>HT-CT-CT-CT</td>
</tr>
<tr>
<td>CT-CT-CT-CT</td>
</tr>
<tr>
<td>C2-C-CD-O</td>
</tr>
<tr>
<td>H-C2-C2-O</td>
</tr>
<tr>
<td>CT-C-CD-OD</td>
</tr>
<tr>
<td>HT-C-CD-OD</td>
</tr>
<tr>
<td>C-CD-O-CO</td>
</tr>
<tr>
<td>OD-CD-O-CO</td>
</tr>
</tbody>
</table>

6) The improper dihedral interaction is described by an oscillatory potential of the form:

\[ U_{\text{improper}}(\xi) = \frac{1}{2} k_{\text{improper}} (\xi - \xi_0)^2 \]

with parameter values as given below.

<table>
<thead>
<tr>
<th>Table 4.8: Parameters of the improper dihedral potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torsions</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>CT-CD-OD</td>
</tr>
<tr>
<td>C-CD-OD</td>
</tr>
<tr>
<td>OD-CD-O-CO</td>
</tr>
<tr>
<td>CT-C-CD-OD</td>
</tr>
<tr>
<td>H-C2-C-C2</td>
</tr>
<tr>
<td>C2-CD-OD</td>
</tr>
<tr>
<td>HT-C-CD-OD</td>
</tr>
<tr>
<td>C-CD-O-CO</td>
</tr>
<tr>
<td>OD-CD-O-CO</td>
</tr>
</tbody>
</table>
### Improper Dihedral Parameters

<table>
<thead>
<tr>
<th>Torsions</th>
<th>$k_{\text{improper}}$ (kcal/mol/rad$^2$)</th>
<th>$\xi_0$ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2-C-C2-CD</td>
<td>20</td>
<td>50 or 130$^&amp;&amp;$</td>
</tr>
<tr>
<td>C2-C-C2-C3</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>

$^\&\&$ the value of $\xi_0$ changes every second monomer along the chain in order the syndiotacticity to be kept.

## 4.3 Equilibration Procedure

The estimation of the elastic constants of the simulated systems was performed at ambient conditions. Before applying the Theodorou and Suter Method$^{85}$, as it described in Chapter 3, a hierarchical procedure should be followed in order to obtain well relaxed and completely independent configurations at room temperature. For that, a 3-step approach was followed as described below:

**Step 1** Generation of a large number of well equilibrated polymer configurations at high enough temperature for which equilibration is easy to achieve within reasonable computational time.

**Step 2** Gradual cooling of a selected number of uncorrelated system configurations down to temperature of interest to obtain an ensemble of systems representative of the glassy phase of the system under study.

**Step 3** Execution of several types of deformation experiments on the glassy structures following the protocol developed by Theodorou and Suter$^{85}$ in order to extract estimates of the two Lamé constants $\lambda$ and $\mu$.

The equilibration simulations of Step 1 are carried out with the Molecular Dynamics (MD) method using the LAMMPS software. The equations of motion were integrated using the velocity - Verlet integrator with a time step of 1fs. Long-range electrostatic interactions were calculated by implementing the Particle-Particle, Particle-Mesh Ewald method (PPPM)$^{69}$. Step 1 entails the following sub-steps:
4.3 Equilibration Procedure

- Generation of an initial configuration which is next subjected to potential energy minimization using the Steepest Descent (SD) Method.
- Exhaustive MD simulation at a high enough temperature (500K) and at a pressure of 1atm in the isothermal isobaric (NPT) statistical ensemble using the Nosé-Hoover thermostat and barostat with relaxation times of 0.01 and 0.3 ps, respectively.

Step 2 involves choosing a rather large number (~8) of independent, totally uncorrelated configurations from the MD simulation at the high temperature of Step 1 and cooling down to room temperature to obtain amorphous structures representative of glassy sPMMA or glassy graphene/sPMMA nanocomposite. To this, an additional equilibration was attempted by running an NPT MD simulation (at T=300K and P=1atm) until the density reached its asymptotic (equilibrium or steady-state) value.

Regarding Step 3, we mention that the entire analysis is based on the amorphous cell method by Theodorou and Suter. Summarizing, the basic assumptions that this methodology makes, as it is already referred from Chapter 3, are:

- The material is isotropic and the model static, i.e., it does not incorporate thermal motion.
- Entropic contributions to the elastic coefficients are neglected and only potential energy effects are considered committing an error on the order of 6%.
- Viscoelastic phenomena associated with relaxation or flow are also neglected.

For glassy polymers (e.g. s-PMMA) these assumptions are all in good order with what actually happens in reality. The steps that are followed in order to get the elastic constants are then summarized in the following sub-steps:

- Start with an undeformed structure, as it emerged from Steps 1 and 2, in detailed mechanical equilibrium and at a local minimum of its total potential energy.
Choose the type of deformation (either uniform hydrostatic compression or uniaxial tension) to be imposed and a small degree of volume deformation (up to 1%).

For the given deformation, re-minimize the total potential energy of the deformed model structure.

Repeat the procedure with different initial (minimum energy) structures.

Average over all deformed model structures to get estimates of those elastic constants of the simulated system that are involved in the given type of deformation, by fitting the numerical results for the potential energy function with a $2^{nd}$ order polynomial.

Repeat the procedure for different types of deformation.

Average again the results for the new deformation experiments to get predictions for other elastic constants.

The minimizations of energy were executed with the very accurate minimization of energy method \textit{hftn} as it described in Chapter 2.6.

4.4 Structural and Dynamical properties

As in Step 1 of the previous section, in order to get representative configurations of each system at room temperature, it was necessary to equilibrate them at a relative high temperature (e.g. 500K). This is completely necessary because for glassy polymers, the relaxation time at temperatures well below their glass transition temperature ($T_g$) is of the order of years, i.e. times that are impossible to follow in a Molecular Dynamics simulation.

By increasing the temperature, the mobility of chains increases, thus the relaxation time drastically reduces. In what follows, parameters that describe the structural and dynamical properties of a polymer material will be represented for each system.

In Figure 4.3 the density of each system at $T=500K$ is depicted with respect to duration of simulation which was on the order of 700ns for the f.Graphene/s-PMMA system.
4.4  Structural and Dynamical properties

![Graph showing density vs time for three systems: System 1 (black), System 2 (red), System 3 (blue).](image)

**Figure 4.4:** Density of each system at temperature equal to 500K.

In Table 4.9, where we report the average value of the density for each system at 500K, we see that the presence of graphene sheets (simple or functionalized) affects the density of the system. This is a sign that the atoms of the polymer chains are attracted by the atoms of graphenes, and as a result the volume for the nanoparticle systems (System 2 and 3) are decreasing resulting in an increase of density.

**Table 4.9:** Average value of the density for each system

<table>
<thead>
<tr>
<th>System</th>
<th>Average Density (g/cm³)</th>
<th>Experimental values (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0655±0.0018</td>
<td>1.067³⁰⁰</td>
</tr>
<tr>
<td>2</td>
<td>1.0818±0.0009</td>
<td>---------------------------</td>
</tr>
<tr>
<td>3</td>
<td>1.0907±0.0012</td>
<td>---------------------------</td>
</tr>
</tbody>
</table>

Experimental data are only available for the pure sPMMA system at 500K suggesting a value equal to 1.067 g/cm³, which is very close to the predicted one from the simulation.
The larger density value of System 3 can be attributed probably to the creation of Hydrogen bonds due to the presence of hydroxilic groups on the surface of the graphenes which attract the oxygen atoms of the polymer. To quantify this we calculate the number of Hydrogen bonds that are developed in System 3 during the MD simulation. In order to decide whether or not an $O-H---O$ interaction is a Hydrogen bond, the following criteria should be met.

- The distance between the two oxygen atoms (acceptor and donor) ($O_1$ and $O_2$ in Figure 4.5) is less than 3.6Å.
- The distance between the oxygen of the donor and the hydrogen of the acceptor (Figure 4.5) is less than 2.4Å
- The angle $\phi$ between the positions of H-donor, O-acceptor and O-donor is less than $30^\circ$.

*Figure 4.5: Schematic representation of the geometrical criteria of a Hydrogen Bond.*

In Figure 4.6 the number of Hydrogen bonds formed in System 3 during the simulation is presented. It is obvious that several H – bonds are developed, with an average value of 2.8 H-bonds. As we can see, the number of H – bonds intensely fluctuates, reaching in some cases values of more than 5 H-bonds. This is a relative high value, taking into account that the available OH groups on the surface of the graphene sheets are 15, and one third of them creates a H – bond with the oxygen atoms of the polymer.
The quantity that we have to monitor in order to decide that one system is fully relaxed is the time decorrelation of the end-to-end vector $\langle R_{ee} \rangle$ autocorrelation function. For a polymer chain, this is the most difficult quantity to be decorrelated. If the end-to-end vector autocorrelation function reaches 0, then any other quantity of the under study system will have lost its memory from its initial configuration and will have reached equilibrium. In the next two figures (Figure 4.7 and Figure 4.8) the decorrelation of the end-to-end vector and the vector between the backbone carbon and the carbon in the branch (atoms 2 and 7 from Figure 4.1(a) respectively) are presented.
From the above two figures it is obvious that the end-to-end vector decorrelates more slowly than the branch vector. For all systems, we can say that at the high temperature they reach equilibrium, since the autocorrelation function reaches 0. Fitting the results to an exponential function of the form:
4.4 Structural and Dynamical properties

\[ P(\varphi(t)) = A \exp\left(-\left(t / \tau_{kww}\right)^{\beta}\right) \]  \hfill (4.1)

the corresponding relaxation time for each system can be calculated by:

\[ \tau_c = \tau_{kww} \left( \frac{\Gamma\left(1 / \beta\right)}{\beta} \right) \]  \hfill (4.2)

where \(\Gamma\) is the \(\Gamma\) function. The values of \(\tau_{kww}\), \(\beta\) and \(\tau_c\) are summarized in Table 4.10.

<table>
<thead>
<tr>
<th>System</th>
<th>(\tau_{kww}) (ns)</th>
<th>(\beta)</th>
<th>(\tau_c) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>208</td>
<td>1.08</td>
<td>202</td>
</tr>
<tr>
<td>2</td>
<td>249</td>
<td>1.57</td>
<td>224</td>
</tr>
<tr>
<td>3</td>
<td>334</td>
<td>0.82</td>
<td>372</td>
</tr>
</tbody>
</table>

From the above Table it is obvious that the dynamics of the polymer chains is strongly affected by the presence of graphene sheets. The relaxation time increases compared to the pure system, especially for the f.graphene/s-PMMA system where oxygen and hydroxilic groups seem to dictate the interactions with the polymer chains. For System No 2 the relaxation time increases by about 11% and for system 3 by almost 85% This can be attributed to the strong attraction between the oxygen atoms of the branches of the polymers and the functional groups of graphene oxide, giving rise to the development of hydrogen bonds which then hinder the movement of chains.

Using the above simulation results for the dynamics of the system, the glass transition temperature \(T_g\) can be extracted. For that, short – time MD simulations were performed in order to be extracted the relaxation time of the branches of sPMMA at various temperatures. This characteristic time is chosen because it is assumed that from the melting point and down to the glass transition temperature, only local motions are
permitted. The branch relaxation times as a function of temperature for all simulated systems are presented in Figure 4.9.

![Graph showing log10(τc) vs. 1000/T (K⁻¹)](image)

**Figure 4.9:** Temperature dependence of the branch relaxation time for the simulated sPMMA and sPMMA/graphene systems.

In order to extract $T_g$ and examine the variations caused due to the presence of graphene sheets, we fit the data of Fig. 4.9 with a Williams – Landel – Ferry (WLF) expression, of the form:

$$
\tau_c(T) = \tau_{c,\infty} \exp \left( \frac{-C_1(T - T_g)}{C_2 + T - T_g} \right)
$$

whith $C_1$, $C_2$, $\tau_{c,\infty}$, $T_g$ being numerical constants. An estimation of the glass transition temperature $T_g$ can be made by assuming values for $C_1$ and $C_2$ equal to 17.44K and 51.6K respectively, which are good approximations for many polymers. In Table 4.11 the predicted values of glass transition temperature for the various simulated systems are reported and compared to the value for bulk sPMMA.
Table 4.11: Estimations of glass transition temperatures for the under study systems

<table>
<thead>
<tr>
<th>System</th>
<th>$T_g$ (K)</th>
<th>Experimental Value</th>
<th>% Difference from bulk value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>408±10</td>
<td>401.15</td>
<td>-----</td>
</tr>
<tr>
<td>2</td>
<td>429±2</td>
<td>-----</td>
<td>17.58</td>
</tr>
<tr>
<td>3</td>
<td>438±3</td>
<td>-----</td>
<td>22.56</td>
</tr>
</tbody>
</table>

We see that our prediction about for the glass transition temperature of sPMMA is in a very good agreement with the available experimental data. The results about systems 2 and 3 show that indeed, the presence of graphene sheets (functionalized or not) increase the $T_g$ of the bulk system. Especially for the f.graphene/sPMMA system this increase is more pronounced which is consistent with the corresponding dynamic properties of this system that are strongly affected by the presence of the functional groups. Our results are in relative agreement with what Ramanthan et. al have reported, namely a shift of the glass transition temperature by nearly 30 °C with 1% insertion of functionalized graphene sheets in the polymer matrix.

The corresponding results for the average value of the square of the end-to-end distance $\langle R_{ee}^2 \rangle$ are reported in Table 4.12. An example of how the $\langle R_{ee}^2 \rangle$ varies with time is also shown in Figure 4.10.
4.5 Self – Assembly of Graphene Sheets

To study how our predictions for the structural, dynamical and mechanical properties are affected by the size of the graphene sheets, systems with more polymer chains were

![Figure 4.10: Time evolution of the $\langle R^2(t) \rangle$.](image)

The average values of the $\langle R^2_{ite} \rangle$ for each system are summarized in the following Table.

**Table 4.12: Average values of the $\langle R^2_{ite} \rangle$**

<table>
<thead>
<tr>
<th>System</th>
<th>$\langle R^2_{ite} \rangle$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>477.94±14.40</td>
</tr>
<tr>
<td>2</td>
<td>541.39±33.33</td>
</tr>
<tr>
<td>3</td>
<td>499.06±21.06</td>
</tr>
</tbody>
</table>

4.5 Self – Assembly of Graphene Sheets

To study how our predictions for the structural, dynamical and mechanical properties are affected by the size of the graphene sheets, systems with more polymer chains were
constructed with the same molecular weight and larger graphene sheets as described in Table 4.1. By increasing the number of chains, the simulation time increases, making it impossible to equilibrate systems 4 and 5 at 500K taking into account that the relaxation times for the small Systems (e.g. 1, 2 and 3) are on the order of hundreds of nanoseconds, and the computational time increases linearly with the number of atomistic units. For that reason, Systems 4 and 5 were equilibrated at 700K. At this higher temperature, the relaxation of a polymeric system is accelerated, because of the more intensive motion of atoms in the polymer chains.

But also, the mobility graphene atoms increases. As a result, after a short simulation time, a very interesting phenomenon was observed: the graphene sheets were monitored to get gradually closer and closer to each other forming eventually a stacked structure (Figures 4.11). For the simulation of System 4 that happen approximately after about 1.25 ns of simulation at 700K despite that in the initial configuration the graphene sheets had been placed far away from each other.
4.5 Self-Assembly of Graphene Sheets

Figures 4.11: Time evolution of the graphene sheets in the polymer matrix. After 1.25ns of an MD simulation, two of the three graphene sheets formed a stacked structure.

A comparison between the initial configuration and the final structure of the entire system after graphene stacking took place is shown in Figure 4.12. A closer view of the stacked graphene sheets is presented in Figure 4.13.
4.5  Self–Assembly of Graphene Sheets

**Figure 4.12:** Typical atomistic snapshots from the NPT simulations of System 4 at the higher temperature in wrapped coordinates: (a) before agglomeration of graphene sheets took place, and (b) after where two of three graphene sheets come close and stacked together.

**Figure 4.13:** Closer view of the two graphene sheets after agglomeration in the directions vertically (a) and parallel (b) to the graphene plane.

The evolution of this phenomenon can be quantified by examining the behavior of the intermolecular radial distribution function $g(r)$ with respect to time as shown in Figure 4.14.
For the first time instances and just before stacking, the distribution is almost uniform with some smooth peaks at very long distances, which proves that the graphene sheets were initially put far from each other. At 1.25\textit{ns} when the stacking of the sheets occurs, $g(r)$ reaches a value of about 1.5 in a distance of 3.75Å, which is very close to the value of $\sigma$ parameter of the Lennard–Jones potential between carbon atoms (3.47Å , Table 4.3). As the time evolves this peak becomes more and more intensive, and from 3.5\textit{ns} and on takes a value almost 30 times larger than the initial value at distance equal to 3.75Å, while the initial small peaks at larger distances decay. It is also observed that after 3.5\textit{ns} the difference in the height of the peak barely changes with time till the end of the simulation (11.00\textit{ns}), something that shows that the stacked graphenes stay strongly one on top of the other moving practically together.

Another size for the quantification of the stacking is to examine the distance separating the centers of masses in pairs, in the course of time. This is presented in Figure 4.15 for System 4, where it is obvious that at about 1.25\textit{ns} of simulation the centers of masses of
graphenes 1 and 2 have come close to a distance of 3.75Å, exactly as was observed in the intermolecular radial distribution function, $g(r)$

![Graphene Sheet Assembly](image)

**Figure 4.15:** Evolution of the distance between the centers of masses of graphenes for every possible pair

As for System 5, the stacking process is a little different to that seen for System 4. The functionalized graphene sheets and move above the other but the stacking is not perfect as the two graphene sheets have the freedom to slide on past the other (Figure 4.16).

Just exactly and above the initial and final configuration of the system is presented (Figure 4.17) as well as a closer view to the stacked functionalized sheets (Figure 4.18). Finally, the evolution of the pair radial distribution function for the atoms of the graphene sheets is given.
Figures 4.16: Time evolution of the graphene sheets in the polymer matrix. After 12.00ns, two of the three graphene sheets come close enough to form a stacked structure.
4.5 Self–Assembly of Graphene Sheets

Figure 4.17. Typical atomistic snapshots from the NPT simulations with System 5 at T=700K in wrapped coordinates: (a) before agglomeration of graphene sheets took place, and (b) after where two of three graphene sheets got stacked together.

Figure 4.18. Closer view of the f.graphene sheets after agglomeration in the directions vertically (a) and parallel (b) to the graphene plane.

Clearly, the two f.graphene sheets not standing completely parallel to each other as it was observed in the aggregation of the pure graphene sheets of System 4. This can be attributed to the presence of the hydroxilic groups which do not let the sheets to take a typical graphite stacked structure.

Finally, in Figure 4.19, we report the time evolution of the intermolecular pair distribution function for carbon atoms in the case of the f.graphene sheets.
4.5 Self–Assembly of Graphene Sheets

Figure 4.19: Evolution of the intermolecular radial distribution function between the carbon atoms of the functionalized graphene sheets before and after agglomeration.

The results for the time evolution of the intermolecular $g(r)$ show significant differences compared to the corresponding ones of System 4. First of all, the aggregation of the graphene sheets does not happen as fast as in graphene/sPMMA system. Also, the aggregation does not happen suddenly as in System 4. By the time that first signs of aggregation show up (10.4ns) till the maximum value of $g(r)$ (15ns) about 4.5ns have passed, something that does not happen in the simple graphene system, where the agglomeration is almost instantaneously. Also the maximum value of $g(r)$ is about 5.5 i.e. noticeably lower compared to maximum value of approximately 30 observed for System 4. Finally, another important thing that has to be mentioned is that $g(r)$ for f.graphene system takes its maximum value at a distance of 6.2Å, which is significantly lower than the value of 3.75Å for the graphene/sPMMA system. This can be attributed to the repelling forces that develop because of the presence of OH groups on the surface of the graphenes, which does not allow the sheets to come closer, as it happened in System 4 where no functional groups exist.
This can be clearer seen by examining the evolution of the distance between the centers-of-mass for every possible pair, as was done for System 4. From Figure 4.20 it is obvious that the centers-of-mass for graphenes 1 and 3 come closer at a later time and not so abruptly as was observed for System 4.

![Figure 4.20: Evolution of the distance between the centers of masses of functionalized graphenes for every possible pair](image)

Also the fluctuations around the equilibrium distance are less intensive in the case of system 5 compared to the corresponding ones of graphene/sPMMA system, as it is shown in Figure 4.21. Again, this can be attributed to the local repulsive forces that develop due to the presence of OH groups on the surface of f.graphene and which do not allow them to come close enough and stay there.
Figure 4.21: Fluctuations around the equilibrium distance of the centers of masses of stacked graphenes for graphene/sPMMA and f.graphene/sPMMA systems

Clearly, graphene agglomeration will lead to a highly inhomogeneous and anisotropic system with very poor mechanical properties, thus methods should be devised in practice so that it can be avoided. This is also the reason that these simulations were stopped and no further analysis was obtained. After the agglomeration of the nano-sheets and the inhomogeneity that forms, a very important assumption behind the estimation of the mechanical properties of a glassy polymeric material collapses: the system is no longer homogenous and the form of the tensor of isothermal elastic coefficients \( C_{LMNK} \) no longer has the form of the expression (3.7). The estimation of the elastic constants, ignoring this assumption, will lead erroneous results. For that reason the estimation of the elastic constants was limited in the small systems (Systems 1, 2 and 3) where the equilibration procedure took place with no graphene stacking observed.

The agglomeration of graphene sheets has been previously reported on the experimental side, along with proposed procedures for avoiding it. In simulation level Park et. al first reported the aggregation of graphene sheets in graphene/water systems and Li et. al reported the self–assembly behavior of graphenes in graphene/Polyethylene systems. To the best of our knowledge, agglomeration of graphene oxide/polymer systems, which is
proposed as one of the methods for avoiding self–assembly behavior, is observed here for the first time.

4.6 Cooling

The main goal of the present thesis has been the estimation of the mechanical behavior of sPMMA – graphene nanocomposites at ambient conditions (T=298K and P=1atm). For that reason, after being sure that the system has fully equilibrated at a high enough temperature, samples of it are subjected to sudden coolings to room temperature. The cooling rate is clearly extremely high (50K/ns) but it is impossible via MD to reach experimental rates. Additional, partial relaxation of the cooled atomistic configurations with MD took place at T=300K until the density reached its asymptotic value. Complete relaxation at ambient conditions is impossible via MD, since the relaxation times of glassy polymers are on the order of years.

4.7 Estimates of the Elastic Constants

By following the procedure described in 3.1.3, representative plots of the change of potential energy $U$ with respect to the volume change are presented in Figures 4.22 – 4.24 for Uniform Hydrostatic Compression and all Uniaxial Tension experiments for one configuration from each system. It is obvious that all points almost fall in a smooth curve, as it is predicted by theory. The behavior is similar for the rest of the 8 chosen, equilibrated and cooled atomistic configurations.
Figure 4.22: $U$ vs fractional volume change for one model structure of System 1: (a) Uniform Hydrostatic Compression, (b) Uniaxial Tension along $x$-direction, (c) Uniaxial Tension along $y$-direction, (d) Uniaxial Tension along $z$-direction
4.7 Estimates of the Elastic Constants

Figure 4.23: $U$ vs fractional volume change for one model structure of System 2: (a) Uniform Hydrostatic Compression, (b) Uniaxial Tension along x-direction, (c) Uniaxial Tension along y-direction, (d) Uniaxial Tension along z-direction
4.7  Estimates of the Elastic Constants

**Figure 4.24:** $U$ vs fractional volume change for one model structure of System 3: (a) Uniform Hydrostatic Compression, (b) Uniaxial Tension along x-direction, (c) Uniaxial Tension along y-direction, (d) Uniaxial Tension along z-direction

On these Figures, a 2$^{nd}$ order polynomial is fitted and the coefficient of the second order term gives then the average value for the corresponding Lamé constants.

For each type of deformation, the values for this coefficient are summarized in Tables 4.13 – 4.15.
### Table 4.13: Values of the 2\(^{nd}\) order fitted coefficient for each type of deformation for System 1

<table>
<thead>
<tr>
<th>Number of Cooling</th>
<th>Uniform Hydrostatic Compression (\frac{\lambda + 2\mu}{\lambda + \mu}) (GPa)</th>
<th>Uniaxial Tension / along x-direction (2\mu + \lambda) (GPa)</th>
<th>Uniaxial Tension / along y-direction (2\mu + \lambda) (GPa)</th>
<th>Uniaxial Tension / along z-direction (2\mu + \lambda) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.14</td>
<td>5.24</td>
<td>4.95</td>
<td>6.46</td>
</tr>
<tr>
<td>2</td>
<td>4.78</td>
<td>5.26</td>
<td>5.54</td>
<td>5.61</td>
</tr>
<tr>
<td>3</td>
<td>5.18</td>
<td>7.68</td>
<td>2.84</td>
<td>2.75</td>
</tr>
<tr>
<td>4</td>
<td>5.18</td>
<td>4.57</td>
<td>9.69</td>
<td>6.44</td>
</tr>
<tr>
<td>5</td>
<td>2.65</td>
<td>5.73</td>
<td>4.74</td>
<td>4.39</td>
</tr>
<tr>
<td>6</td>
<td>5.53</td>
<td>6.96</td>
<td>3.53</td>
<td>6.60</td>
</tr>
<tr>
<td>7</td>
<td>2.75</td>
<td>6.53</td>
<td>7.26</td>
<td>1.89</td>
</tr>
<tr>
<td>8</td>
<td>4.33</td>
<td>6.01</td>
<td>5.58</td>
<td>4.04</td>
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</table>

### Table 4.14: Values of the 2\(^{nd}\) order fitted coefficient for each type of deformation for System 2

<table>
<thead>
<tr>
<th>Number of Cooling</th>
<th>Uniform Hydrostatic Compression (\frac{\lambda + 2\mu}{\lambda + \mu}) (GPa)</th>
<th>Uniaxial Tension / along x-direction (2\mu + \lambda) (GPa)</th>
<th>Uniaxial Tension / along y-direction (2\mu + \lambda) (GPa)</th>
<th>Uniaxial Tension / along z-direction (2\mu + \lambda) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.76</td>
<td>3.95</td>
<td>8.46</td>
<td>3.51</td>
</tr>
<tr>
<td>2</td>
<td>4.38</td>
<td>12.68</td>
<td>5.26</td>
<td>3.89</td>
</tr>
<tr>
<td>3</td>
<td>5.22</td>
<td>8.36</td>
<td>7.75</td>
<td>5.94</td>
</tr>
<tr>
<td>4</td>
<td>5.22</td>
<td>7.91</td>
<td>5.68</td>
<td>8.24</td>
</tr>
<tr>
<td>5</td>
<td>4.40</td>
<td>6.16</td>
<td>6.07</td>
<td>5.94</td>
</tr>
<tr>
<td>6</td>
<td>6.50</td>
<td>7.16</td>
<td>6.69</td>
<td>6.64</td>
</tr>
<tr>
<td>7</td>
<td>4.35</td>
<td>5.81</td>
<td>5.50</td>
<td>9.75</td>
</tr>
<tr>
<td>8</td>
<td>3.57</td>
<td>4.84</td>
<td>6.53</td>
<td>4.68</td>
</tr>
</tbody>
</table>
Table 4.15: Values of the 2nd order fitted coefficient for each type of deformation for System 3

<table>
<thead>
<tr>
<th>Number of Cooling</th>
<th>Uniform Hydrostatic Compression</th>
<th>Uniaxial Tension / along x-direction</th>
<th>Uniaxial Tension / along y-direction</th>
<th>Uniaxial Tension / along z-direction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \frac{\lambda + \frac{2}{3} \mu}{\text{(GPa)}} )</td>
<td>( (2\mu + \lambda) \text{(GPa)} )</td>
<td>( (2\mu + \lambda) \text{(GPa)} )</td>
<td>( (2\mu + \lambda) \text{(GPa)} )</td>
</tr>
<tr>
<td>1</td>
<td>4.89</td>
<td>8.45</td>
<td>5.64</td>
<td>7.63</td>
</tr>
<tr>
<td>2</td>
<td>4.61</td>
<td>8.97</td>
<td>5.34</td>
<td>7.80</td>
</tr>
<tr>
<td>3</td>
<td>3.69</td>
<td>4.18</td>
<td>4.15</td>
<td>8.32</td>
</tr>
<tr>
<td>4</td>
<td>4.60</td>
<td>7.46</td>
<td>6.13</td>
<td>7.68</td>
</tr>
<tr>
<td>5</td>
<td>5.17</td>
<td>8.64</td>
<td>9.41</td>
<td>5.59</td>
</tr>
<tr>
<td>6</td>
<td>6.89</td>
<td>11.54</td>
<td>9.94</td>
<td>8.63</td>
</tr>
<tr>
<td>7</td>
<td>5.10</td>
<td>7.79</td>
<td>7.50</td>
<td>11.72</td>
</tr>
<tr>
<td>8</td>
<td>5.39</td>
<td>6.42</td>
<td>12.24</td>
<td>13.91</td>
</tr>
</tbody>
</table>

We average the Tension results over all structures and all directions. For the Uniform Hydrostatic Compression experiments we average only over all structures. Mean values and standard deviations of the means thus obtained are listed below:

Table 4.16: Mean values and standard deviations for the corresponding expressions for \( \lambda \) and \( \mu \)

<table>
<thead>
<tr>
<th>System</th>
<th>Uniform Hydrostatic Compression</th>
<th>Uniaxial Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( B = 4.32 \pm 0.71 \text{ GPa} = \lambda + \frac{2}{3} \mu )</td>
<td>( \frac{1}{3} (C_{11} + C_{22} + C_{33}) = 5.43 \pm 0.22 \text{ GPa} = 2\mu + \lambda )</td>
</tr>
<tr>
<td></td>
<td>( B = 4.68 \pm 0.04 \text{ GPa} = \lambda + \frac{2}{3} \mu )</td>
<td>( \frac{1}{3} (C_{11} + C_{22} + C_{33}) = 6.56 \pm 0.52 \text{ GPa} = 2\mu + \lambda )</td>
</tr>
<tr>
<td></td>
<td>( B = 5.04 \pm 0.84 \text{ GPa} = \lambda + \frac{2}{3} \mu )</td>
<td>( \frac{1}{3} (C_{11} + C_{22} + C_{33}) = 8.13 \pm 0.70 \text{ GPa} = 2\mu + \lambda )</td>
</tr>
</tbody>
</table>
Now, having two equations with two unknowns ($\lambda$ and $\mu$) we can extract the estimates for the elastic constants for each system. The results are summarized in the Table below:

**Table 4.17:** Estimation of the elastic constants for each system and comparison with available experimental data. For systems 2 and 3 an extra comparison has been made with the corresponding values of the pure sPMMA system.

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>System 1</th>
<th>System 2</th>
<th>System 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ (GPa)</td>
<td>3.38</td>
<td>3.73</td>
<td>3.50</td>
</tr>
<tr>
<td>$\mu$ (GPa)</td>
<td>1.27</td>
<td>1.41</td>
<td>2.31</td>
</tr>
<tr>
<td>$E$ (GPa)</td>
<td>3.45</td>
<td>3.85</td>
<td>6.02</td>
</tr>
<tr>
<td>$B$ (GPa)</td>
<td>4.22</td>
<td>4.68</td>
<td>5.04</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>1.27</td>
<td>1.41</td>
<td>2.31</td>
</tr>
<tr>
<td>$v$</td>
<td>0.36</td>
<td>0.36</td>
<td>0.30</td>
</tr>
</tbody>
</table>

As summary of the elastic constants for each system normalized to the values of the pure sPMMA system are given in Figure 4.25.
4.7 Estimates of the Elastic Constants

To validate our whole methodology, we carried out a thorough comparison between available experimental data and our predictions for the elastic constants. At this point, it has to be noticed that the experimental data for the elastic constants refer to atactic poly(methyl methacrylate), but under the assumption that these values are not far from the ones for syndiotactic PMMA a comparison is permissible. As shown in Table 4.17, our results are in a very good agreement with the experimental values, which means that our predictions about the elastic constants for the nanocomposite systems (Systems 2 and 3) are compatible with what is measured experimentally.

The comparison between Systems 2 and 3 and the pure sPMMA elastic constants shows a significant improvement of their mechanical behavior compared to the bulk values. More specifically, for graphene/sPMMA system, the improvement of the elastic constants is up to 12% compared to the values of the pure sPMMA system with only 5.85% enhancement on graphene sheets.

The outstanding results though are those of f.graphene/sPMMA system, where an amazing improvement of the elastic constants by almost 82% is recorded with only 6.54% insertion of f.graphene sheets. Rammanath et. al have reported an improvement of 80% of Young modulus with only 1% reinforcement in f.graphene sheets. This shows
that our predictions are in qualitative agreement with the experimental data, and prove that the insertion of both graphene and f.graphene in a polymer matrix improves its mechanical behavior.

Another important observation is that the improvement that System 3 shows is about eight times larger than that of System 2. This is something that was expected because the structural and dynamical analysis above, showed that the functional groups in f.graphene affects much more the behavior of the polymer matrix compared to the graphene/sPMMA system, and this is reflected in the mechanical behavior of the nanocomposite.
In the present thesis, results have been presented from a hierarchical computational methodology aiming at the prediction of the mechanical properties of graphene-based polymer nanocomposites. As test systems we have chosen sPMMA and sPMMA enhanced with graphene or graphene oxide sheets. Experimental measurements have shown that the addition of a small fraction of graphene sheets in PMMA can lead to a remarkable enhancement of its elastic constants.

Our methodology involves the following steps: exhaustive equilibration of the systems at a high enough temperature (~500K) , cooling down to room temperature (300K) to obtain a good number of configurations representative of their glassy structure, and computational deformation experiments to calculate their mechanical properties.

At the equilibration temperature, we have also carried out a detailed analysis of the structural and dynamic properties of the simulated systems. We found that the sPMMA matrices containing graphene or graphene oxide sheets are denser; this is the result of the strong affinity of sPMMA chains with graphene, especially with graphene oxide. An important result of our work is that the characteristic times describing local and terminal relaxation in sPMMA increase in the presence of graphene or graphene oxide sheets due to adsorption of sPMMA chains on the graphene sheets, causing an increase also in the value of the glass transition temperature.

We have also found that graphene sheets in sPMMA tend to come closer one to the other, forming eventually a stacked (layered) structure due to very favorable side-side (carbon-carbon) interactions, with each graphene sheet in the stack arranged practically perfectly above the other. The tendency to self-assemble was obvious even in the case where functionalized graphene sheets were used in the simulations. But in this case, the phenomenon took place later and the stacking was not perfect.
Summary and Future work

For the predictions of the mechanical properties of these systems to be more relevant from a practical point of view, the subsequent calculation of the mechanical properties of the nanocomposite systems were done with systems before self-assembly took place. They are therefore representative of systems characterized by a uniform dispersion of graphene sheets.

Computed values of the elastic constants of the pure sPMMA glassy matrix were found to be in a very satisfactory agreement with experimentally measured values. The addition of small fractions of graphene sheets was seen to lead to substantial improvement of these properties, especially when functionalized graphene sheets were used. The relative increase in the Young modulus was also found to agree remarkably well with measured values.

In the future we plan: a) to address systems containing longer sPMMA chains to assess the dependence of the mechanical properties on the MW of the polymeric matrix, b) to analyze the dependence of the computed mechanical properties on the size of the graphene sheets (in the present study, the larger graphene sheets considered were 24Å x 20 Å large). We also plan to carry out a more detailed analysis of the dependence of the size (radius of gyration) of sPMMA chains on the concentration of graphene sheets in the matrix. This is very important in light of recent theoretical arguments that the relative size of polymer chains and of the particles that are inserted in the polymer matrix governs the mixing properties of the resulting nanocomposite material (the miscibility or degree of particle dispersion).
Bibliography


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