

Forschungszentrum Jülich



Institut für Festkörperforschung

***Density Functional Study of
Organic Systems:
Molecules, Polymers, and Crystals***

Barbara Montanari

Jüli-3624

***Density Functional Study of
Organic Systems:
Molecules, Polymers, and Crystals***

Barbara Montanari

Berichte des Forschungszentrums Jülich ; 3624
ISSN 0944-2952
Institut für Festkörperforschung Jül-3624
D 38 (Diss. Universität Köln)

Zu beziehen durch: Forschungszentrum Jülich GmbH · Zentralbibliothek
D-52425 Jülich · Bundesrepublik Deutschland
☎ 02461/61-6102 · Telefax: 02461/61-6103 · e-mail: zb-publikation@fz-juelich.de

Abstract

Density functional calculations have been performed on three polymeric systems, namely *isotactic* polypropylene (*it*-PP), polyethylene (PE) and systems related to bisphenol-A polycarbonate (BPA-PC). The structure of an isolated chain of *it*-PP and of several of its segments have been optimized. The results agree well with experiment and show that the structural properties of the small molecules can be used to predict the energy surfaces of the infinite chain. The computation of the equilibrium structure of PE confirms the reliability of the method in the description of the *intra*-molecular interactions in hydrocarbons. Different approximations for the exchange-correlation energy have been tested to describe the weak *inter*-molecular interactions on two types of molecular crystals: crystalline PE and a crystalline analog of BPA-PC. The local density approximation overestimates the intermolecular bonds in both, and the Becke-Perdew functional gives no intermolecular binding in the former and a very weak bond in the latter. The functional of Perdew, Burke, and Ernzerhof leads to a better description of the binding in both systems. The study of BPA-PC has then been extended to structural and vibrational properties of several fragments of the infinite chain. The calculation of the energy barriers for characteristic molecular motions provides insight into the relation between these properties and the intra- and inter-molecular arrangement. In order to extend the size and time scales of the calculations, all these results have been used to tune a classical force field, which has then been applied in Monte Carlo simulations of polycarbonate systems containing several thousand atoms. The results concern bulk and surface properties of an amorphous system.

Contents

Introduction	1
1 Theoretical Tools	5
1.1 Density Functional Theory	6
1.1.1 Local and Semi-local Approximations to E_{xc}	8
1.1.2 Plane-Wave Expansion	10
1.1.3 Pseudopotentials	11
1.1.4 Electronic Structure Optimization	13
1.2 Molecular Dynamics	14
1.2.1 The Car-Parrinello Method	17
1.2.2 Ionic Structure Optimization	18
1.2.3 Remarks about the DFT/MD method	19
2 Isotactic Polypropylene	21
2.1 Calculation Details	23
2.2 Chain Fragments	24
2.3 Structure of the Infinite Chain	26
2.4 Structural Transferability	31
3 Polyethylene	32
3.1 Calculation Details	33
3.2 Geometric and Electronic Chain Structure	35
3.3 Crystalline Structure	37

4 Polycarbonates	40
4.1 DFT Study of Chain Fragments	42
4.1.1 Computational details	42
4.1.2 Carbonic Acid	45
4.1.3 Benzene and Phenol	46
4.1.4 Monophenyl Carbonate and BPA	49
4.1.5 DPBC	50
4.2 DFT Study of a Crystalline Analog	57
4.2.1 Volume Optimization	58
4.2.2 Geometrical Structures	60
4.2.3 Vibration Properties	64
4.2.4 Rotation Energy Barriers	64
4.3 DFT Study of Cyclic Oligomers	67
4.3.1 Geometrical structures	69
4.3.2 Vibrational properties	73
4.4 Combined DFT/Classical FF Study	75
4.4.1 Tuning the Force Field	76
4.4.2 Details of the Monte Carlo Simulation	82
4.4.3 Preliminary Monte Carlo Results	84
Conclusions	99
Acknowledgments	103
Appendix: Monte Carlo Method	105
Bibliography	107
List of Publications	117

Introduction

Organic compounds are the compounds containing carbon. The word “organic” is misleading, and comes from the days when chemists thought that they could only be obtained from living organisms. Also when it became clear that these compounds do not have to come from living sources but could be made in the laboratory, the name did not change. The reason why carbon compounds are separated from the compounds of all the other elements of the periodic table is that there are so very many compounds of carbon, and their molecules can be so large and complex. Indeed, the number of organic molecules is many times greater than the number of inorganic molecules. Nearly ten million compounds of carbon are known today, and this number is growing by half a million a year. This is due to the ability of carbon atoms to attach themselves to one another to an extent not possible for atoms of any other element. Carbon atoms can form chains thousands of atoms long, or rings or cages of all sizes; the chains and rings can have branches and cross-links. To the carbon atoms of these chains and rings there are attached other atoms, mainly hydrogen, but also fluorine, chlorine, bromine, iodine, oxygen, nitrogen, sulphur, phosphorus and many others. Another important reason of interest for these compounds is that organic molecules are the building blocks of all living organisms.

In this work I present a study of a special class of organic molecules, the organic *polymers*. Polymers are very large molecules built up by repetition of small, simple chemical units linked by covalent bonds. For example, polyethylene consists of a long chain of repeating $\text{—(CH}_2\text{)—}$ groups. In nature there is an abundance of organic polymeric materials. Proteins, nucleic acids (DNA,

RNA), and enzymes are the most complex polymers. Other naturally occurring organic polymers, like cellulose, starch, and natural rubber, have a simpler structure. In comparison to them synthetic polymers produced by man have a primitive molecular architecture.

Aside from the biological importance of organic polymers, their industrial relevance deserves special mention. They are in fact the constituent of two classes of materials, rubbers and plastics, that increasingly gained importance during the last century. Since the introduction of synthetic organic polymers on the market indeed, they have challenged the other materials (wood, metals, natural fibers, etc.) for their uses, and it is difficult to conceive how many everyday features of modern life could ever have been developed without these two groups of materials. For example, the automotive industry is now a major user of plastics, with the weight of plastics being used per car increasing year by year. Among the other main applications of plastics and rubbers there are electrical insulation, food packaging, domestic goods, and toys.

The widespread use of these materials has not been achieved without largescale investment in research. Polymer properties have been closely studied and slowly a relationship has been built up between structure and properties of polymers. Modern materials science indeed is based on the experience that the properties of materials are to a large extent influenced by their microstructure. Knowing the microstructure helps to understand, and therefore to predict, the macroscopic properties of these materials, and could provide essential information for designing new plastics with tailor-made properties. The study of the microstructure consists in studying the forces acting among the atoms. In this concern, polymers are very interesting and manifold systems, since different kinds of interactions, with different origin and different range of action, are involved in the determination of the structure. Going more into detail, the predominant effect of the intramolecular interactions is the presence of covalent bonds, which are characterized by short bond distances (1.1 to 1.6 Å) and high energies (1.5 to 6.5 eV/particle). A very different nature characterizes the intermolecular interactions. Amongst them, the van der Waals forces play here an important role. These forces are non

INTRODUCTION

local, and involve long distances (2 to 10 Å) and low energies (0.04 eV/pair of atoms). Special mention deserves a particular type of interaction, which forms the so called *hydrogen bond*, where an hydrogen atom acts as a bridge between two electronegative atoms (e.g. O—H...O, O—H...N). For this kind of bond, the typical energy range is 0.1–0.3 eV/bond, and the typical length is in the range from 2.4 to 3.2 Å. Because of the variety of these interactions, organic polymers represent a challenging subject of investigation, and they can be used to test the versatility of a method.

This work is mainly focused on the investigation of the microstructure of three important plastics materials, i.e., polyethylene, *isotactic* polypropylene, and polycarbonates. The traditional methods for investigating the atomistic structure of organic molecules and polymers are mostly semi-empirical or based on force-fields of uncertain validity and transferability. We approach the problem using the density functional theory (DFT). This method, supported by the enormous growth of computer power in the last decades, plays nowadays a central role in analysing the structure and properties of matter in detail, and its importance has been this year recognized, with the assignment of the Nobel Prize in Chemistry “to Walter Kohn for his development of the density functional theory”. In fact, DFT calculations, applied here also in combination with molecular dynamics (MD) techniques, enable us to study complex systems retaining the details of their quantum mechanical nature. This theory has a long and triumphant history in solid state physics, where it routinely predicts correct crystal structures, lattice constants, bulk moduli and vibrational frequencies, and provides a reliable method for calculating binding properties of molecules and clusters. In particular, previous studies of carbon-containing molecules have demonstrated the reliability of DFT in predicting electronic [1], structural [2, 3] and vibrational properties [4], as well as energy barriers [3] and reaction energy surfaces [5, 6] for these systems. Besides its predictive power, DFT has an important advantage with respect to the traditional semi-empirical and force-field-based methods: it free of adjustable parameters. The disadvantage is that its application must be limited to systems of smaller size. For those specific polymer science applications that

require very large systems, DFT can still play an important role, providing data to improve the quality of the force fields.

In Chapter 1, I shall present the theoretical framework of these calculations. The basic theorems of the density functional theory, and the approximations, not avoidable for its practical use and implementation, are illustrated. The combination of DFT with molecular dynamics techniques, which leads to the Car-Parrinello method, is described in details, and the success and limitations of the approach are discussed. The next chapters comprise the results obtained for three different systems: in Chapter 2, the study of **isotactic polypropylene** shows the capability of DFT to reproduce the experimental geometries of isolated organic molecules and polymers. The comparison with the calculated structures of some fragments of the infinite chain allows to identify the extent to which the structural parameters of small hydrocarbons can be used to parametrize the forces in larger systems. In Chapter 3, the study of **polyethylene** is presented. The calculation of the equilibrium structure of an isolated chain of polyethylene evidences the reliability of the DFT description for *intra*-molecular electronic and geometrical structures in organic systems. More difficult is instead the description of the weak *inter*-chain interactions present in the crystalline polyethylene. Several different energy functionals are here challenged to reproduce the measured interchain distances and binding energies. This study continues in the chapter concerning the **polycarbonates**, with an application to a crystalline analog of bisphenol-A polycarbonate. Several polycarbonate systems are then investigated. Their study includes a detailed analysis of the geometrical structures, rotation energy barriers, vibration spectra, and electronic properties. All the results obtained using DFT have then been used to optimize a force field that has been applied for studying thermodynamical properties of a polycarbonate amorphous system containing several thousand atoms.

Chapter 1

Theoretical Tools

From the microscopic point of view, organic molecules, like any other material, consist of interacting ions and electrons, and their properties could be in principle determined by solving the Schrödinger equation. In practice, this is not feasible, and the solution of the problem requires several approximations. Firstly, the Born-Oppenheimer approximation [7] is introduced, which states that, because of the large difference between electronic and ionic masses, the nuclei can be described as fixed charges in the treatment of the electronic problem, so that their coordinates appear in the Hamiltonian only as parameters. The electrons move in the “external” potential V_{ext} of the nuclei, following adiabatically their slow motion and remaining close to the quantum-mechanical ground state. In other words, this approximation decouples the ionic and electronic degrees of freedom, and allows us to divide the problem in two parts: the part concerning the electronic degrees of freedom will be treated in Sect. 1.1, where we will consider a system of N electrons in an external potential V_{ext} described by the Hamiltonian:

$$\mathcal{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_{ext}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (1.1)$$

[Atomic units $e = \hbar = m_e = 1$ are used throughout this work.] The second part, presented in Sect. 1.2, will concern the time evolution of the ions, treated as classical particles in the effective potential determined by the electronic ground state.

1.1 Density Functional Theory

The density functional theory (DFT) provides an appropriate mathematical framework for determining the ground state of a many-electron system, which is the only required knowledge for the study of a great number of physical properties. This theory is based on the Hohenberg-Kohn theorem [8], which consists of two statements:

- The external potential V_{ext} acting on a system of electrons is determined (up to an additive constant) by the ground-state electronic charge density $n(\mathbf{r})$ *alone*.

As a consequence, also $E = \langle \Psi | \mathcal{H} | \Psi \rangle$, where Ψ is the N -particle wave function, is a unique functional of $n(\mathbf{r})$, and can be written as:

$$E[n] = \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n], \quad (1.2)$$

where $F[n]$ does not depend on the external potential, i.e., it is *universal*.

- The ground-state total energy E_{GS} of the system is the minimum of the functional $E[n]$ with respect to variations of the electronic charge density $n(\mathbf{r})$.

In this framework, the determination of the ground state of the system is reduced to the minimization of $E[n]$ under the constraint

$$\int n(\mathbf{r})d\mathbf{r} = N, \quad (1.3)$$

i.e., to the solution of the Euler-Lagrange equation:

$$\frac{\delta}{\delta n} \left[E - \mu \int n(\mathbf{r})d\mathbf{r} \right] = 0, \quad (1.4)$$

where the Lagrange multiplier μ is introduced to impose the condition in Eq. (1.3). More details about this theory can be found in several review papers and books [9, 10, 11, 12]. For the present purpose we limit ourselves to the basic concepts illustrated above. It is important to stress, anyway, the focal point of the theory: for the ground state, the electron density suffices for the

determination of *all* properties. This means that the N -particle wave function Ψ (depending on $3N$ variables) and the associated Schrödinger equation can be replaced by the electron charge density $n(\mathbf{r})$ (depending only upon three variables) and the minimization problem of Eq. (1.4), and the problem is greatly simplified.

The usual implementation of the DFT is due to Kohn and Sham [13] who wrote the electron density in terms of an orthonormal set of N independent one-particle wave functions ψ_i , the *KS orbitals*:

$$n(\mathbf{r}) = \sum_{i=1}^N f_i |\psi_i(\mathbf{r})|^2, \quad (1.5)$$

where f_i are the occupation numbers. In the Kohn-Sham (KS) formulation, the universal functional F is then written in the form:

$$F[n] = T_0[n] + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n]. \quad (1.6)$$

Here $T_0[n]$ is the kinetic energy that a system with density n would have in the absence of electron-electron interaction, and the second term is the classical (Hartree) electrostatic term. This expression defines the so called *exchange-correlation energy* E_{xc} , which is the unknown part of the problem. The step backwards to a description in terms of wave functions has the role of providing a reliable approximation of the kinetic energy term that cannot be obtained in terms of the density alone. If we assume the KS orbitals to be our basic variables, the solution for the Euler-Lagrange equation (1.4) can be found by solving a set of coupled single-particle Schrödinger-like equations for non-interacting electrons:

$$\left(-\frac{1}{2} \nabla^2 + \underbrace{V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + v_{xc}(\mathbf{r})}_{V_{KS}} \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (1.7)$$

where:

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (1.8)$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}. \quad (1.9)$$

These are the *KS equations*, whose solution is found via a self-consistent iterative procedure: starting from a given set of ψ_i we determine the density and the potential V_{KS} , and then we solve the Eq. (1.7) to determine new orbitals ψ_i . This cycle is repeated, using the new orbitals as input wave functions, until the input and the output orbitals are identical.

The KS procedure introduces a single-particle Hamiltonian, that can be interpreted as describing each electron in the mean field created by all other electrons; but it must be pointed out that the KS eigenstates and eigenvalues do not have any formal interpretation, and the only physical observables here are the ground-state total energy and density.

1.1.1 Local and Semi-local Approximations to E_{xc}

The DFT described above is formally exact but useless for practical purposes, because all difficulties related to the many-body character of the problem are still unsolved. They are all contained in the exchange-correlation energy E_{xc} , which is formally well defined by the equation (1.6), but unknown. In order to apply the theory, an approximation of E_{xc} is necessary. The most common and simplest approach is the *local spin density* approximation (LSD). It relies on the idea of replacing the exchange-correlation energy of a *non uniform* interacting electron system with the E_{xc} computed as if locally it had the same exchange-correlation energy of a *uniform* interacting system with the same density:

$$E_{xc}^{\text{LSD}} = \int \varepsilon_{xc}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] n(\mathbf{r}) d\mathbf{r}, \quad (1.10)$$

where $\varepsilon_{xc}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})]$ is the exchange-correlation energy per particle of a homogeneous, spin-polarized electron gas with spin-up and spin-down densities $n_{\uparrow}$ and $n_{\downarrow}$, respectively¹. This quantity depends locally upon the density at the point $\mathbf{r}$, and it has been determined with high accuracy using quantum Monte Carlo simulations [14, 15], which provided the total ground-state energy of the uniform interacting electron gas at several densities. These energies have

¹The local density approximation (LDA) is obtained from the LSD approximation in the limit of no spin polarization ($n_{\uparrow} = n_{\downarrow}$).

been interpolated by several authors. For our computations we have chosen the recipe of Perdew and Zunger [16].

The LSD approximation, free of experimental input, is exact only in the limit of uniform systems, and its application is formally justified for systems with slowly varying electron density. Somewhat surprisingly, the application of the LSD approximation to a large variety of systems has shown that this approximation reproduces satisfactorily many measurable quantities [10], including ground-state structures of molecules and solids, vibrational properties, etc. The reason for the success of the LSD approximation relies on its ability in predicting energy variations upon displacing atoms, forming or breaking bonds, etc.. In turn, the reason for this is that the LSD approximation preserves certain properties of the exact *exchange-correlation hole*, which describes the depletion hole around each electron due to the anti-symmetry of the wave function and to the repulsive electron-electron potential. The preservation of such properties constrains the energy to a reasonable value in a variety of different bonding configurations [17].

Nevertheless, there are some drawbacks: the LSD overestimates the cohesive energies of solids, whereas the lattice constants are often underestimated. Errors in the structural properties are usually small for solids with covalent or metallic bonds, but the description of weaker bonds like hydrogen bond [18], or intermolecular bonds arising from dispersion forces [19, 20] is not accurate enough.

A natural extension beyond the LSD is represented by the so called *generalized gradient approximations* (GGA), where the E_{xc} depends not only upon the density, but also on its gradient, and, more generally, on higher derivatives. In the usual implementation, the dependence on the density gradient is expressed in terms of the dependence upon a dimensionless quantity ζ :

$$\zeta(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{n^{4/3}(\mathbf{r})}. \quad (1.11)$$

The general expression for E_{xc} in the generalized gradient approximations then reads:

$$E_{xc}^{GGA}[n] = \int f_{xc}[n(\mathbf{r}), \zeta(\mathbf{r})] n(\mathbf{r}) d\mathbf{r}. \quad (1.12)$$

It has been found that GGA modifications often lead to better agreement with measured formation energies in small molecules [21] and solids [22], and to a more accurate description of hydrogen bonds [23, 24].

Many different recipes have been invented for the function f_{xc} in Eq. (1.12). Most of them have been produced by fitting existing data, e.g. tuning their shapes to reproduce the total energies of specific atoms. One of the most popular GGA schemes owes the exchange part to Becke [25] and the correlation to Perdew [26], and it is referred to as BP.

A more recent GGA, the so called PBE, is due to Becke, Perdew, and Ernzerhof [27]. With respect to previous GGA recipes, PBE has the advantage of being simpler and free of empirical input. Moreover, it incorporates an accurate description of the linear response of the uniform electron gas, and results in a smoother potential than in previous approximations.

In this work we have tested the capability of LSD and both these GGA schemes in the description of the different sources of bonding in organic systems.

1.1.2 Plane-Wave Expansion

The equation (1.7) can be solved by expanding the KS orbitals ψ_i in a finite basis of known functions $\{\phi_j(\mathbf{r})\}$:

$$\psi_i(\mathbf{r}) = \sum_j c_j^i \phi_j(\mathbf{r}), \quad (1.13)$$

and then diagonalizing the corresponding KS Hamiltonian matrix. Among all possible basis functions, the plane-wave (PW) functions have several advantages: besides their simplicity, they are independent of the atomic positions. In this way also the accuracy of the calculation is independent of the positions and the forces are easy to calculate [28]. The plane-wave expansion is especially favourable in case of periodic systems, because it leads to a very simple formulation of the problem in the reciprocal space². Moreover, the

²Most of the calculations presented here were performed using periodic boundary conditions.

accuracy of the calculation can be easily evaluated and improved if the basis dimension is determined using all plane waves whose corresponding kinetic energy is smaller than a chosen cutoff, E_{cut} :

$$|\mathbf{k} + \mathbf{G}\rangle = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}, \quad (1.14)$$

with

$$\frac{1}{2}(\mathbf{k} + \mathbf{G})^2 \leq E_{cut}. \quad (1.15)$$

Here $\mathbf{k}$ belongs to the first Brillouin zone, $\mathbf{G}$ is a vector of the reciprocal lattice, and Ω is the volume of the system.

Unfortunately, only a very large plane-wave basis is able to accurately reproduce the rapid spatial variation of the orbitals in the region around the nuclei. However, the orbitals closer to the nuclei (i.e. the *core* orbitals) are very well localized, energetically well separated from all valence states, and they do not play a role in the interatomic bonds, i.e. in most properties of the system. These considerations justify the elimination, from the KS equations, of the degrees of freedom associated with the core electrons, and only the “chemically active” electrons are explicitly included in the computation.

1.1.3 Pseudopotentials

The switch from the all-electron (AE) problem to an equivalent problem that involves only the valence electrons is exploited by replacing the nuclear potential V_{ext} in the Hamiltonian of equation (1.1) with a new potential, the so-called *pseudopotential* (PP) [29]. In this formalism the interaction of the valence electrons with the nuclei and the core electrons is replaced by a potential describing it as if the atomic cores were an “external” source of interaction, and the degrees of freedom associated with them are left out from the system described by the KS equations. The reduction of the explicitly treated degrees of freedom is not the only advantage of the pseudopotential formalism. In this approach in fact, the AE valence wave functions, which present rapid oscillations in the region close to the cores, are replaced by *smoother* PP wave functions. Therefore, the size of the PW basis required to compute electronic properties within a given accuracy is drastically reduced.

The modern techniques for pseudopotential design are based on the following requirements:

- (a) The PP eigenvalues relative to the occupied states are equal to the AE eigenvalues for the same states, and the corresponding PP wave functions are free of radial nodes.
- (b) The PP wave functions for the valence electrons coincide with the AE wave functions outside a fixed core radius r_c .
- (c) The logarithmic derivatives of the PP eigenfunctions coincide with the ones of the AE eigenfunctions for $r \geq r_c$.

The condition (b) implies the *norm conservation*, i.e., the norm of the PP and AE atomic wave functions is the same outside the radius r_c . In turn, the norm conservation implies, via the Gauss theorem, that the electrostatic potential produced by the PP charge density coincides, outside r_c , with the one derived from the AE density. The combination of (b) and (c) implies that the derivative of the PP eigenfunctions with respect to the energy coincide with the ones of the AE eigenfunctions for $r \geq r_c$ [30]. These pseudopotentials are built to be not singular at the origin, and the smoothness of their corresponding PP wave functions ensures an accurate description with a relatively small plane-wave basis. This smoothness arises because the strong Coulomb attraction in the core region is compensated by the orthogonality constraint between valence and core orbitals, which produces a large kinetic energy resulting in a strong repulsive potential for the valence states.

The orthogonality constraint between valence and core orbitals gives rise to another important characteristic of these pseudopotentials. In fact, since every valence state must be explicitly orthogonalized only to core states corresponding to the same angular momentum (the scalar product between them gives automatically zero otherwise), the pseudopotential is different for s , p , d , ... valence states, i.e. it depends on the angular momentum of the valence configuration. This forces the pseudopotential to be *non-local*, whereas the AE nuclear potential V_{ext} is local.

Pseudopotentials can be produced by fitting measured quantities (such as energy bands [31]) or can be generated starting from parameter free (DFT) atomic calculations [30, 32]. In both cases they can suffer the drawback of being valid only for the atomic configuration to which the measurements or the calculations refer. Therefore, their quality is measured by their *transferability*, i.e. their ability to describe a given atom in different valence-electron configurations. In other words, a “good” pseudopotential must be able to describe the atom in its isolated configuration, but also with different electronic configurations, including its ionized state, or in a molecule, a cluster or a solid.

In the present calculations we have chosen the pseudopotential form suggested by Troullier and Martins [33] which is norm-conserving, relatively smooth, and whose transferability has been tested by many different applications published in the literature.

1.1.4 Electronic Structure Optimization

The procedure depicted in the previous sections for the resolution of the KS equations conventionally involves the diagonalization of a $N_{pw} \times N_{pw}$ matrix, where N_{pw} is the number of PW functions. Since the cost of a standard diagonalization grows as $\mathcal{O}(N_{pw}^3)$, this procedure becomes very expensive for large systems. This cost can be reduced by exploiting the fact that we are interested only in the eigenvalues and eigenvectors relative to the bands occupied in the ground state configuration, i.e., the bands corresponding to the lowest KS eigenvalues. The computation of selected eigenvalues and eigenfunctions of a large matrix is nowadays a well-developed technique, and it can be efficiently applied for solving the KS equations. Going more into the details of the problem, once we have expanded the occupied KS orbitals in a finite basis of known functions, as shown in Eq. (1.13), we choose a set of initial expansion coefficients c_j^i . In this way the electron density n is calculated, and its explicit expression is inserted in the functional $E[n]$. Consequently, $E[n]$ can be expressed as a function of the (many) variables c_j^i , and the minimization required to compute the electronic ground-state energy can be performed with any of the modern techniques for solving multidimensional minimization

problems.

The simplest of these techniques is the so-called *steepest descent* [34]. It introduces a fictitious time variable t , used only to label different configurations in the space of the ψ_i . Then one calculates:

$$\dot{\psi}_i(\mathbf{r}, t) = -\frac{1}{2} \frac{\delta E}{\delta \psi_i^*(\mathbf{r}, t)}. \quad (1.16)$$

The system is driven towards a minimum moving a bit down the gradient $\delta E_{tot}/\delta \psi_i^*(\mathbf{r}, t)$ at each step. The orthonormality constraint on the ψ_i must be kept during the minimization procedure.

This method does not necessarily provide the best strategy to reach the minimum point [34]. More efficient methods, e.g. the *conjugate gradient* [35], accumulate information on the second derivatives of the energy by a feedback process that monitors the progress of the minimization.

1.2 Molecular Dynamics

We now focus our attention on the ionic degrees of freedom, considering the evolution of the ionic coordinates, with the aim of simulating dynamical processes and of determining the most stable structures.

Molecular Dynamics (MD) methods have been described extensively by several authors [36], and we restrict ourselves to the basic concepts. The time evolution of a system of M classical particles is governed by the Lagrangian:

$$\mathcal{L} = T - V. \quad (1.17)$$

Usually, the kinetic energy T takes the form:

$$T = \sum_{I=1}^M \frac{1}{2} m_I \dot{\mathbf{q}}_I^2, \quad (1.18)$$

where $\dot{\mathbf{q}}_I$ and m_I are the velocity and the mass of the I -th particle, respectively. The potential energy V contains the interesting information regarding the interactions between the particles. Once the expression for V is given, we can compute the forces on the particles:

$$\mathbf{F}_I = -\nabla_{\mathbf{q}_I} V, \quad (1.19)$$

CHAPTER 1. THEORETICAL TOOLS

and solve the Newton's equations of motion, which give the time evolution of the system.

For systems fulfilling the ergodicity condition, MD can be used to compute thermal averages for a variety of properties. Under this condition, in fact, it can be proved that the thermal expectation value of a physical observable $\mathcal{A}$ is given by the time average of $\mathcal{A}$ over the trajectory followed by the system:

$$\begin{aligned}\langle \mathcal{A} \rangle &\equiv \int \frac{\mathcal{A}(\mathbf{q}^M) e^{-\beta \mathcal{H}}}{\int e^{-\beta \mathcal{H}} d\mathbf{q}^M} d\mathbf{q}^M = \\ &= \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \mathcal{A}(\mathbf{R}_1(t), \mathbf{R}_2(t), \dots, \mathbf{R}_M(t)) dt.\end{aligned}\quad (1.20)$$

Here $\mathbf{q}^M = (\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_M)$ are the configurational variables, $\mathcal{H}$ is the Hamiltonian governing the system, $\beta = 1/kT$, and k is the Boltzmann constant. Therefore, in this case the time evolution provided by the MD simulations suffices to calculate the values of many physical quantities.

The key to an accurate description of the system is the set-up of a reliable expression for the potential V . In the usual approach, the “real” potential is modelled by an effective potential containing adjustable parameters that are fitted to reproduce measured or computed quantities. For instance, the properties of rare gas dimers are well reproduced by the Lennard-Jones potential:

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1.21)$$

where r is the distance between the two atoms, and ϵ and σ are adjustable parameters; pair potentials are often able to describe ionic systems, etc. In many cases of interest, however, these simple models are not able to provide a reliable description of the “real” potential surface. They fail, for example, to describe the breaking or forming of bonds, or in the description of systems whose chemical or physical state changes. An adequate description of these phenomena must explicitly take into account the electronic structure.

According to DFT, we can calculate the potential V acting on the ions by solving the instantaneous electronic problem. In fact, this potential is given

by:

$$V(\{\mathbf{R}_I\}) = \min_{\{\psi_i\}} E_{tot}[\{\psi_i\}, \{\mathbf{R}_I\}], \quad (1.22)$$

where E_{tot} is obtained by adding the potential energy of the ion-ion interaction to the KS expression for the total energy of the electronic system:

$$\begin{aligned} E_{tot}[\{\psi_i\}, \{\mathbf{R}_I\}] = & -\frac{1}{2} \sum_i^{occ} \langle \psi_i(\mathbf{r}) | \nabla^2 | \psi_i(\mathbf{r}) \rangle + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \\ & + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n] + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \end{aligned} \quad (1.23)$$

Therefore, a combined DFT/MD scheme can be implemented, where the time evolution of the ions is governed by the potential, free of adjustable parameters, produced by the DFT electronic structure optimization. An advantage of combining the two schemes is that parameter-free potentials are general and versatile, and represent a significant improvement over the potentials fitted to reproduce experimental and/or theoretical data. A molecular dynamics with DFT-based interatomic potentials could be performed in the following way:

- (1) begin with a likely configuration of the ions,
- (2) solve the KS equations for this ionic configuration,
- (3) use the electronic structure and the Hellmann-Feynman theorem [37] to calculate the forces on the ions,
- (4) move the ions according to the classical equation of motion,
- (5) take the new ionic coordinates, go to step (2) and continue.

Although this procedure is conceptually possible, it is not practicable. The solution of the electronic-structure problem according to the DFT requires matrix diagonalization calculations, which must be iterated until the self-consistency is reached. These computations take long, and if this time is multiplied by the number of the ionic configurations visited during the dynamical process (of the order of 10^4 – 10^5), it becomes evident that only very small systems could be studied with this method.

1.2.1 The Car-Parrinello Method

The success of combined DFT/MD calculations is due to a different approach introduced in 1985 by Car and Parrinello [38]. The idea on which the Car-Parrinello (CP) method is based is to consider a fictitious dynamical system where the ionic and electronic degrees of freedom are treated on the same footing. This is achieved associating a fictitious classical kinetic energy to the electronic degrees of freedom (the KS orbitals ψ_i), i.e., adding a kinetic energy term for the electrons in the Lagrangian of the system. The Lagrangian reads then:

$$\begin{aligned} \mathcal{L} = & \mu \sum_i^{\text{occ}} \int |\dot{\psi}_i|^2 d\mathbf{r} + \frac{1}{2} \sum_I m_I \dot{\mathbf{R}}_I^2 - E_{\text{tot}}[\{\psi_i\}, \{\mathbf{R}_I\}] + \\ & + \sum_{ij} \Lambda_{ij} \left(\int d\mathbf{r} \psi_i^* \psi_j - \delta_{ij} \right). \end{aligned} \quad (1.24)$$

Here μ is the fictitious electron mass, m_I are the ionic masses, and Λ_{ij} are the Lagrangian multipliers arising from the orthonormality constraint on the ψ_i , which must be satisfied at any time t during the dynamical process. The equations of motion associated with the Lagrangian $\mathcal{L}$ are:

$$\mu \ddot{\psi}_i(\mathbf{r}, t) = -\frac{\delta E_{\text{tot}}}{\delta \psi_i^*(\mathbf{r}, t)} + \sum_j \Lambda_{ij} \psi_j(\mathbf{r}, t) \quad (1.25)$$

and

$$m_I \ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I} E_{\text{tot}}. \quad (1.26)$$

The dynamics is then performed in the following way:

- (1) start from a likely ionic configuration,
- (2) solve the electron-structure problem, i.e. calculate

$$\min_{\{\psi_i\}} E_{\text{tot}}[\{\psi_i\}, \{\mathbf{R}_I\}], \quad (1.27)$$

- (3) compute the forces on ions ($\nabla_{\mathbf{R}_I} \mathcal{L}$) and electrons ($\delta_{\psi_i^*} \mathcal{L}$),
- (4) move electronic wave functions and ions *simultaneously*, go to step (3) and continue.

In other words, the fictitious electronic optimization dynamics and the proper ionic dynamics are run in parallel: in the same time step the ions are moved according to the self-consistent forces, while the electron variables are moved according to the energy gradients and constraints. In this way the costly electron-structure calculations at every step of the ionic motion are replaced by *only one* initial optimization of the electronic wave functions and by their relatively inexpensive update at each MD step. The fictitious electron dynamics and the assumption $\mu \ll m_I$ prevent energy transfer from the ionic to the electronic degrees of freedom over the time scale of the simulation, so that the electronic wave functions are automatically updated to follow *adiabatically* the nuclear motion, i.e., they remain in their ground state.

Since its establishment, the CP method has extended the range of conventional electronic-structure calculations, and it has been applied to a great variety of problems. Examples are the determination of physical properties of disordered systems, the study of relevant dynamical processes in the area of semiconductors, surface reconstruction, atomic clusters and more. This method, born and traditionally applied in the realm of solid state physics, has recently attracted the attention of the quantum chemists, and it is increasingly used to study chemical reactions and even biological systems. Further details about this method and its applications can be read in numerous review articles published in the last decade [39, 40, 41, 42, 43, 44].

1.2.2 Ionic Structure Optimization

In principle, the most stable structure of a system can be determined by calculating its total energy for each possible set of ionic coordinates $\{\mathbf{R}_I\}$ and selecting the geometry with the lowest energy. Unfortunately, such a procedure is feasible only for systems with very few ionic degrees of freedom. A more convenient optimization scheme is then required and, moreover, since the number of local energy-minima increases very rapidly with the number of atoms, we need a procedure able to provide the absolute minimum, i.e., a *global* minimization procedure. The *simulated annealing* [45] optimization procedure satisfies this requirement. Using MD or Monte Carlo (see Appendix)

as basic tools, it exploits the analogy with the way in which the molecules of a liquid find their minimum potential-energy configuration as the liquid is cooled. At a given instant, the system is represented by a point in the phase space, exploring the configurations allowed by the total energy. As the temperature T (kinetic energy) is lowered, the region allowed for exploration by this constraint is reduced until eventually only the point of minimum potential remains when $T=0$.

In the CP method, the process of wandering around in the phase space is simulated by the MD, the energy function is $E_{tot}[\{\psi_i\}, \{\mathbf{R}_I\}]$, and the temperature T is measured by the kinetic energy of the ions:

$$\frac{1}{2} \sum_{I=1}^M m_I \dot{\mathbf{R}}_I^2 = \frac{3}{2} M k_B T. \quad (1.28)$$

During the dynamical process, the ions will move, on average, in the directions that minimize the ionic forces, and the configuration will move on the energy surface, losing potential energy and gaining kinetic energy. To anneal the system, it should be allowed to keep this high kinetic energy long enough in order to fully explore the phase space. Then a small portion of the kinetic energy is removed to “cool” the system, which should maintain a lower kinetic energy for a time. This process is continued, slowly cooling the system, until $T=0$ and the system has settled into its optimal configuration.

The MD annealing is often performed using Langevin dynamics [46], with a friction term and a stochastic external force that progressively dissipate the kinetic energy of the atoms.

1.2.3 Remarks about the DFT/MD method

The DFT/MD method of Car and Parrinello shares the advantages of the parameter-free DFT: it has predictive power, is general and versatile, and it explicitly takes into account the electronic degrees of freedom. Moreover, the unified approach allows this parameter-free method to access a range of problems and physical quantities that cannot be studied with a pure electronic structure method. For example, time averages can be computed, and processes involving thermal variations can be simulated by varying the $\{\dot{\psi}_i\}$ and

the $\{\dot{\mathbf{R}}_I\}$. Furthermore, it allows us to study chemical reactions and other problems not addressable with a semi-empirical potential scheme.

The gain of having a method closer to the fundamentals of electrons and ions is not without cost. Indeed, the CP method is more expensive than the standard classical MD because

- the computation of the forces on the electrons is expensive,
- the separation of the electronic and ionic time scales leads to a small time step, typically 10^{-16} s,
- the method scales as $\mathcal{O}(M^3)$, where M is the number of atoms, whereas classical MD scales as $\mathcal{O}(M)$ (for systems with short range potentials) or $\mathcal{O}(M^2)$ (for systems with Coulomb potentials).

These limitations restrict the range of CP simulations to smaller system sizes and shorter simulation times (of the order of 10^{-12} s) if compared to the classical MD methods. But present-day computers and the development of parallel programming techniques have helped to extend the range of applicability of the DFT/MD method, and allow us to study systems containing several hundred atoms over longer simulation times at a reasonable price.

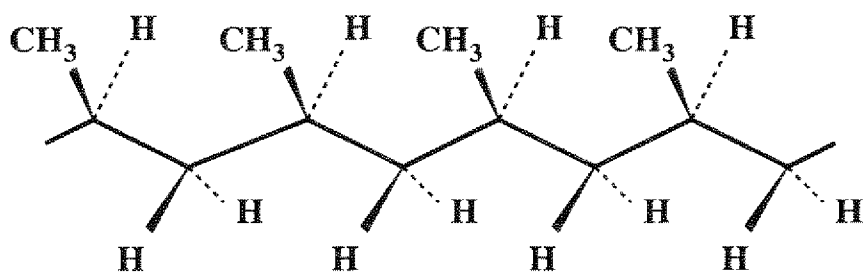
Chapter 2

Isotactic Polypropylene

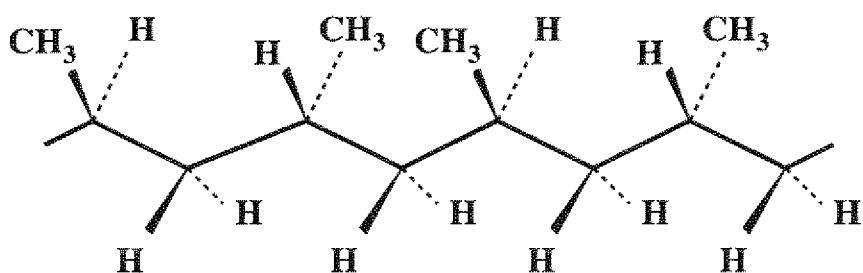
In 1954 Natta, following the work of Ziegler, was able to produce different types of polypropylenes that differed extensively in their properties. These types were characterized by different *tacticity*, as it is illustrated in Fig. 2.1. One form, known as isotactic polypropylene (*it*-PP), was marketed by Montecatini as Moplen as early as 1957, and it is now the second most widely used polymer in the world, after polyethylene. The importance of the work of Ziegler and Natta in the field of polymer synthesis was quickly recognized, and in 1963 they were awarded the Nobel Prize in Chemistry for the development of what are now known as Ziegler-Natta catalysts.

The widespread industrial applications of polypropylene induced in the last four decades numerous studies of its structure, morphology, mechanical properties and their interrelationships.

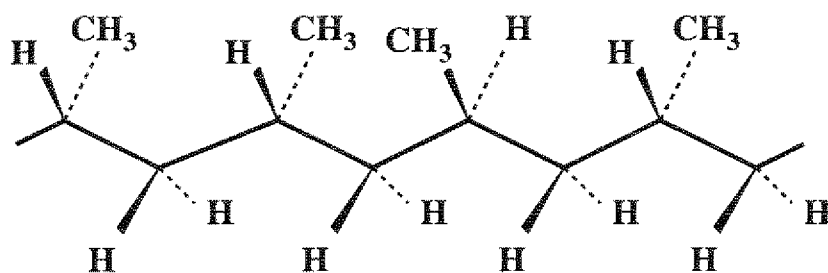
Two major aims motivate the present study: first, *it*-PP is one of the simplest among the nontrivially stereoregular polymers synthesized so far. With three C_3H_6 units (27 atoms) in the unit cell, its structure has not yet been optimized *fully* using a method free of adjustable parameters. We perform such an optimization using the DFT approach. Second, it is interesting to investigate the extent to which the structural properties of small molecules can be used to predict the energy surfaces of larger systems, i.e. those containing the smaller molecules as structural units. A similar study using the Hartree-Fock approximation was carried out some years ago for some small



Isotactic Polypropylene



Syndiotactic Polypropylene



Atactic Polypropylene

Figure 2.1: In the *isotactic* form the configurations of the H atoms and methyl groups around the main-chain C atoms are all the same along the chain. In the *syndiotactic* form these configurations are always opposite in successive structural units. In the *atactic* form the sequence of this configurations along the chains is random.

straight-chain [47] and branched [48] hydrocarbons, with particular focus on the conformational behavior (the dependence of the dihedral angles along the carbon chains). We perform a similar study, based on the DFT, and compare the results for the structure of *it*-PP and several of its segments. If the local bonding properties of the polymer chain can be determined reliably by (much more economical) calculations on small segments, there is a justifiable hope that the latter can be used to parametrize the forces and energies in the former.

2.1 Calculation Details

The optimization of the structure of *it*-PP was performed by calculating the forces on the atoms, which were then allowed to relax to the structure with minimum energy [49]. The minimization used the Hellmann-Feynman forces [37] and the Broyden-Fletcher-Goldfarb-Shanno [34] algorithm. The unit cell was chosen to be simple tetragonal, with lattice constants in the directions perpendicular to the chain that were large enough (10.98 Å) to ensure a minimal interchain interaction. The lattice parameter in the direction of the chain axis was initially set equal to the experimental value (6.50 Å) [50]. The optimization of the structure was then repeated with different lattice parameters along the direction of the chain, in order to optimize *all* structural parameters for the single *it*-PP chain. The integration in the reciprocal space employed the special points technique [51] and a thorough check showed that eight special points and a kinetic energy cutoff of 60 Ry gave well-converged results.

The calculations for the segments C_3H_8 and C_5H_{12} of *it*-PP were performed using simple cubic unit cells. The lattice constants were chosen to be large enough to ensure that there is a negligible interaction between neighboring molecules (9.5 Å for C_3H_8 and 11.3 Å for C_5H_{12}). The integration in reciprocal space used a single point ($\mathbf{k}=0$) in the Brillouin zone.

All the calculations mentioned so far were done first using the LSD approximation for the exchange-correlation energy, and then repeated using the GGA-BP gradient corrected approximation.

For isopentane and $C_{10}H_{22}$ we have also performed all-electron DFT calculations with a Gaussian basis set [52].

2.2 Chain Fragments

We have optimized the structures of several fragments of the *it*-PP chain, which are shown in Fig. 2.4: propane (C_3H_8), isopentane (C_5H_{12}), and 2,4,6-trimethyl heptane ($C_{10}H_{22}$). We focus here our attention on the smallest branched fragment, i.e., isopentane (IP). This molecule has a variety of conformers, and we have performed calculations on those shown in Fig. 2.2. Conformer IP(2) is obtained from IP(1) by rotating the $C(CH_3)(CH_3)(H)$ group by 60° with respect to the $C(CH_3)(H)(H)$ group; IP(3) is obtained from IP(2) and IP(4) from IP(3) by rotating the same group in the same way by 120° and 60° , respectively. The conformer denoted (3, rotated methyl) is related to IP(3) by rotating the methyl group containing C_5 by 60° , and it is less stable than IP(3) by 3.07 kcal/mol. As shown in Table 2.1, there is satisfactory agreement between the optimized structures obtained here with the LSD approximation and those obtained with Hartree-Fock (HF) calculations [48]. Our DF calculations lead to C-H bonds that are slightly longer than the HF values, which is consistent with earlier findings [53] that the LSD approximation tends to overestimate the lengths of bonds between H and main group elements.

The most stable structure of isopentane is found to be (3), which is indeed that found as a structural unit in both $C_{10}H_{22}$ and *it*-PP. Conformer (2) lies 0.83 kcal/mol higher, followed by (4) and (1). The ordering is the same as that found in HF calculations [48], and the relative energies are in reasonable agreement. Fig. 2.3 shows Newman plots of structures (1-4) viewed down the axis from C_2 to C_3 (see Fig. 2.2 for the labelling of atoms) and makes plausible the relative stability of IP(3). IP(1) has two eclipsed CH_3 groups on opposite sides of the molecule, and these steric interactions result in the highest energy. IP(4) also has an eclipsed form, but each methyl group eclipses a single hydrogen atom. While both IP(2) and IP(3) are staggered, the former

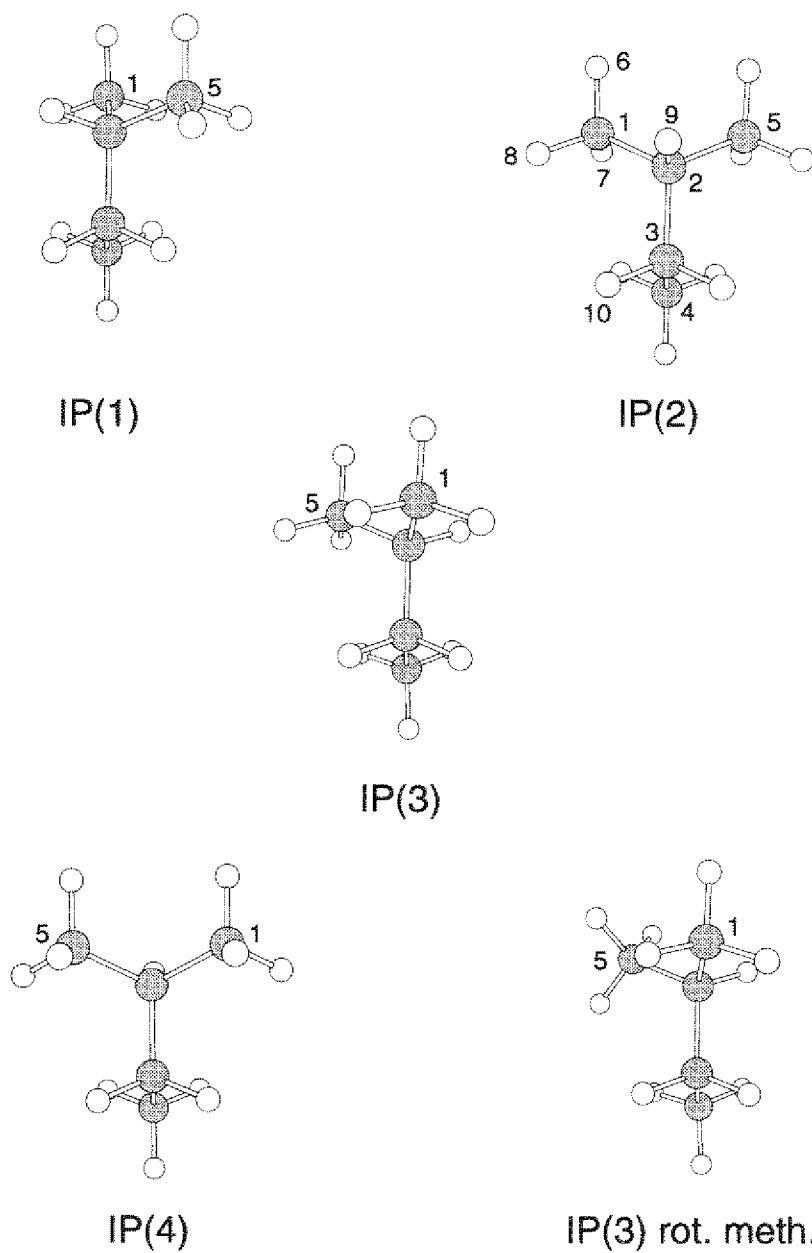


Figure 2.2: Optimized structures of five conformers of isopentane (IP, C_5H_{12}). Carbon atoms are gray, hydrogens are white.

2.3. STRUCTURE OF THE INFINITE CHAIN

Table 2.1: Optimized bond distances and angles for conformers (1-4) of isopentane (bond lengths d in Å, bond angles α in degrees). The relative energies ΔE are given in kcal/mol.

Param	(1) ^{a,b}	(2) ^{a,b}	(3) ^{a,b}	(4) ^{a,b}
ΔE	5.6, 5.19	0.9, 0.83	0.0, 0.0	3.0, 3.41
$d_{C_2C_1}$	1.544, 1.515	1.543, 1.519	1.543, 1.518	1.542, 1.519
$d_{H_6C_1}$	1.084, 1.107	1.084, 1.108	1.084, 1.109	1.084, 1.109
$d_{C_3C_2}$	1.572, 1.552	1.550, 1.532	1.547, 1.526	1.562, 1.542
$d_{H_9C_2}$	1.084, 1.113	1.086, 1.116	1.086, 1.118	1.085, 1.117
$d_{C_4C_3}$	1.543, 1.514	1.542, 1.516	1.542, 1.516	1.542, 1.516
$d_{H_{10}C_3}$	1.084, 1.112	1.085, 1.112	1.085, 1.112	1.084, 1.112
$\alpha_{H_7C_1H_6}$	107.9, 107.2	107.8, 107.1	108.1, 107.3	108.2, 107.4
$\alpha_{H_8C_1C_2}$	111.7, 112.5	110.9, 111.7	111.0, 111.8	110.8, 111.6
$\alpha_{C_3C_2C_1}$	114.8, 114.6	112.2, 112.4	110.0, 110.8	111.4, 112.0
$\alpha_{H_9C_2C_3}$	107.4, 107.1	107.5, 107.3	108.4, 108.0	107.7, 107.5

^aHartree-Fock calculations (Ref. [48]).

^bPresent work.

has a higher energy since the two front methyl groups are *gauche* to the back CH₃ group, while one of the front methyl groups in IP(3) is *gauche* and the other *trans*.

2.3 Structure of the Infinite Chain

Isotactic polypropylene occurs in three different crystalline structures: a monoclinic α -form, first reported by Natta and Corradini [50], a hexagonal β -form and a triclinic γ -form. In spite of structural differences, there is a considerable experimental evidence [50, 54, 55] that these forms comprise just two enantiomorphic chain conformations: right-handed and left-handed $(3/1)^1$ helices, with a periodicity of 6.50 Å (the helical structure of *it*-PP is shown in Fig. 2.5).

¹The notation (u/t) gives a conformation in which the period along the chain axis comprises u chemical units in t turns of helix.

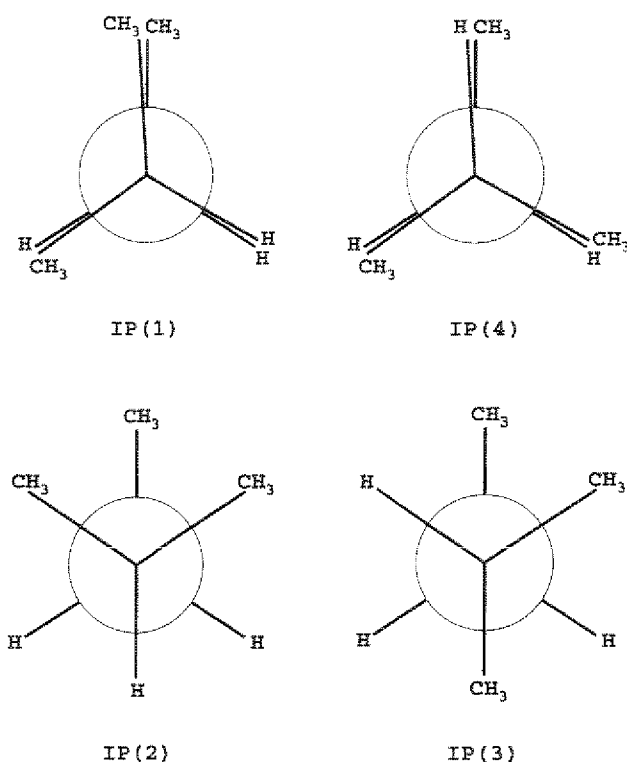


Figure 2.3: Structures of conformers (1–4) of isopentane shown as Newman projections, viewed down the axis from C₂ to C₃.

This suggests that intramolecular forces play a central role in the conformation of the chains in the crystalline structure. The helix is such that the backbone dihedral angles alternate between *trans* and *gauche*. Although the *gauche* torsions have the higher energy, the (3/1) helix structure leads to a lower energy than the all-*trans* planar zigzag structure, because the intramolecular steric interactions between the methyl side groups are minimized. To the best of our knowledge, a calculation performing a global optimization of *all* structural parameters of a single *it*-PP chain has not been performed previously. The parameters commonly adopted are $d_{CC} = 1.54 \text{ \AA}$, $d_{CH} = 1.09 \text{ \AA}$, and bond angles derived from tetrahedral values. An example is the recent exploratory study of single chains of isotactic and two syndiotactic forms of polypropylene, using Hartree-Fock methods [56] to determine the total energies and the energy eigenvalue spectra. An analysis of X-ray diffraction data [57], performed

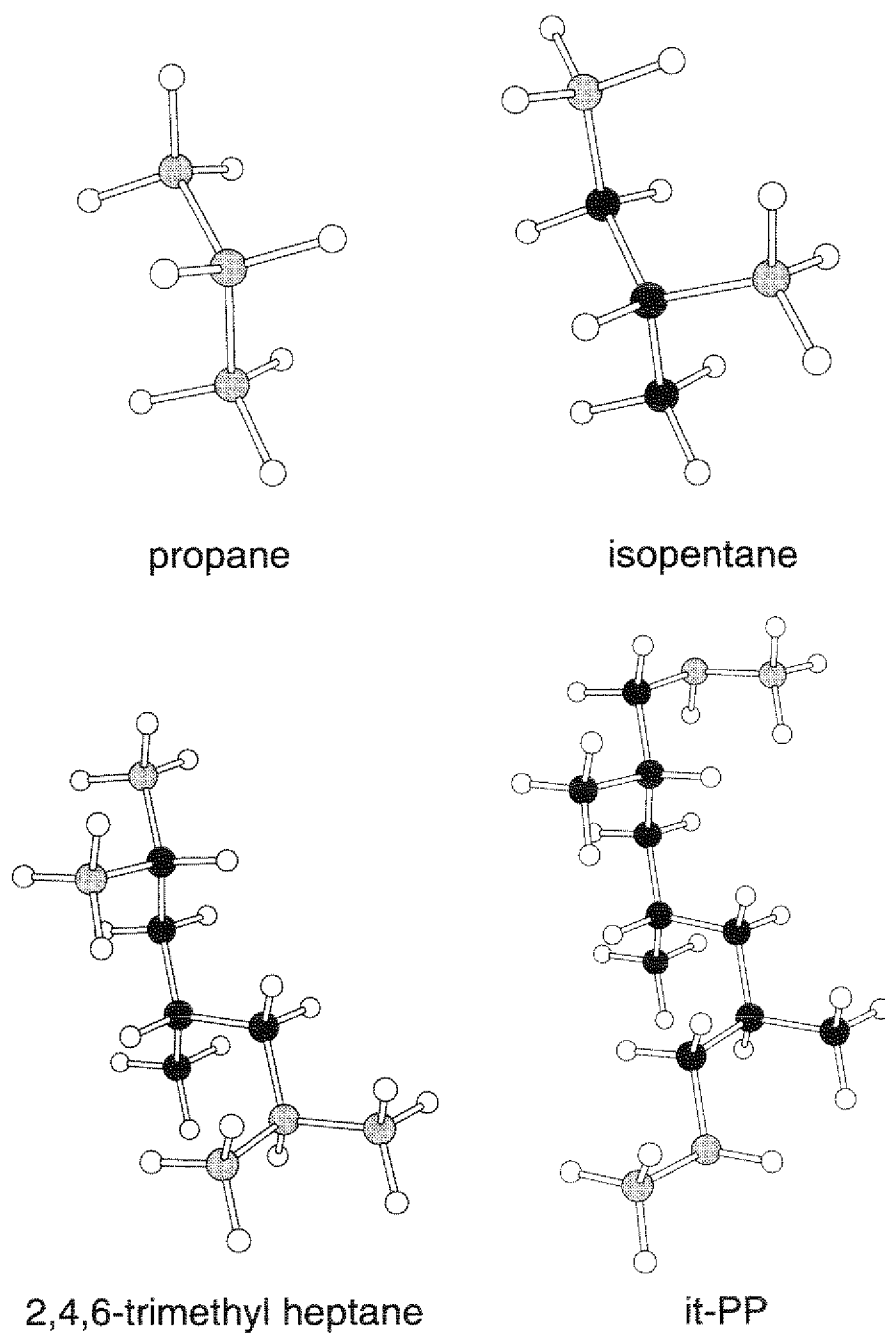


Figure 2.4: Structure of *it*-PP and of its submolecules. Carbon atoms in black indicate the structure of the previous molecule in the series.

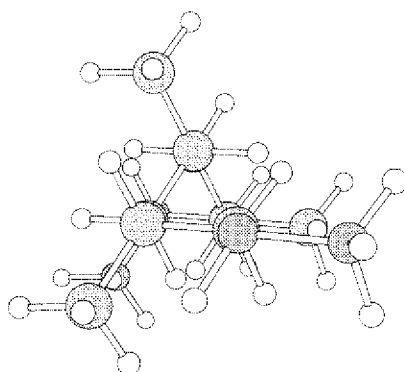


Figure 2.5: View of *it*-PP along the axis of the polymer chain. Carbon atoms are gray, hydrogens are white.

assuming a chain conformation with fixed bond lengths and three-fold helical symmetry, gave C-C-C chain angles of 116.9° and 112.4° , chain dihedral angles of 178° and 59° , and methyl-to-chain bond angles of 108.2° . These values are close to those obtained from partial structural optimization using total energy calculations [58, 59].

Our calculations also lead to a (3/1) helix, and the optimized structure has repeat distances along the chain of 6.36 Å and 6.49 Å using LSD and GGA-BP approximations, respectively, for the exchange-correlation energy. The LSD structure has then a slightly ($\sim 2\%$) shorter repeat distance than the GGA-BP structure along the chain, and the latter gives a value in excellent agreement with the measured repeat distance [50]. The other structural parameters, most of which are reported in Table 2.2 for the case where the repeat distance is constrained to have the experimental value, agree well with the “standard” distances and with the optimized angles reported above [57]. The small differences between the optimized LSD structure (repeat distance 6.36 Å) and the constrained values are most evident in the bond angles. If the bond angles in the optimized structures are replaced by the values in Table 2.2, for example, the repeat period of the chain increases by 0.07 Å. The corresponding changes to the bond lengths and dihedral angles extend the repeat distance by 0.03 Å and 0.04 Å, respectively.

2.3. STRUCTURE OF THE INFINITE CHAIN

Table 2.2: Structural parameters of (*it*-PP) and of its segments $C_{10}H_{22}$, C_5H_{12} , and C_3H_8 (bond lengths in Å, bond angles in degrees). See Fig. 2.6 for labelling of atoms.

Param	isotactic PP ^a	$C_{10}H_{22}$ ^b	C_5H_{12} ^b	C_5H_{12} ^a	C_3H_8 ^a
$r_{C_2C_3}$	1.517, 1.530	1.529	1.522	1.516, 1.524	
$r_{C_3H_{16}}$	1.112, 1.099	1.108	1.107	1.114, 1.104	1.106, 1.098
$r_{C_4C_9}$	1.509, 1.522	1.524	1.524	1.518, 1.525	1.518, 1.530
$r_{C_4H_{17}}$	1.112, 1.098	1.106	1.106	1.117, 1.106	1.107, 1.099
$r_{C_9H_{29}}$	1.107, 1.094	1.102	1.105	1.109, 1.099	1.106, 1.098
$\alpha_{C_4C_3H_{15}}$	108.2, 108.1	108.4	108.5	108.2, 108.3	110.7, 111.0
$\alpha_{C_4C_3H_{16}}$	107.8, 107.8	108.3	108.2	108.1, 108.5	110.7, 111.0
$\alpha_{C_3C_4C_9}$	109.7, 109.8	109.0	110.0	110.8, 110.4	110.9, 112.6
$\alpha_{C_9C_4H_{17}}$	108.0, 107.5	108.3	108.7	108.1, 108.2	110.0, 109.5
$\alpha_{C_4C_9H_{27}}$	112.4, 112.1	112.3	111.8	111.6, 111.3	112.6, 111.8
$\alpha_{C_4C_9H_{28}}$	111.4, 111.1	110.2	111.6	111.8, 110.5	110.7, 111.0
$\alpha_{C_4C_9H_{29}}$	110.5, 111.4	110.95	110.0	110.4, 111.5	110.7, 111.0
$\phi_{C_3C_4C_9H_{27}}$	-175.8, -173.5	-176.1	-178.7	-178.0, -178.1	-180.0, -180.0

^aDFT calculations (LSD and GGA-BP results, respectively).

^bAll-electron calculations (Ref. [52]), LSD approximation.

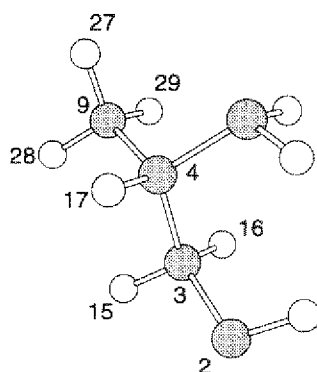


Figure 2.6: Section of isopentane (C_5H_{12}) with labelling of atoms used in Table 2.2. Carbon atoms are gray, hydrogens are white.

2.4 Structural Transferability

The qualitative relationship between the infinite chain of *it*-PP and its segments is quite evident in Fig. 2.4. An aim of this study, however, is to examine the structures in detail and to determine the extent to which the structural parameters – such as the bond lengths, and the bond and dihedral angles – are transferable.

In Table 2.2 we compare the structural features (bond lengths, and bond and dihedral angles) of sections of isotactic polypropylene, $C_{10}H_{22}$, C_5H_{12} and C_3H_8 , with those of the infinite *it*-PP chain. Fig. 2.6 shows the labelling of the atoms in a representative section of C_5H_{12} . The bond lengths in the different molecules generally agree well, with substitution of H by CH_3 leading to very small increases in the lengths of C-C bonds at the substituted atoms. The bond angles agree well unless H atoms or C groups are close to other groups containing carbon. This effect can be seen comparing the $C_4-C_3-H_{15}$ bond angle in the molecules, where the open environment of H_{15} in C_3H_8 leads to a larger $C_4-C_3-H_{15}$ bond angle than in the remaining molecules.

Propane is the smallest and the only unbranched molecule amongst those considered, and it is evidently too small to provide accurate estimates of the structural parameters of larger hydrocarbons. The additional C atoms in isopentane and the higher steric strain result in a structure that agrees better with those of $C_{10}H_{22}$ and *it*-PP. Therefore, we can conclude that, with the exception of propane, there is a remarkable transferability of the structural parameters between molecules with the same local environment.

Chapter 3

Polyethylene

The discovery of polyethylene (PE) provides an excellent lesson in the value of observing an unexpected experimental result. In 1931 two chemists, E. W. Fawcett and R. O. Gibson, carried out a research program to investigate the effect of pressure up to 3000 atmospheres on organic systems. Many systems were investigated but the results of the experiments did not show immediate promise. However, they noticed that in the experiment in which ethylene was used a small amount of a white waxy solid had been formed. On analysis this was found to be a polymer of ethylene. After this discovery, attempts were made to reproduce the polymer, and it was discovered eventually that a trace of oxygen was necessary to bring about the formation of polyethylene. In the original experiment this had been present accidentally, owing to a leak in the apparatus.

Polyethylene was soon seen to have many properties suitable for a wide range of applications, and it is today the largest tonnage plastics material in the world. The main attractive features of PE, in addition to its low price, are excellent electrical insulation properties, very good chemical resistance, good processability, flexibility, and transparency in thin films of certain grades. Such an important polymer has the simplest molecular structure of all polymers (see Fig. 3.1) and more has probably been written about it than any other polymer. Thanks to the experimental work, PE is nowadays synthesized with a high degree of purity, and is the best experimentally characterized polymer.

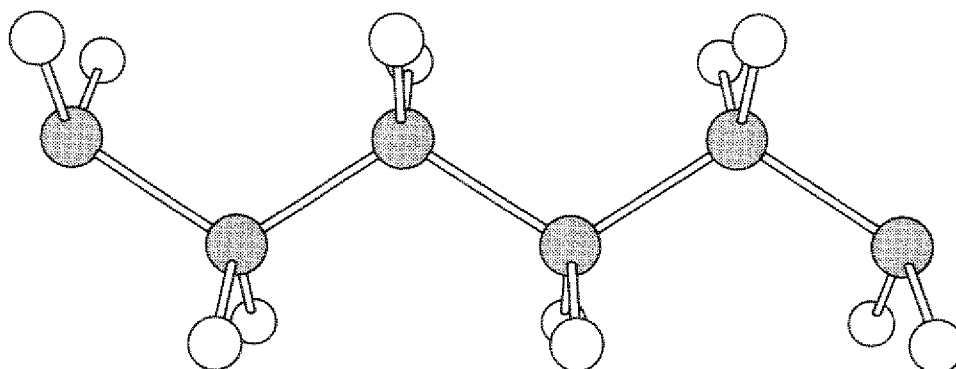


Figure 3.1: Section of a single chain of polyethylene. The white atoms are hydrogens and the gray are carbons.

On the theoretical side, because of its simple structure and the reliability of the measured data, PE has been used as a benchmark in the development of theoretical techniques for polymer research.

We have applied the DFT approach to the study of the geometrical and electronic structure of an isolated infinite chain of PE, and checked the reliability of our calculations comparing our results with experimental data and previous calculations. Then we have performed structure optimizations for the crystalline form of PE, applying the LSD approximation for the exchange-correlation energy and two gradient-corrected modifications: the GGA-BP and GGA-PBE. The goal is to examine the description of *inter*-chain interactions in organic polymers provided by these different functionals.

3.1 Calculation Details

The method applied for the study of PE is analogous to the one used for isotactic polypropylene (see Section 2.1) [49]. For both the isolated chain and the crystalline structure it assumes periodic boundary conditions in three dimensions. The initial structure of the isolated chain had the experimental lattice constant along the chain and large lattice constants perpendicular to it, and the optimum geometry was found by minimizing the forces on all atoms. The calculation was repeated for different chain lengths to minimize the energy

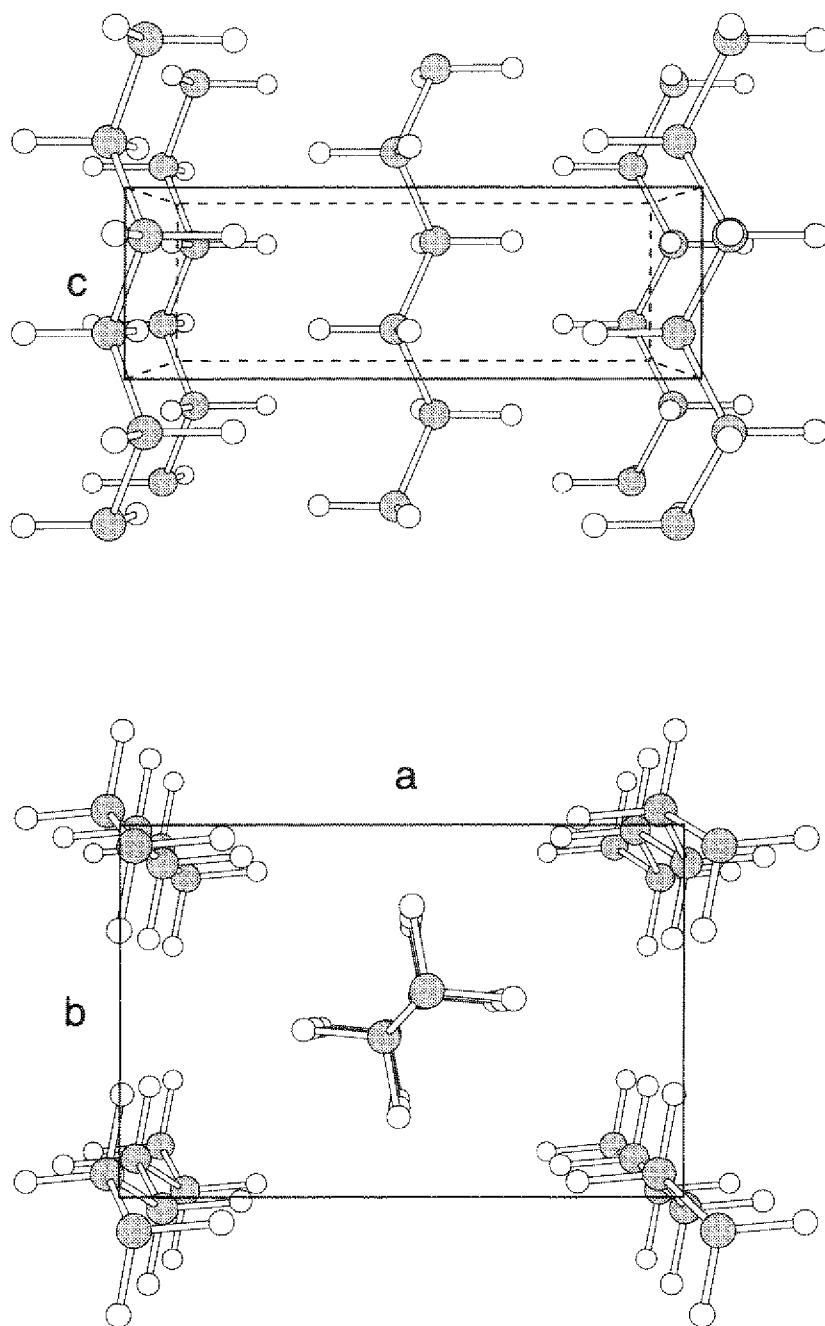


Figure 3.2: Views of the orthorhombic structure of polyethylene along the b-axis (top panel) and the c-axis (bottom panel). Carbon atoms are gray, hydrogens are white.

as a function of *all* atomic positions. An analogous procedure was used for crystalline PE, whose most stable structure is the experimentally determined orthorhombic structure shown in Fig. 3.2.

Detailed convergence tests of the plane-wave basis have shown that reliable energy differences can be obtained using a kinetic energy cutoff of 60 Ry. The integration in reciprocal space employed the special points technique [51], and the convergence of the total energy was tested with 3, 6, 12 and 24 such points. Six $\mathbf{k}$ -points give a well-converged total energy and were used to obtain the results presented here.

The calculations were first performed using the LSD approximation for the exchange-correlation energy, and then repeated using two different gradient-corrected modifications: the GGA-BP and the GGA-PBE (see Section 1.1.1).

3.2 Geometric and Electronic Chain Structure

The optimized structures calculated for a single chain with LSD and GGA (both BP and PBE) approximations are compared in Table 3.1 with the results of other calculations and with experimental values for crystalline PE. Gradient corrections lead to an increase of $\sim 1\%$ in the C–C bond length. In view of the experimental uncertainties, however, both approximations give reasonable agreement with the measured values and with the results of earlier calculations. Apart from a deviation of 4.5° in the H–C–H bond angle, the present LSD values are very close to the DFT(LSD) results of Miao *et al.* [67].

Recent advances in polymer electronic have focused attention on their excitation and band structures. Polyethylene was indeed the first organic polymer for which measured band structures were reported [68]. We show in Fig. 3.3 the energy bands calculated for a single chain using both the LSD and the GGA-BP approximations (the band structure calculated using the PBE approximation, not reported here, is very similar to that obtained with the BP functional). The overall form of the band structure in both approximations is the same as found in the measurement [68] and in previous band structure calculations [67, 69]. A more detailed comparison also shows similarities. The

3.2. GEOMETRIC AND ELECTRONIC CHAIN STRUCTURE

Table 3.1: Measured structural parameters of crystalline PE and calculated structures for a single chain. Bond lengths are in Å, angles in degrees. Values marked with an asterisk (*) were assumed, and not measured or calculated directly.

Method	r_{CC}	r_{CH}	α_{CCC}	α_{HCH}
X-rays [60]	1.53	-	112	-
X-rays [61]	1.534	1.09*	112.0	109.5*
X-rays [62]	1.533	1.07	111.9	107.0
X-rays [63]	1.527	1.091*	112	-
neutrons (4K) [64]	1.578	1.06, 1.10	107.7	109.0
neutrons (90K) [64]	1.574	1.07	108.1	110.0
Hartree-Fock [65]	1.536	1.083	112.7	106.8
Hartree-Fock [66]	1.541	1.087	112.5	107.2
DFT (PZ) [67]	1.515	1.10*	113.0	109.7
DFT (XO) [67]	1.534	1.10*	113.0	110.0
This work (LSD)	1.512	1.111	114.3	105.2
This work (BP)	1.536	1.111	113.8	105.6
This work (PBE)	1.523	1.110	113.0	105.8

width of the lower valence band in single chain LSD calculations (6.8 eV), for example, is in reasonable agreement with calculated (7.2 eV [69], 6.0 and 6.1 eV [67]) and measured values (7.2 eV [68]). The value obtained for the upper valence band (5.2 eV) is very close to previous DFT results (5.4 and 5.3 eV [67]), and underestimates the experimental value 6.7 eV [68]. Gradient corrections lead to a negligible change in the valence band widths and to an increase in the gap between valence and conduction bands from 5.7 to 6.0 eV. The experimental value for the band gap is (8.8 eV) [70]. In the literature concerning DFT calculations, the underestimation of the experimental band gap appears to be a typical feature of the Kohn-Sham approach. In fact, the identification of KS eigenvalues with excitation energies is not a rigorous procedure (see Section 1.1). Anyway, the qualitative description provided by

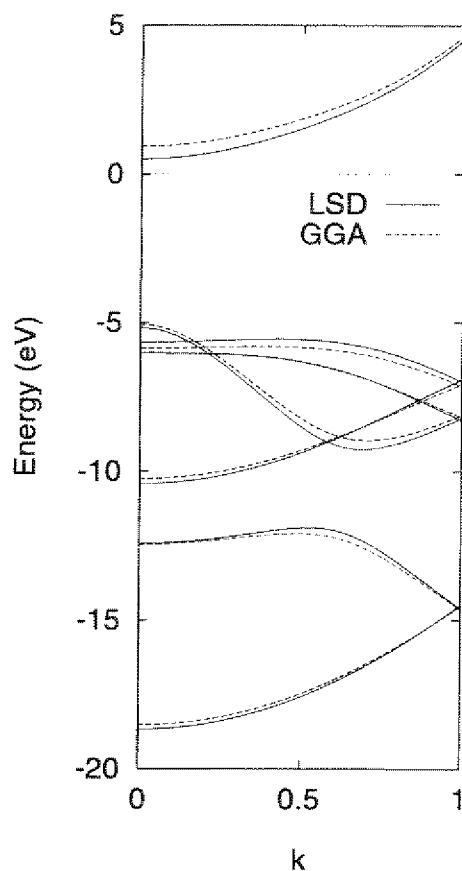


Figure 3.3: Band structure of a single chain of polyethylene calculated with LSD (full curves) and GGA (broken curves) approximations. Wave vectors $\mathbf{k}$ are in units of $2\pi/c$.

these calculations is valuable. Indeed, the large values for energy gap provided by both LSD and GGA approximations indicate that our calculation are able to reproduce the strong insulating character of this polymer.

3.3 Crystalline Structure

The optimization of the orthorhombic crystalline structure with the LSD and GGA approximations led to strikingly different results. The LSD calculations yielded a well-defined minimum in the binding energy curve (Fig. 3.4), and the length of the unit cell parameter parallel to the chain axis (referred to as c in Fig. 3.2) is in excellent agreement with all experimental data (Table 3.2).

3.3. CRYSTALLINE STRUCTURE

Table 3.2: Comparison of measured and calculated equilibrium lattice constants and interchain structural parameters in PE. The shortest distance between C atoms in different chains is $d_{C...C}$, and ϕ is the angle between the ac -plane and the plane of the C atoms in the chain. Distances are in Å, angles in degrees.

Method	a_0	b_0	c_0	ϕ	$d_{C...C}$
X-rays [61]	7.42	4.945	2.546	41.4	4.14
X-rays [62]	7.42	4.96	-	47.7	4.15
X-rays [63]	7.388	4.929	2.539	45	4.59
This work (LSD)	6.73	4.53	2.52	41.3	3.67
This work (PBE)	8.28	5.64	2.57	47.4	4.66

The structure of the chain is modified by the lower symmetry of the crystal, but the changes are small (r_{CC} is 0.007 Å less, there is a small splitting in the values of r_{CH} , and the bond angles are $\sim 0.4^\circ$ smaller). The *inter*-chain separations, however, are underestimated by $\sim 9\%$ (Table 3.2). The GGA-BP binding energy curve, by contrast, shows no minimum (Fig. 3.4), and there is a weak minimum in the case of GGA-PBE functional corresponding to an interchain distance $\sim 12\%$ larger than the measured value. Similar curves for the binding energies computed with the LSD and GGA-BP functionals were recently found in DFT studies of inter-molecular interactions in rare gas dimers [19] and benzene dimers [20]. For all these systems, the inter-molecular interactions are dominated by dispersion forces, which arise from correlated fluctuations of dipole moments on distant atoms. Therefore, these interactions have a *non-local* nature, which cannot be described by local functionals (e.g. LSD) or by semi-local GGA functionals. The need of new strategies for including this feature in approximate exchange-correlation energy functionals provides a stimulus for further development and several new functionals have been recently proposed [71, 72, 73]. Previous applications [74, 75] of the PBE functional to a wide range of systems, including also rare-gas diatomic molecules, confirm the improved description of weak inter-molecular interactions provided by this functional in the present work.

The differences between the descriptions of bonding provided by the LSD and GGA approximations are reflected in the electron density distribution. We have compared such distributions obtained with the two approximations for the experimental geometry plotting the surfaces with equal electron density at fixed values of the density. Although the density differences are small, the net effect of the GGA is to lower the electron density both between the C atoms and between the chains. There is also an overall transfer of electrons from the neighbourhood of the C nuclei to that of the H nuclei. These differences are small, but suffice to give the qualitatively different descriptions of the interchain interactions found here.

A similar study will be presented below, in Section 4.2.1, for the interchain interactions in a crystalline analog of bisphenol-A polycarbonate.

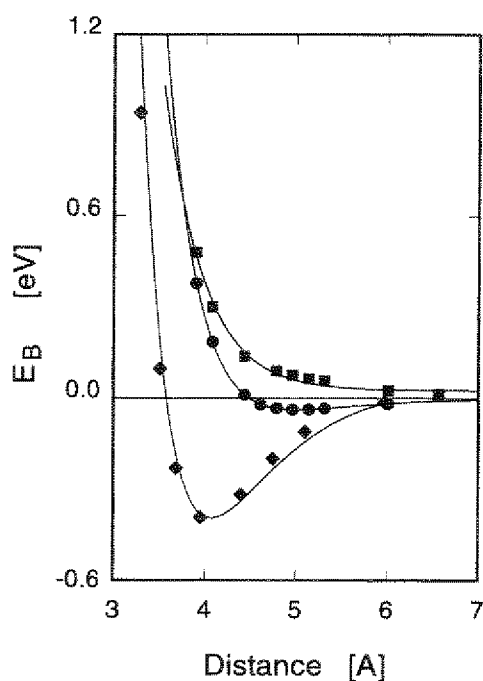


Figure 3.4: Binding energy of PE (in eV per unit cell) as a function of inter-chain separation (in Å) for LSD (diamonds), GGA-BP (squares) and GGA-PBE (circles) approximations.

Chapter 4

Polycarbonates

In the mid 1950s Farbenfabriken Bayer in Germany initiated a program in search of useful polymers containing phenylene rings in the main chain. The reaction between bisphenol-A (see Fig. 4.3) and carbonic acid derivatives produced a polymer, bisphenol-A polycarbonate (BPA-PC) of immediate promise. Independently at General Electric Company in the USA a research team also produced polycarbonates from bisphenol-A. Later, other kinds of polycarbonates were produced, but BPA-PC is still the most important. Because of its outstanding optical and mechanical properties (in particular high glass and melting temperature, and good impact resistance) it has uses as disparate as shatterproof windows, lightweight eyeglass lenses, compact disks, mobile telephones, and artificial kidneys. Many experimental and theoretical studies have investigated its microscopic structure and dynamics, and tried to establish a relationship between them and the good macroscopic properties of this material. One of the most active areas of these studies has been the attempt to understand the phenylene ring rotational motions and how these motions affect the mechanical properties of BPA-PC, in particular its good impact resistance.

Scheme 4.1 shows the strategy used for the present study of BPA-PC. The first step is reminiscent of the approach described in Chapter 2 for the study of *isotactic* polypropylene: the study of isolated fragments in the chain, presented in Section 4.1, allows us to isolate the effects of their mutual interactions within

the molecule. The investigation of crystal polycarbonate systems (Section 4.2 and 4.3), together with that of their isolated molecular units, point out the influence of the inter-molecular interaction in the condensed phase. The noise due to the disorder in the inter-molecular arrangement is introduced with the study of the amorphous phase (Section 4.4), which is the typical phase of the commercial polycarbonates. The DFT approach will be applied to the study of structural, dynamical, and vibrational properties of the chain segments and of the crystals, and will give an insight into the influence of the structure upon dynamical processes on the atomistic scale. All these DFT results are then applied to parametrize a classical force-field that is used for Monte Carlo simulations of an amorphous polycarbonate system.

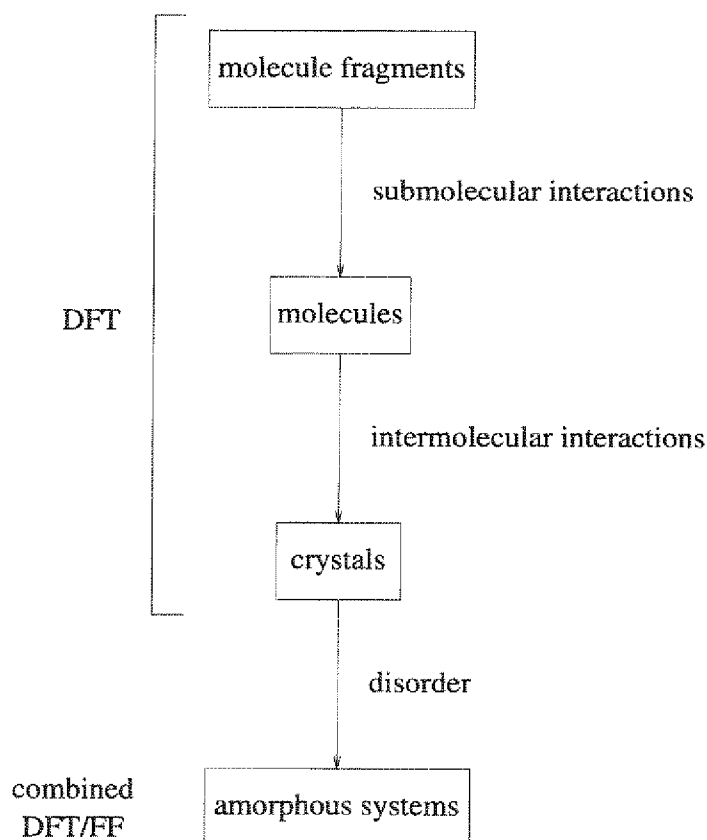


Figure 4.1: Schematic representation of the strategy for addressing the study of BPA-PC in this chapter.

4.1 DFT Study of Chain Fragments

In order to identify the origin of the structural details of BPA-PC, we have performed calculations of isolated molecules representing fragments of increasing size of the infinite chain of BPA-PC. In Fig. 4.2 we show (a-c) isomers of carbonic acid, (d) benzene, (e) phenol, and (f, g) isomers of monophenyl carbonate. Fig. 4.3 shows (a) 2,2-bis(4-hydroxyphenyl)propane, BPA, and (b) 4,4'-isopropylidenediphenylbis(phenylcarbonate), DPBC. Chart 4.4 shows the labelling of the atoms used throughout this chapter. For each molecule we have optimized the geometrical structures and computed the vibration spectra. We report all the data, together with the comparison with experiment and previous calculations, in our work of Ref. [76]. There, the agreement of our results with the measured structures and vibrations is shown, and we conclude that these calculations confirm the reliability of the DFT results in the description of such systems. The data are reported here only partially, and we focus our attention on the most significant trends identified in this large set of data.

A similar analysis could be carried out on the experimental atomic positions. However, presently available data are generally less homogeneous than the results of a series of well converged calculations performed with the same method. Moreover, additional points of detail can be investigated with relative ease performing computations on modified or artificial structures. This is usually not the case in an experimental study.

4.1.1 Computational details

The structures have been optimized using the Car-Parrinello method [77] and a simulated annealing strategy (see Section 1.2.2). The computations were started using the experimentally determined atomic coordinates and performed without constraint (on symmetry or otherwise) until the magnitude of the *maximum* force on any atom was less than 5×10^{-4} a.u. and the *average* force on the atoms was an order of magnitude less. We emphasize that *all* atomic coordinates were allowed to relax. We use a plane-wave basis, and

CHAPTER 4. POLYCARBONATES

tests showed that reliable energy differences can be obtained for these systems using a kinetic energy cutoff of 70 Ry. The expansion of the orbitals assumes a single point ($\mathbf{k}=0$) in the Brillouin zone. The calculations are performed using periodic boundary conditions, and we adopt a simple cubic unit

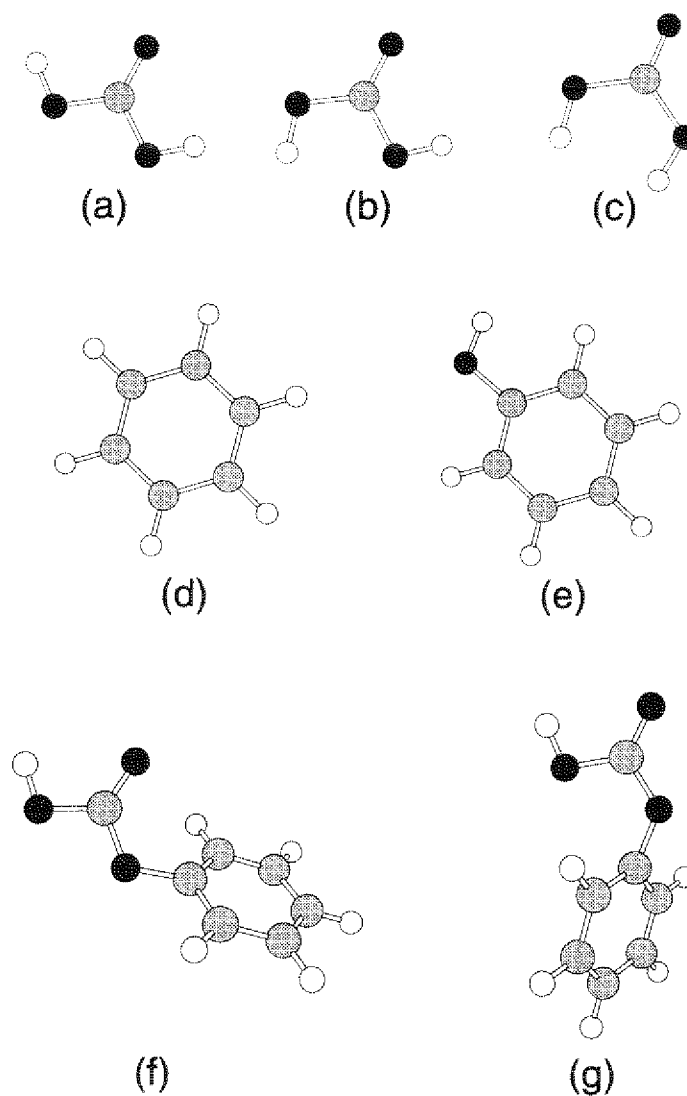
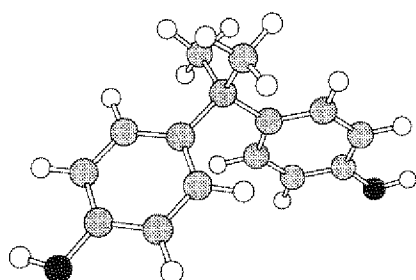


Figure 4.2: Molecular structures of fragments of BPA-PC chains. (a) *trans-trans*, (b) *cis-trans*, and (c) *cis-cis* isomers of carbonic acid, (d) benzene, (e) phenol, (f) *trans-trans* and (g) *trans-cis* isomers of monophenyl carbonate. Carbon atoms are gray, oxygens black, and hydrogens white.

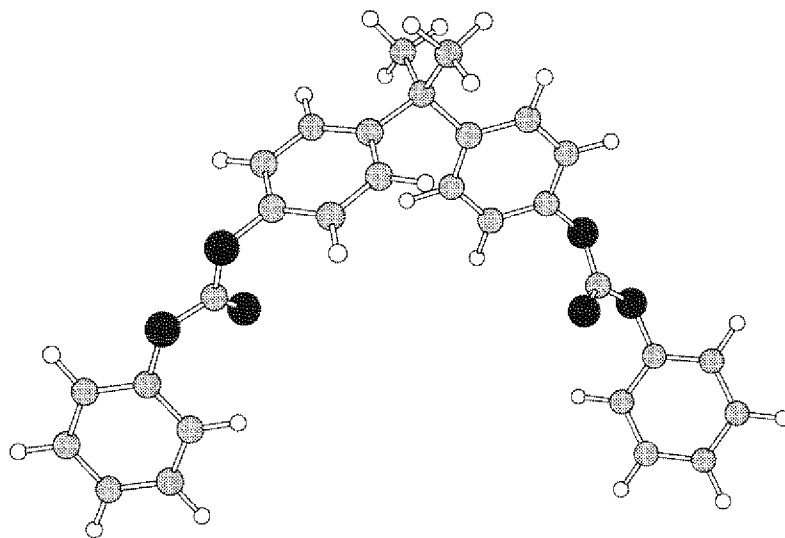
4.1. DFT STUDY OF CHAIN FRAGMENTS

cell with lattice constant of 40 a.u. for the isolated molecules. The GGA-PBE approximation for the exchange-correlation energy is applied for these calculations.

The vibration frequencies and eigenvectors of all these molecules are calculated for the optimized geometries. The dynamical matrix $\mathbf{D}$ is evaluated



(a) BPA



(b) DPBC

Figure 4.3: Molecular structures of fragments of BPA-PC chains. (a) bisphenol-A (BPA) and (b) DPBC.

by a finite difference approximation with atomic displacements δ of the order of 0.005 Å. The computed frequencies change by at most a few cm^{-1} upon increasing or decreasing δ by a factor of three, so that anharmonic contributions are very small.

The intensity of the infrared fundamentals in absorption for a mode with frequency ν_j is estimated by associating an electrostatic charge q_I with each atom I and evaluating

$$\alpha(\nu_j) = \frac{8\pi^3 N \nu_j}{3ch} \left| \sum_I q_I \delta \mathbf{r}_I^{(j)} \right|^2, \quad (4.1)$$

where $\delta \mathbf{r}_I^{(j)}$ is the displacement of atom I for the j -th vibrational eigenvector, and N is the molecular density. The atomic charges are computed by a least squares fit to the electrostatic potential around each molecule [78]. Equation (4.1) is an approximation to the quantum mechanical expression [79], but should be accurate for the weakly polar, closed shell molecules considered here.

4.1.2 Carbonic Acid

We have optimized the structure of the three isomers of carbonic acid (H_2CO_3) reported in Fig. 4.2 (a-c), which represent well-defined minima in the energy surface. The energy differences between the three structures show that the *trans-trans* conformer is the most stable, this stability being due to the attractive interaction between O19 and the hydrogen atoms. The *trans-trans* conformation is conserved in most cases that will be considered below, where the $\text{O}-\text{C}(=\text{O})-\text{O}$ part of this molecule, called *carbonate group*, appears as a functional group of larger molecules. The carbonate group is found in a different conformation only in the cyclic dimer carbonate, where the *cis-trans* geometry is forced by the strain due to ring closing (see Section 4.3). The energy of the *cis-trans* conformation of carbonic acid is higher by only 1.5 kcal/mol, while the high energy of the *cis-cis* isomer ($\Delta E=10.0$ kcal/mol) with respect to the *trans-trans* arises from the short separation of the two terminal hydrogens (equal to 2.02 Å, i.e., considerably less than the sum of

their Van der Waals radii).

The most prominent features in the vibrational spectrum of the *trans-trans* isomer of H_2CO_3 are the stretching of the hydroxyl (OH) groups (3533 cm^{-1}) and the stretching of carbonyl (C=O) group (1787 cm^{-1}). The out-of-plane mode with the highest frequency (759 cm^{-1}) involves oscillations of C with respect to the plane of the oxygen atoms. The different conformations of the hydroxyl groups in the *cis-trans* and *cis-cis* isomers is reflected in slight shifts ($\sim 10\text{ cm}^{-1}$) in the frequencies of the first two modes, while the out-of-plane motion of carbon is almost unaffected.

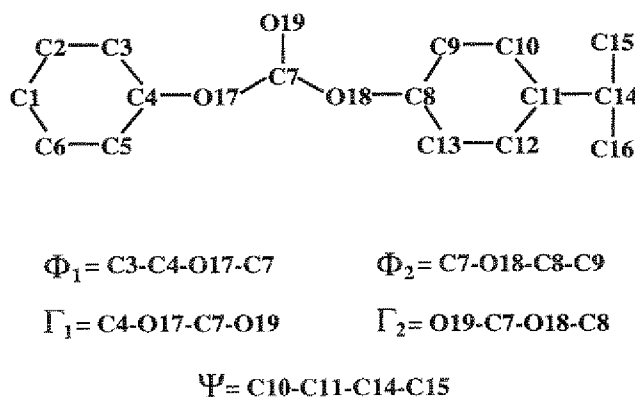


Figure 4.4: Schematic structure of the repeat unit of BPA-PC, with the atomic numbering and the torsion angles of interest. In the text and in the tables, the hydrogen atoms take the same number as the adjacent C or O atom.

4.1.3 Benzene and Phenol

Benzene is one of the best studied hydrocarbons and has served as a benchmark for both methods of calculation and measurements on other systems [80]. Table 4.1 reports the structural parameters obtained by our calculations, in comparison with experiment [81], as an example of the reliability of the DFT results. The table compares also the present results, obtained using the recently developed PBE functional, with previous DFT calculations [20], which applied the LSD approximation and a commonly used GGA functional, the so-

Table 4.1: Bond lengths ($\text{\AA}$) and angles (degrees) in the benzene molecule.

Atoms	PBE (this work)	Exp.[81]	LSD[20]	BLYP[20]
C-C	1.397	1.399	1.385	1.400
C-H	1.093	1.101	1.092	1.086

called BLYP functional [82]. The results obtained with the three functionals are very close.

Benzene rings are studied here because they are the molecules obtained if we isolate the so-called *phenylene* or *aromatic* groups in the chain. As it will be shown in the following sections, the molecular environment does not affect the stiff structure of these rings, which is very close to that of the isolated molecule for all systems considered below.

The simplicity and high symmetry of benzene allow a detailed comparison of computed vibrational frequencies with experimental data. It is important to note that the peaks in measured spectra are affected by anharmonic effects and do not correspond exactly to the harmonic frequencies. In benzene, for example, the observed peaks in the vibrational spectrum can differ by up to 120 cm^{-1} from the corresponding harmonic frequencies [80]. As shown in Ref. [76], our computations describe the (corrected) harmonic frequencies in benzene well. Apart from the lowest energy modes, for which the finite difference scheme of computation is less reliable, the calculated and experimental values differ by at most 3%, and this level of agreement shows that modern DFT schemes lead to vibration frequencies that are within a few percent of experiment.

If an hydrogen atom in the benzene ring is replaced by a OH group, the phenol molecule is obtained. This change in the chemical composition has important structural effects that are present in the molecules we will consider below. In fact, the structure is still planar, but the C3-C4-O17 angle, adjacent to the OH group, is larger than the C5-C4-O17 angle. We attribute this difference partly to an intrinsic asymmetry of O17, which has the hydrogen atom on one side and two lone pairs on the other, and partly to the short

distance between OH and the closest hydrogen (H3) in the ring.

About the accuracy of the calculated vibration frequencies

As it is illustrated in our article of Ref. [76], the calculated harmonic frequencies can differ by a few percent from the experimental frequencies, the absolute error in the highest energy modes being $\sim 50 \text{ cm}^{-1}$. However, most errors introduced by the PBE approximation should be systematic and lead to frequency *differences* that are much more reliable than the frequencies themselves.

This expectation is confirmed by the comparison of the frequency for three representative modes (C-H and C-C stretch, C out-of-plane) in benzene and phenol (Table 4.2). Since anharmonic corrections have not been estimated for phenol, we compare the computed harmonic frequencies with the *observed* ones for both molecules. The *shift* in the individual frequencies from benzene to phenol is reproduced very well, and frequency *differences* of the order of 10 cm^{-1} can be identified reliably. Moreover, properties related to low moments of the vibrational density of states, such as the zero point energy (zpe), should be relatively insensitive to the numerical uncertainties and given accurately. This is confirmed by the comparison of the computed and measured zpe for benzene and phenol, which differ by at most 1 %.

Table 4.2: Comparison of computed (first line) and measured (second line, in parentheses) frequencies (cm^{-1}) for: (1) C-H and (2) C-C stretching, and (3) C out-of-plane modes in benzene and phenol.

Mode	Benzene	Phenol	Δ
1	3127.5	3133.6	6.1
	(3073.9)	(3087)	16.1
2	1587.8	1596.1	8.3
	(1601.0)	(1610)	9
3	997.5	974.6	-22.9
	(993.1)	(973)	-20.1

4.1.4 Monophenyl Carbonate and BPA

For the two isomers of monophenyl carbonate shown in Fig. 4.2 (f,g) we have optimized the structures and found that the *trans-trans* isomer is more stable (by 3.36 kcal/mol) than the *cis-trans*. Comparison of this energy difference with that found for the carbonic acid shows that the difference increases by only 2 kcal/mol if an hydrogen in the carbonic acid molecule is replaced by a phenylene ring.

Some structural parameters of both isomers of monophenyl carbonate present important deviations with respect to the structures of its isolated fragments. The most interesting feature is the asymmetry in the O17-C4 (1.413 Å) and O17-C7 (1.359 Å) bond lengths¹. As noted in Ref. [83] and discussed below in Section 4.1.5 for the DPBC molecule, this asymmetry reflects the enhanced π -bonding contribution to the O17-C7 bond. The CO₃ unit is close to planar as a result, and this feature should persist in the oligomers of BPA-PC discussed below. As in phenol, the C3-C4-O17 and C5-C4-O17 angles deviate from the ideal value (120°) by $\sim 4^\circ$ in both the *trans-trans* and *cis-trans* isomers. Moreover, the O17 atom is slightly (0.1 Å) out of the plane of the phenylene ring. This effect is probably due to the short range repulsion between H3 and the carbonyl oxygen (O19), which also forces the C3-C4-O17-C7 ($= \Phi_1$) torsional angle to deviate significantly from planar ($\Phi_1 = 48^\circ$ in both isomers).

The calculation of the vibrational frequencies shows that the OH stretching frequency is the same in the *trans-trans* and *cis-trans* forms, and remarkably close to the frequency observed in the smallest fragment, H₂CO₃, while the modes localized on the carbonyl (C=O) group are more sensitive to the local bonding environment. The highest C-H stretching frequency involves the C3-H3 bond, with the other C-H stretching modes being at least 20 cm⁻¹ lower in energy. This feature is found in all molecules with a short O19-H3 distance and appears to be a consequence of the interaction between these two atoms.

The BPA molecule represents, in the BPA-PC chains, the vertex joining

¹The distances refer to the *trans-trans* isomer. The *cis-trans* isomer displays a very similar asymmetry.

successive monomers. The optimized structure obtained by our calculations has C_2 symmetry, with the methyl groups (CH_3) in the eclipsed geometry. The orientation of the two phenylene rings is determined by the short range repulsion between the phenylene and methyl hydrogen atoms (minimum H-H distance of 2.19 Å). As a result, the two phenylene groups are nearly perpendicular. The relative positioning of these two phenylene rings is one of the structural features that are affected by the π -flip of the phenylene ring in the BPA-PC chains, which will be studied in detail below.

4.1.5 DPBC

The DPBC molecule (Fig. 4.3) is the largest chain fragment we have studied. It extends over almost two repeat units of the infinite chain of BPA-PC, and it has been synthesized in two different crystalline phases that are analogs of crystalline BPA-PC. The analysis of these crystal phases will be presented in Section 4.2, while its amorphous phase is addressed in Section 4.4.2. A detailed study of this structural unit is a prerequisite for understanding the structural and dynamical properties of the condensed phases. For this reason, we have performed a careful investigation of its structural and vibrational properties. Moreover, we have extended our analysis to the energy barriers associated to the rotation of all functional groups in the molecule, and electrostatic properties have also been considered.

I. Geometrical structure

We have optimized the structure of this molecule, which has C_2 symmetry in the ground state, and report the most significant parameters in Table 4.3. The comparison between these data and those relative to the other segments shows that the bonding within the phenylene, carbonate and isopropylidene ($\text{CH}_3\text{--C--CH}_3$) groups is not influenced strongly by intra-molecular interactions. For example, the phenylene rings have bond angles and lengths that are very close to those of benzene, with minor fluctuations around the average C–C and C–H distances (1.396 Å and 1.092 Å, respectively), and the isopropylidene group

Table 4.3: Selected interatomic distances (Å) and angles (degrees) in DPBC. See Chart 4.4 for numbering of atoms. Hydrogen atoms take the same number as the adjacent C atom.

Atoms	
C4-O17	1.411
O17-C7	1.365
H3...O19	2.494
H9...O19	3.000
C3-C4-O17	123.2
C5-C4-O17	115.1
C4-O17-C7	119.2
O17-C7-O19	128.0
C3-C4-O17-C7 (Φ_1)	44.8
C9-C8-O18-C7 (Φ_2)	69.3
C4-O17-C7-O19 (Γ_1)	0.0
C8-O18-C7-O19 (Γ_2)	0.5
C10-C11-C14-C15 (Ψ)	8.4

at the molecular vertex has bond distances and angles close to the ideal sp^3 bonds in hydrocarbons.

The region of the molecule connecting phenylene rings and carbonate groups, and in particular the relative orientation of these two groups, are of central importance. The first thing we notice is that, as in the case of monophenyl carbonate, the C4–O17 bond in the carbonate group is longer than the C7–O17 bond, although they might appear at first sight to be equivalent. Projection of the Kohn-Sham orbitals onto atomic states (see Paragraph IV) and the computation of the Mayer bond order [84] show that both bonds have a significant π character, and that this is stronger in C7–O17. This difference is reflected in the force constants associated with the $\Phi_{1,2}$ and $\Gamma_{1,2}$ torsional angles: the delocalization of the π -electrons, which is an important contribution to stability [83, 85], favours the planar configuration for both

angles ($\Phi_{1,2} = \Gamma_{1,2} = 0, 180^\circ$), but rotations around the O17–C4 bond (associated with the $\Phi_{1,2}$ angles) require significantly less energy than around the O17–C7 (associated with the $\Gamma_{1,2}$ angles), as it will be illustrated in Paragraph III.

Second, also for this molecule the angles C3–C4–O17 and C5–C4–O17 deviate by $\sim \pm 5^\circ$ from ideal 120° . This asymmetry is significant when the C–C–O–R torsional angle Φ is close to planar and vanishes when $\Phi \sim 90^\circ$, independent of the residue R. The underlying C3–C4–C5 angle is close to 120° in all cases. This feature, already discussed above for phenol and monophenyl carbonate, is due to an intrinsic asymmetry in the electron distribution around the O atom, and to a relatively strong interaction of H3 with the residue R when their distance is below $\sim 3 \text{ \AA}$.

The same H3–R interaction causes a small ($\sim 0.1 \text{ \AA}$) deviation of the O17 atom from the plane of the adjacent phenylene ring, observed also for the monophenyl carbonate molecule.

II. Vibrational properties

We have calculated the vibrational eigenvalues and eigenvectors for the DPBC molecule, and the results are reported in Fig 4.5. We show the vibrational density of the infrared active states and – in the inset – the density of states of all modes.

The infrared active modes involve mainly vibrations of the carbonate group, the most ionic part of the molecule. The peaks at 725 cm^{-1} and 1139 cm^{-1} are out-of-plane and in-plane bending modes, respectively, of this group. The bending mode for the C8–O18–C7 angle is at 1580 cm^{-1} , and the stretching of the carbonyl group is at 1774 cm^{-1} . The peak at 3135 cm^{-1} arises from stretching modes of the (aromatic C)–H atoms. The overall infrared spectrum determined by our calculation is in good agreement with the measured spectrum [86]. On the basis of symmetry we find that Raman activity is allowed for modes localized on the carbonate group, the isopropylidene unit (1217 and 3078 cm^{-1}), and on the phenylene groups (1471 and 1586 cm^{-1}).

We now turn to the total vibration spectrum, using the vibration spec-

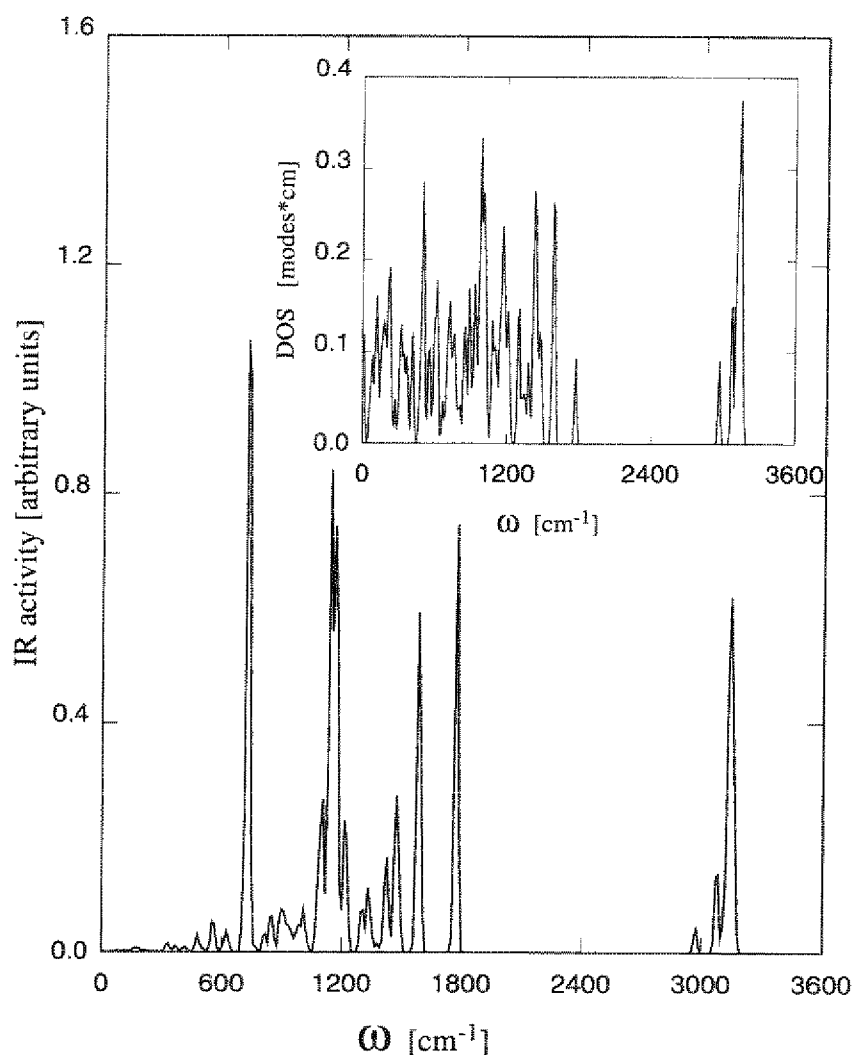


Figure 4.5: The infrared active vibrational spectrum of the isolated DPBC molecule. The inset shows the total vibrational density of states. Each mode is represented by a Gaussian distribution of width 12 cm^{-1} .

tra of the smaller fragments as a basis for interpretation. The modes are discussed in the order of decreasing frequency. The highest frequencies arise from stretching modes of the (aromatic C)-H bonds and range from 3113 and 3166 cm^{-1} , i.e., with a broader spread and higher frequencies than in the isolated benzene ring (3097-3128 cm^{-1}). Part of this shift arises from the change in the masses, which decreases the frequency of H more in the small fragment

(benzene) than in the DPBC unit, and the broadening probably originates from intra-molecular interactions. The highest frequency is associated with the hydrogen closest to O19. A similar shift is present in the spectrum of the monophenyl carbonate (Fig. 4.2 (f)), confirming that it is due to the steric repulsion between the H atom and the carbonyl O19 atom. The stretching modes of the C–H bonds belonging to the two methyl groups occur in the $[2970\text{--}3070]$ cm^{-1} range, that is slightly higher but not significantly broader than that of the BPA fragment ($2969\text{--}3063$ cm^{-1}), suggesting that these modes are determined by the local interactions at the molecular vertex. The carbonyl C=O stretch (at 1775 cm^{-1}) is also only slightly higher than in the isolated molecule of carbonic acid. The wide band from $1470\text{--}1600$ cm^{-1} corresponds to the stretching modes of the carbon backbone. Carbon stretching is mixed with C–H bond bending at lower frequencies, and the stretching of the carbon-tetrahedral oxygen occurs at 1210 cm^{-1} . There are bending modes between $1010\text{--}1200$ cm^{-1} that preserve the planarity of the phenylene and carbonate groups. The out-of-plane vibrations of these groups follow between 400 and 1000 cm^{-1} . About 30 low-frequency modes can not be identified reliably by our calculation, but this frequency range covers the rotations and librations of the constituent groups.

III. Rotation energy barriers

The energy barriers for the rotation of the phenylene, carbonyl and methyl groups have been calculated as follows: First, we define a reaction coordinate ξ (usually an angle) that transforms the initial structure into the rotated one. For selected values of ξ we then optimize *all* atomic positions, subject only to the constraint $\xi=\text{constant}$. The potential energy of the relaxed structure provides information about the rotational barriers, while the structural changes occurring as the barrier is crossed allow us to identify the interactions determining it. The differences between barriers and relaxations found in the isolated molecules and in the condensed phases allow us to distinguish *intra*- from *inter*-molecular contributions.

Table 4.4: Rotational energy barriers (in kcal/mol) for the functional groups of the isolated DPBC molecule. (a), (b) refer to rotations about the C7-O18 and O17-O18 axes, respectively.

Group	Energy barrier
Methyl	2.86
Int. Ring	1.98
Ext. Ring	1.20
Carbonyl (a)	8.7
Carbonyl (b)	18.5

The considerations about the structure of the DPBC molecule (see Paragraph I of this section) help understand which forces contribute to the energy barriers for the rotation of either functional group. Rotations of the phenylene rings involve only a torsional restoring force and will be facile, with the exception of a narrow range of angles corresponding to close contact between O and H atoms. Rotations of the carbonyl group will be more difficult because of the enhanced π -character of the O17-C7 and O18-C7 bonds. The rotations of the methyl groups should involve barriers comparable to those observed in saturated hydrocarbons. Since steric interactions between the H in the rings and either O (carbonyl) or H (methyl) are likely to contribute most to the energy barriers, the simultaneous rotation of two groups – avoiding the shortest H-H or O-H distances – should lead to energetically most favorable path.

These predictions are confirmed by our calculations of rotational barriers, which are reported in Table 4.4. Analysis of the relaxed atomic positions for fixed values of the dihedral angles confirm that all barriers are lowered by the simultaneous relaxation of the neighbouring groups. The phenylene rings and the carbonate group are nearly planar along the entire path in all cases. The large difference between the barriers of the π -flip of the rings in the isolated molecule and the experimental estimate in the crystal phases (reported in Section 4.2.4) shows that the rotational rigidity of the latter arises from intermolecular interactions.

IV. Other properties

Fig. 4.6 shows the energetic distribution of the KS eigenvalues for the isolated DPBC molecule. The eigenvalues with higher energy contribute to the π bonds, those with the lowest energies to the σ bonds, and the intermediate band corresponds to the sp^2 and sp^3 bonds.

The charge distribution in the DPBC molecule has been analyzed in terms of both Mulliken populations and ESP charges, the atomic charges obtained by fitting the electrostatic potential outside the molecule [87]. The electrostatic interactions are localized at the carbonyl group and well screened by the

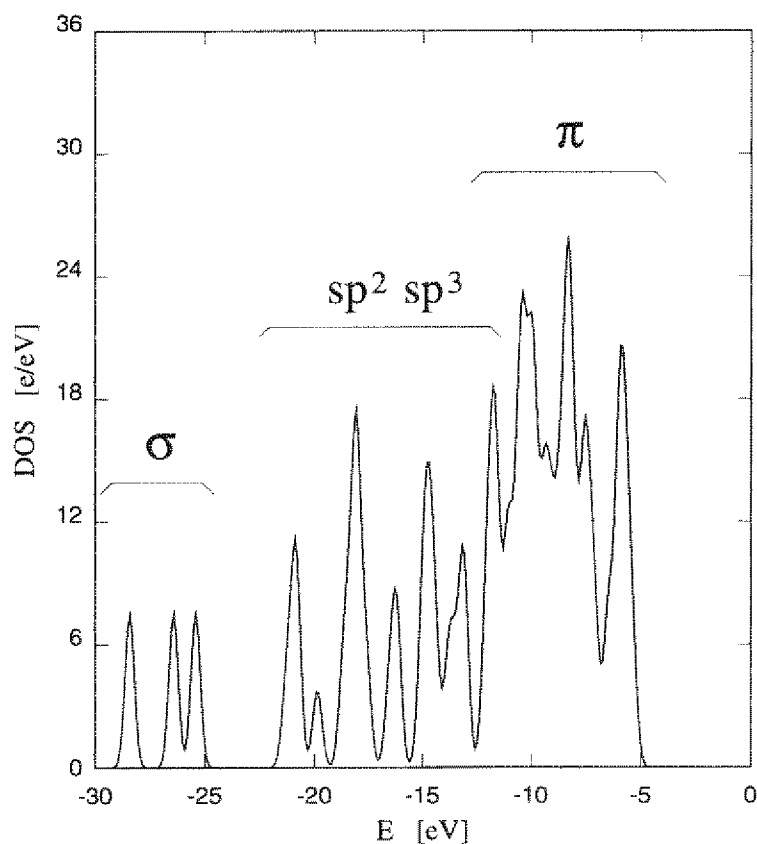


Figure 4.6: The eigenvalues of the Kohn-Sham equations for the isolated DPBC molecule. Each eigenvalue is represented by a Gaussian distribution of width 0.3 eV. The contributions from different bands are also shown.

neighbouring atoms, and the dipole moment of the molecule (1.0 D) points towards the molecular vertex. The effective charges change little if groups are rotated around “easy” axes, and they should provide valuable input for modelling the force field in the molecule (see Section 4.4).

4.2 DFT Study of a Crystalline Analog

The most precise structural information available on molecules closely related to BPA-PC has come from x-ray diffraction studies. Early data on oriented chains were given by Prietzschk [88], and there are two crystalline forms of DPBC molecule, containing 118 and 236 atoms, respectively, in the unit cells, which are analogs of the crystalline polymer. The first form was synthesized by Perez and Scaringe [89], and was designed the “immobile” form because of the low rate of π -flips of the phenylene rings [90]. The same motion is facile in a second crystalline modification, which is referred to as “mobile” form [91]. We have performed DFT calculations for both the “immobile” and “mobile” form in a way analogous to that described for the chain fragments of BPA-PC. The availability of experimental data allows us to check the reliability of the results provided by our calculations. The comparison of structural parameters, energy barriers, and vibrational properties obtained for the DPBC molecule in the isolated (see Section 4.1.5) and crystalline configuration gives insight into the influence of *intra*- and *inter*-molecular interactions upon all these properties. In particular, the analysis of the π -flips of the phenylene rings, which is believed to be related to the high impact resistance of the polymer, provides new information. Finally, in line with the study of crystalline polyethylene reported above in Section 3.3, we have tested, also for the present system, the reliability of three different approximations of the exchange-correlation energy in the description of the equilibrium volume and cohesive energy for this molecular crystal. It is important to point out that, thanks to the present-day powerful computers and to the development of efficient programming techniques, it is now possible to perform calculations of such systems, containing several hundred atoms, optimizing *all* atomic posi-

tions with a method free of adjustable parameters. The numbering of atoms used throughout this section follows the numbering shown in Chart 4.4.

4.2.1 Volume Optimization

The optimization of the *inter*-molecular structure for the “immobile” form has been performed finding the optimum structure at different volumes, obtained via a uniform scaling of the experimental unit cell. The high cost of the calculation did not allow an independent optimization of the three lattice constants. As in the case of crystalline polyethylene (see Section 3.3) the calculations were repeated for three different approximations of the exchange-correlation energy: the LSD approximation, and both the BP, and PBE generalized gradient approximations.

The binding energy of the “immobile” crystal phase relative to the energy of two isolated molecular units is shown in Fig. 4.7 for the LSD, GGA-BP and GGA-PBE approximations. The abscissa is the scaling factor for the linear dimensions, with unity corresponding to the experimental structure. The three curves differ significantly, as in the case of PE (see Section 3.3), but all lead to a finite equilibrium volume and a positive cohesive energy. The LSD calculation underestimates the equilibrium volume (the scaling factor is 0.97) and predicts a cohesive energy of 3.4 eV per unit cell. The equilibrium volumes for the GGA-BP and GGA-PBE are larger, with the optimum scaling factors found by fitting the energy curves with a Morse potential (also shown in Fig. 4.7) being 1.08 and 1.12, respectively. Although the two gradient-corrected functionals have similar forms and lead to similar equilibrium densities, the cohesive energy predicted by the GGA-PBE functional (0.78 eV) is almost three times the GGA-BP value (0.28 eV). We know of no experimental data on the low temperature cohesive energy of crystalline polycarbonates, which would provide a useful criterion for preferring a functional form for describing such molecules. Comparison with data for glassy polycarbonates suggests a cohesive energy of ~ 2 eV per molecular unit [92], which would point in favour of the GGA-PBE functional. Moreover, the GGA-PBE functional leads to a unit cell volume in better agreement with experiment

than the GGA-BP modification.

Nevertheless, the GGA-PBE is still far from giving a good quantitative description of the interchain interactions in this system: what is the main source of cohesion not described by the GGA-PBE functional? If we calculate the cohesive energy for the optimal GGA-PBE structure and add *ad hoc* attractive pair potentials of the form C_{ij}/r^6 , with the C_{ij} taken from standard potentials for organic molecules, we find a cohesive energy in the correct range [92]. This indicates that the attractive part of the Van der Waals potential is the main feature that is not included in the PBE functional. Since the Van der Waals forces have a weak structural dependence – they act as a background “glue”

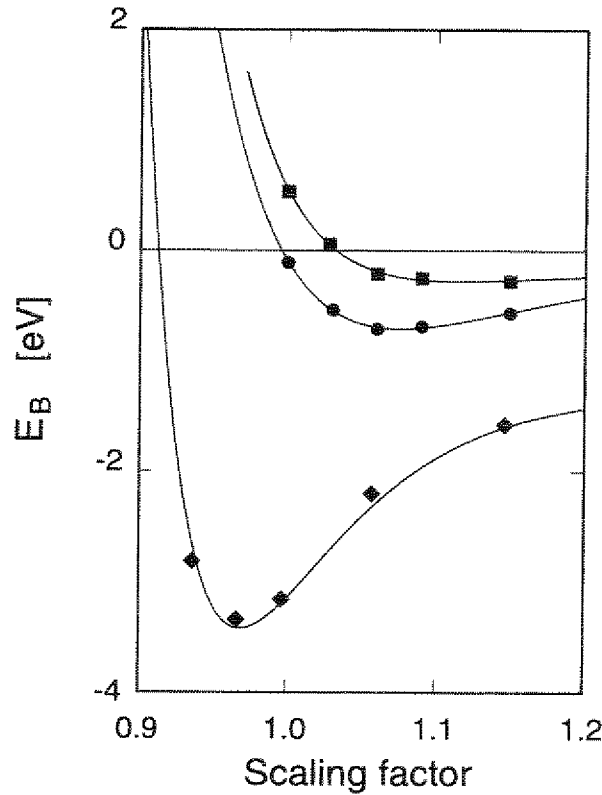


Figure 4.7: Variation of the binding energy of the “immobile” crystalline analog of BPA-PC (in eV per unit cell) as a function of linear dimension scaling factor for constant unit cell shape for LSD (diamonds), BP (squares), and PBE (circles) approximations.

giving rise to cohesion – the GGA-PBE is able to reproduce the measured geometries very well if the unit cell is constrained to have the experimental dimensions.

This result is still not enough to explain the behavior of the curve relative to the GGA-BP functional in Fig. 4.7, because this approximation gives purely repulsive $E(V)$ curves in systems with van der Waals bonds [19]. The weak minimum present in this curve suggests the presence of weak bonds of another type, and a careful observation of the interchain structure, in combination with an extensive series of calculations, have provided insight. We note first that a detailed analysis of the electrostatic interactions indicate that these forces can contribute only very little to the cohesion of the system. In fact, in both “mobile” and “immobile” forms the ESP charges are ~ 0.5 eV/molecule, and the crystal packing is such that the total dipole moment of the unit cell – and the long-range components of the electrostatic interactions – are small in both crystalline forms. The relatively weak electrostatic forces in these systems are consistent with the small dielectric constant measured for glassy polycarbonates (equal to 3.17) [93], which is typical of weakly ionic organic systems. A probable source of cohesion instead, described also by the GGA-BP functional, is the network of weak bonds between H atoms and O or aromatic C atoms in neighbouring molecules. We estimate that their contribution to cohesion is of the order of 10% of that of the Van der Waals forces. A detailed description of these bonds is presented in Section 4.2.2.

4.2.2 Geometrical Structures

The “immobile” and “mobile” crystalline structures are shown in Fig. 4.8 and Fig. 4.9, respectively. Since existing exchange-correlation energy functionals do not predict quantitatively the equilibrium volume and unit cell of the “immobile” form, as it was described in Section 4.2.1, the structure optimization for the crystalline systems have been performed with the experimental unit cell. The relaxed atomic positions agree well with the experimental data (for a detailed comparison see Ref. [94]).

The density is 10% higher in the “immobile” form than in the “mobile”

form, and we have noted that the molecular arrangements in both mimic the head-to-tail arrangement of the polymeric system. The geometry of the molecular units (see Section 4.1.5) changes little on forming either crystal. The most pronounced changes are in Φ_1 and Φ_2 , which define the orientation of the external ring in the molecules. With one exception in the “immobile” form (see Table 4.5), these angles open up significantly in the crystal, with

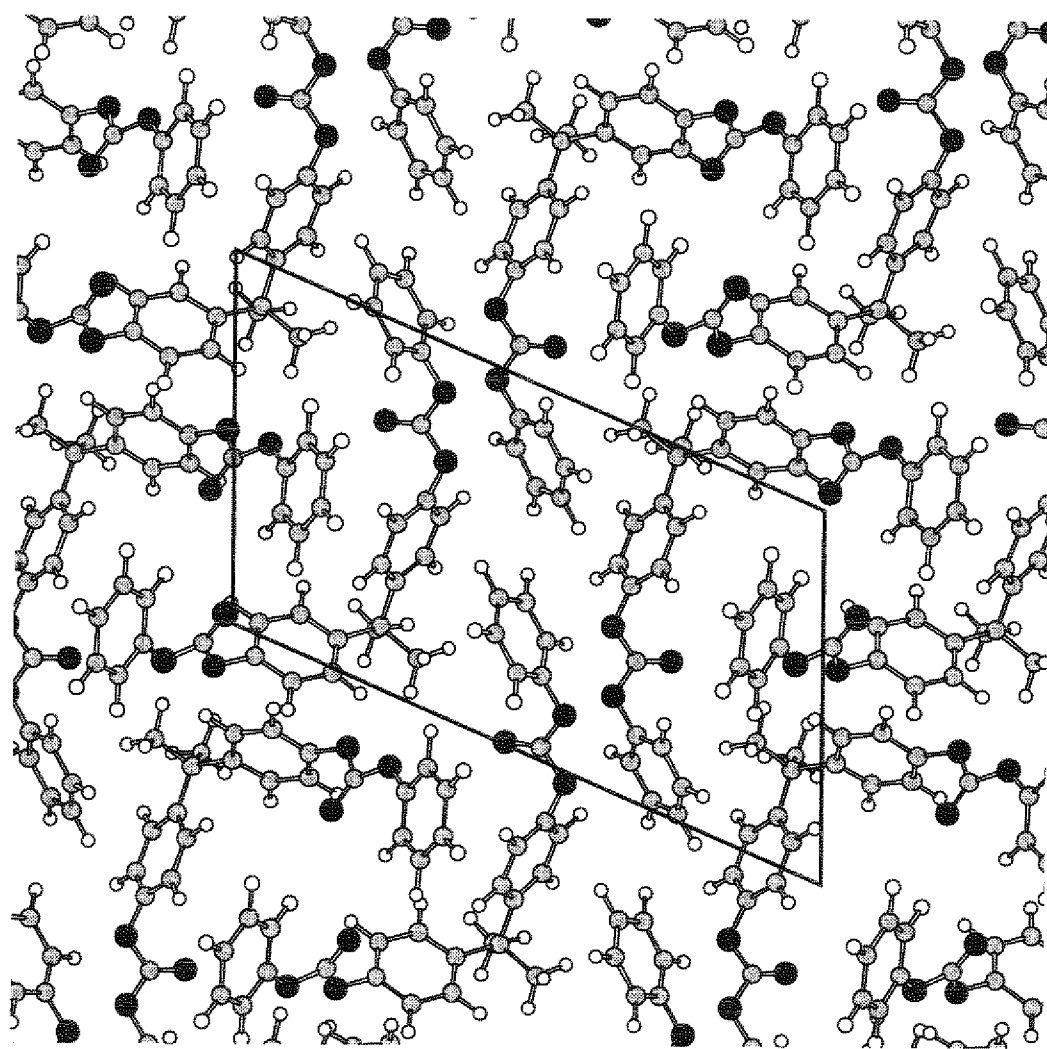


Figure 4.8: Projection of the monoclinic “immobile” crystalline analog of BPA-PC onto the ac -plane. Carbon atoms are gray, oxygen atoms black, and hydrogen atoms white.

4.2. DFT STUDY OF A CRYSTALLINE ANALOG

a related increase in the O19–H3 distance. As we have pointed out for the isolated DPBC, monophenyl carbonate, and phenol molecules, O19–H3 separations below ~ 3 Å force the the C3–C4–O17 and C5–C4–O17 angles to deviate from their ideal values (120°). According to this analysis, the increase of the O19–H3 separation observed in this case causes these angles approach the ideal geometry. The variation in bond lengths with changing volume shows that inter-molecular packing is limited mainly by H–H contacts, with contacts between H and aromatic C atoms playing a secondary role.

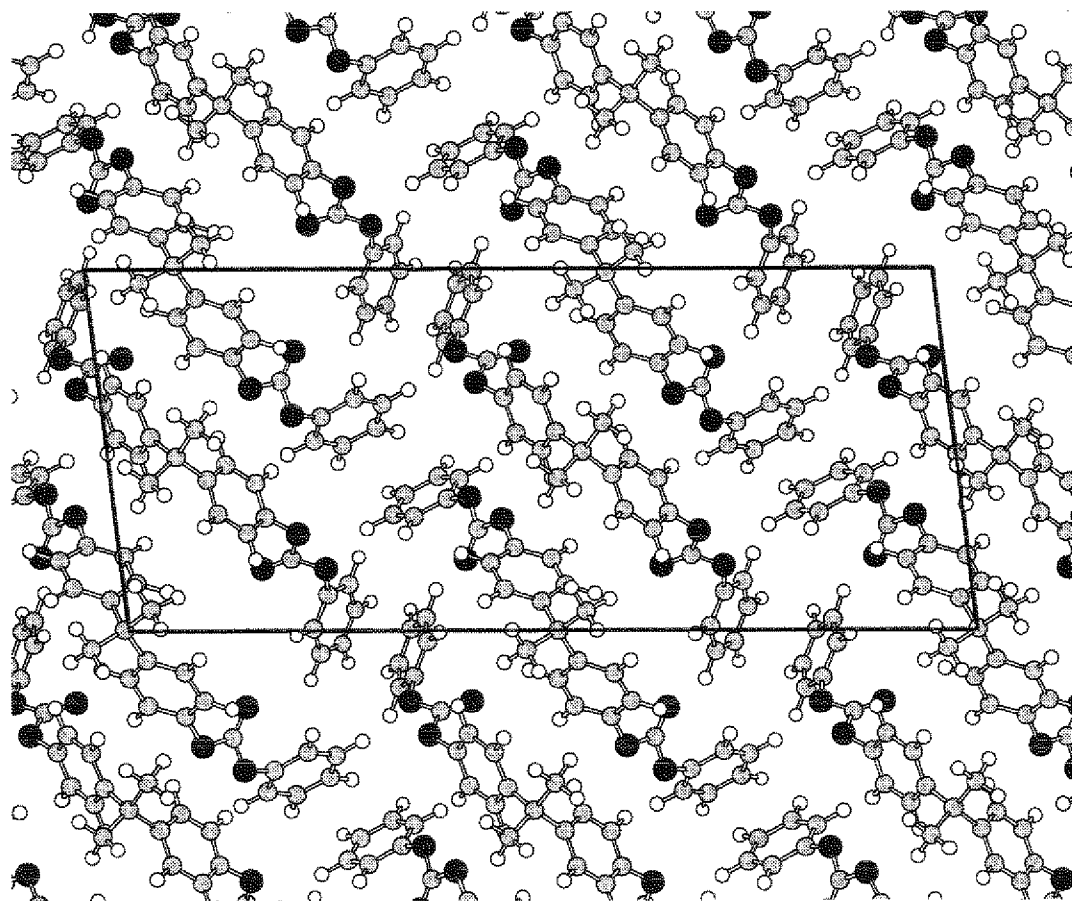


Figure 4.9: Projection of the monoclinic “mobile” crystalline analog of BPA-PC onto the ac -plane. Carbon atoms are gray, oxygen atoms black, and hydrogen atoms white.

Table 4.5: Torsional angles (in degrees) defining the orientation of the phenylene groups in the molecular unit (DPBC molecule) and in the crystal forms.

	Angle	Multiplicity	Value
Molecule	Φ_1	2	45.1
	Φ_2	2	69.2
	Ψ	2	8.3
Immobile	Φ_1	2	33.3
		2	87.7
	Φ_2	2	88.8
		2	82.0
	Ψ	2	36.5
		2	4.4
Mobile	Φ_1	4	60.0
		4	49.8
	Φ_2	4	89.0
		4	71.9
	Ψ	4	22.4
		4	9.6

As we mentioned previously, there is a network of weak inter-molecular links between H atoms and either O or aromatic C atoms. Their presence become evident if we observe the structural changes occurring during uniform dilation of the unit cell. In fact, the distances between these atoms *decrease* with increasing volume, indicating the presence of bonding. Most of these bonds are between phenylene H atoms and O atoms in neighbouring molecules, and there is similar attraction between H atoms and aromatic C–C bonds. Neither family involves “hydrogen bonds” in the sense of linking two highly electronegative ions, but the basic mechanism is also a weak hydrogen attraction towards electron-rich regions of the systems.

Projection of the Kohn-Sham orbitals relative to these crystals onto atomic states gives results very close to those obtained for the molecular unit of the

crystal (see Paragraph IV of Section 4.1.5), indicating that the electronic structure of the DPBC molecule changes little on forming the solids, with the density of states (DOS) being the superposition of the molecular DOS.

4.2.3 Vibration Properties

We have calculated the Γ -point phonons of these two crystalline forms in the same way described in Section 4.1.1, and compared them with the vibration spectrum of the isolated molecular unit (see Paragraph II of Section 4.1.5). In going from the isolated DPBC molecule to the “immobile” crystalline forms, we observe a slight upward shift of the spectral center of mass, the zero point energy of “immobile” crystal form being 7.8 kcal/mol (per crystal unit cell, i.e., two molecules) higher than that of the corresponding free molecules. The vibrational bands are, of course, broader in the crystal than in the molecular spectra. The most apparent effect is in the (aromatic C)-H stretching modes: in the crystal they occur between 3110 cm^{-1} and 3192 cm^{-1} , i.e., this band is broader and $\sim 30\text{ cm}^{-1}$ higher than in the isolated DPBC molecule. Analysis of the eigenvectors suggests that the shift is due to the repulsive contact between the phenylene hydrogen atoms belonging to different molecules.

4.2.4 Rotation Energy Barriers

We have calculated the energy barriers for the rotation of the methyl and carbonyl groups, as well as for the π -flip of the internal and external phenylene groups in both “immobile” and “mobile” crystal forms. To minimize systematic errors in comparing the results for the rotation energy barriers in the two crystal phases, we use a simulation cell of 236 atoms for both forms. This corresponds to two unit cells for the “immobile” form, arranged so that the simulation cell is nearly cubic, and to the experimental unit cell in the “mobile” form [91]. The results are reported in Table 4.6 and compared with those of the isolated molecular unit, described in Paragraph III of Section 4.1.5.

CHAPTER 4. POLYCARBONATES

Table 4.6: Rotational energy barriers (in kcal/mol) for the functional groups of the DPBC molecule, and for both its “immobile” and “mobile” crystalline phases. (a), (b) refer to rotations about the C7-O18 and O17-O18 axes, respectively.

	Methyl	Int. Ring	Ext. Ring	Carbonyl (a)	Carbonyl (b)
Molecule	2.9	2.0	1.2	8.7	18.5
Immobile	3.4	16.3	16.3	-	19.0
Mobile	3.4	7.7	12.5	-	19.0

This comparison helps understand whether the energy barriers arise from *intra*- or *inter*-molecular interactions. We discuss first the results for the phenylene rings, because this is the most prominent motion in NMR studies of polycarbonates.

In the “immobile” form the external phenylene group has a rotational barrier of 16.3 kcal/mol. Analysis of the relaxed geometry at the saddle point shows that the intra-molecular relaxation is small, while there is a strong coupling with the motion of the *internal* ring in two adjacent molecules: by changing Φ_1 by 90° , Φ_2 and Ψ on the same molecule change by less than 3° , while the largest value of $\Delta\Phi_1$, $\Delta\Phi_2$, and $\Delta\Psi$ on the two nearest molecules are 7° , 31° and 22° respectively. The relaxation of the internal rings in the neighbouring molecules implies a small but definite rotation of one of the methyl groups. The synchronous motion of internal and external rings in adjacent molecules suggests the existence of a single mechanism for rotating either group in the “immobile” form, i.e., the rotation barrier for the internal phenylene ring (not computed) should be close to the one computed for the external ring. The 16.3 kcal/mol barrier arises from the short-range repulsion of several H-H pairs (the minimum separations are 1.90 Å at the saddle point and 2.09 Å in the ground state) and the local expansion of intra-molecular distances around the rotating phenylene group.

The barrier for the π -flip of the external ring in the “mobile” form is 12.6 kcal/mol. The intra-molecular relaxation at the saddle point is greater than

in the “immobile” form ($\Delta\Phi_2=13^\circ$, $\Delta\Psi=26^\circ$, $\Delta\Phi_1=90^\circ$), while weaker inter-molecular coupling affects mainly the nearest external phenylene ring in the head-to-tail arrangement ($\Delta\Phi_1=21^\circ$, $\Delta\Phi_2=8^\circ$, and $\Delta\Psi=2^\circ$). The relaxation of the internal rings in adjacent molecules is small ($\sim 3^\circ$), and the barrier arises predominantly from local expansion to accommodate the rotating phenylene group. While some H–H distances shrink (the minimum separation is 1.96 Å), most of the interatomic separations increase near the rotating ring.

Finally, rotation of the internal phenylene ring in the “mobile” form is associated with the smallest energy barrier (7.7 kcal/mol) and relaxation. The strongest couplings are with the isopropylidene group and the other internal ring in the same molecule ($\Delta\Psi=70^\circ$ for the ring whose Φ_2 changes by 90° ; $\Delta\Phi_1=5^\circ$, $\Delta\Phi_2=18^\circ$, and $\Delta\Phi=20^\circ$ for the other half of the same molecular unit). The relaxation most evident in the neighbouring units involve one isopropylidene group ($\Delta\Psi \sim 10^\circ$ on both sides of the group) with smaller changes ($\sim 3^\circ$) in Φ_1 and Φ_2 . In this case there is a small homogeneous expansion around the rotating ring. The previous estimates of the barriers for phenylene ring rotation are 9–10 kcal/mol [95], 8–9 kcal/mol [96], 10.4 kcal/mol [97], and 9.6 kcal/mol [98]. Our results agree satisfactorily with experiment and allow us to identify the mobile group observed as the internal phenylene group. A molecular dynamics simulation for BPA-PC led to higher value (12.6 kcal/mol) [99].

The values obtained for the rotation barrier of the methyl groups in the crystals and in the isolated molecular unit shows that it is almost independent of the chain packing, and determined primarily by intra-molecular interactions. An earlier semi-empirical estimate of this barrier was 6.6 kcal/mol [95].

The rotation of the carbonyl group around the O18–C7 axis, which gives the smallest barrier for the rotation of this group in the isolated structural unit, would require substantial inter-molecular relaxation in the condensed phases. The lowest energy path in the crystals is found to be the rotation around the O17–O18 axis. This barrier (19 kcal/mol) is nevertheless close to the same barrier calculated for the DPBC molecule, and therefore we conclude

that it is due mainly to intra-molecular interactions.

4.3 DFT Study of Cyclic Oligomers

The cyclic dimer, trimer, and tetramer carbonates of BPA have been isolated and analyzed spectroscopically, and the structures of their crystalline forms determined by x-ray diffraction [100]. The ring topologies of these cyclic oligomers are more closely related to the chain structure of the polymer than are the isolated molecular units of the “immobile” and “mobile” forms. Therefore, these rings provide insight into the structural trends as the molecules increase in length and are important molecules in their own right, not least because polymerization in ring systems (ring-opening polymerization, ROP) is an active research area in polymer chemistry [101]. Our calculations focus

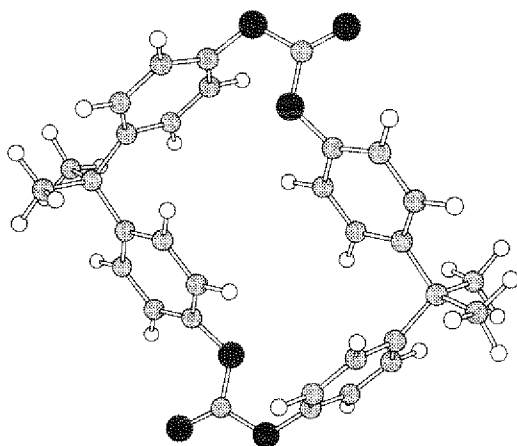


Figure 4.10: Structure of BPA cyclic dimer carbonate. Carbon atoms are gray, oxygen atoms black, and hydrogen atoms white.

4.3. DFT STUDY OF CYCLIC OLIGOMERS

on the investigation of the geometrical structures and vibrational properties of dimer and tetramer, both in the isolated and in the crystalline configurations. These calculations are performed in the same way illustrated for the segments of BPA-PC chains (see Section 4.1), using the experimental unit cells for the crystalline systems, and, for the isolated molecules, unit cells large enough to ensure a minimal inter-molecular interaction. The tetramer tends to include solvent molecules on crystallization, and the stable crystals were obtained using *m*-xylene (1,3-dimethylbenzene) as a solvent [100]. The coordinates of the solvent molecules were also relaxed in the calculations. Labelling of atoms in this section follows that reported in Chart 4.4.

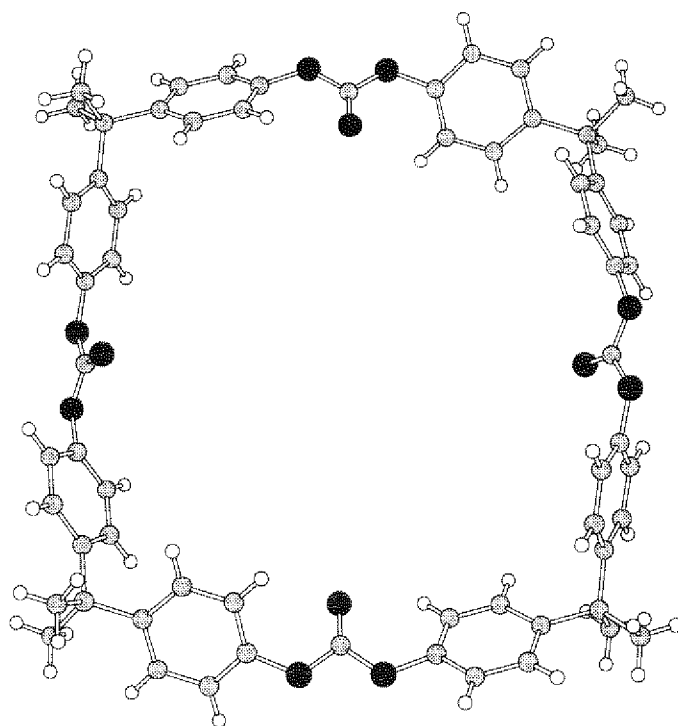


Figure 4.11: Structure of BPA cyclic tetramer carbonate. Carbon atoms are gray, oxygen atoms black, and hydrogen atoms white.

4.3.1 Geometrical structures

The structural parameters for isolated dimer and tetramer have been calculated, and are reported in Table 4.7. A comparative analysis of these structures with that of the isolated DPBC molecule is very enlightening. In fact, this molecule has a chemical composition similar to that of the dimer (which has one isopropylidene ($\text{CH}_3\text{-C-CH}_3$) unit more), but it is open. Dimer and tetramer instead, are both closed structures, and they have the same relative composition of phenylene, carbonyl, and isopropylidene groups. As in the case of the DPBC molecule, the bond lengths and angles at the isopropylidene vertices and in the phenylene rings in both dimer and tetramer are almost identical to those in the corresponding fragments (see Section 4.1). The structures show some differences close to the junction of the carbonate and phenylene groups.

Ring closing generally induces strain and an increase in the total energy, and both should be greater in the dimer than in the tetramer. Indeed, the dimer has less flexibility than tetramer and DPBC, and adopts – unique in this family – the *cis-trans* conformation. The total energy (without zero point energy corrections, see Section 4.3.2) of the tetramer is 27 kcal/mol lower than that of two dimer molecules. Some of the features already pointed out for the DPBC molecule are not affected by ring closing or size increasing of the molecules. Indeed also in dimer and tetramer the O17-C4 bond is longer and weaker than in O17-C7 bond, and small deviations of the O17 atom from the plane of the adjacent phenylene ring are observed also in some of the carbonate groups in the dimer and tetramer. In the tetramer, the C3-C4-O17 and C5-C4-O17 angles deviate from the ideal value (120°) by $\pm 5^\circ$, as in the case of DPBC and smaller molecules. These angles assume the ideal value only in the dimer molecule. The strain present in the latter modifies also the $\Gamma_{1,2}$ angles, which depart significantly from the planar configuration assumed in the other molecules. Because of the asymmetric *cis-trans* conformation of the dimer, the O19-C7-O17 and O19-C7-O18 angles, which are equivalent in the DPBC and tetramer molecules, differ here by 5° . Also the angle O17-C7-O18 in the dimer is affected by the different conformation, being 5° smaller

4.3. DFT STUDY OF CYCLIC OLIGOMERS

Table 4.7: Selected interatomic distances (Å) and angles (degrees) in DPBC, dimer and tetramer carbonates. Hydrogen atoms take the same number as the adjacent C atom.

Atoms	DPBC	Tetramer	Dimer
H3-O19	2.494	2.662, 2.337	2.954
H9-O19	3.000	2.717, 2.558	4.533
C3-C4-O17	123.2	122.7, 125.3	123.5
C5-C4-O17	115.1	116.2, 114.0	115.0
C4-O17-C7	119.2	118.7, 121.5	121.3
O17-C7-O19	128.0	127.6, 128.1	127.5
O18-C7-O19	126.9	127.4, 127.2	122.8
O17-C7-O18	105.1	105.0, 104.7	109.6
C9-C8-O18	121.2	122.3, 123.1	119.4
C13-C8-O18	117.5	116.6, 115.9	119.8
C3-C4-O17-C7 (Φ_1)	44.8	52.7, 31.4	70.3
C9-C8-O18-C7 (Φ_2)	69.3	55.4, 46.8	73.4
C4-O17-C7-O19 (Γ_1)	0.0	2.0, 3.8	21.0
C8-O18-C7-O19 (Γ_2)	0.5	3.0, 4.3	194.9
C10-C11-C14-C15 (Ψ)	8.4	12.8, 12.0	5.8

than in the other molecules.

Only the opposite edges are equivalent in the tetramer structure. There are two types of conformation about the carbonate, as it is shown in Fig. 4.11): one has a nearly symmetric position of the phenylene rings with respect to the plane of the carbonate ($\Phi_1 \simeq \Phi_2$), while in the other Φ_1 and Φ_2 differ by $\sim 15^\circ$. As in the DPBC molecule, Γ_1 and Γ_2 are close to zero, indicating *trans-trans* geometry. All bond lengths and angles in the tetramer molecule are very close to those in the DPBC molecule.

The structures of the crystalline forms of the cyclic dimer and tetramer have been optimized, starting from the experimental coordinates [100]. In line with our earlier experience with the “immobile” form of DPBC (see Section

4.2.1), all computations have been performed with the experimental unit cells. The relaxed atomic positions agree well with the experimental data. For example, the r.m.s. deviations for the coordinates of non-hydrogen atoms (0.018 Å and 0.041 Å for dimer and tetramer, respectively) arise from slight rotations of the functional groups, while computed and experimental values for interatomic distances and bond angles agree very well.

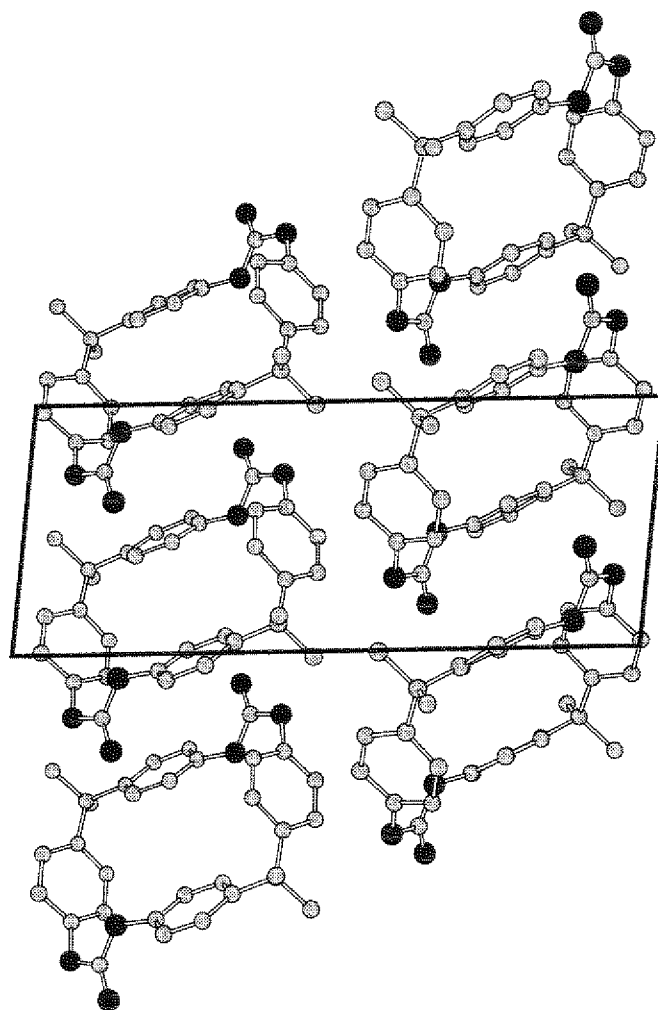


Figure 4.12: Projection of the monoclinic crystalline structure of BPA cyclic dimer carbonate onto the ac -plane. Carbon atoms are grey and oxygen atoms black. Hydrogen atoms are not shown.

4.3. DFT STUDY OF CYCLIC OLIGOMERS

Compared with the wide range of torsional angles in the different oligomers, and some variations in the carbonate geometries, both dimer and tetramer show only minor structural differences on forming the crystals. According to what was observed for the DPBC crystal system (see Section 4.2.2), the inter-molecular interaction affect mainly the soft $\Phi_{1,2}$ torsional angles and are less pronounced in the dimer than in the tetramer. This reflects the fact that the strain present in the dimer structure makes this molecule less susceptible to the relatively small inter-molecular perturbations induced by condensation.

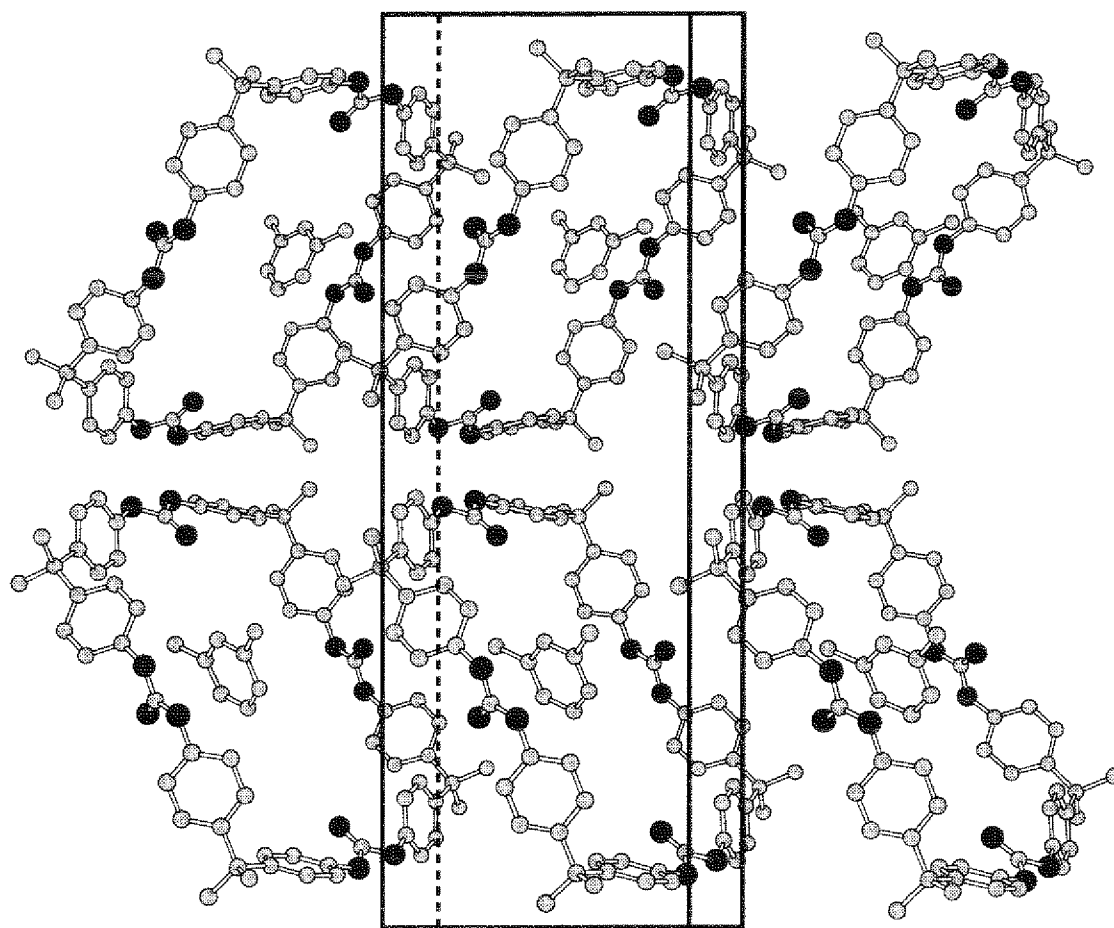


Figure 4.13: Projection of the monoclinic crystalline structure of BPA cyclic tetramer carbonate onto the bc -plane. Carbon atoms are grey and oxygen atoms black. Hydrogen atoms are not shown.

4.3.2 Vibrational properties

The vibration spectra for the isolated dimer and tetramer oligomers and the Γ -point phonons for the corresponding crystalline structures were calculated following the method described in Section 4.1.1. We report here only the spectrum of the isolated dimer molecule, which is shown in Fig. 4.14. Again, the calculated vibrational properties of the smaller oligomers, in particular the DPBC molecule (see Section 4.1.5), provide the basis for the interpretation of the data.

The strain in the isolated dimer is reflected in the vibration frequencies, which are higher than those in DPBC and tetramer. For instance, the band

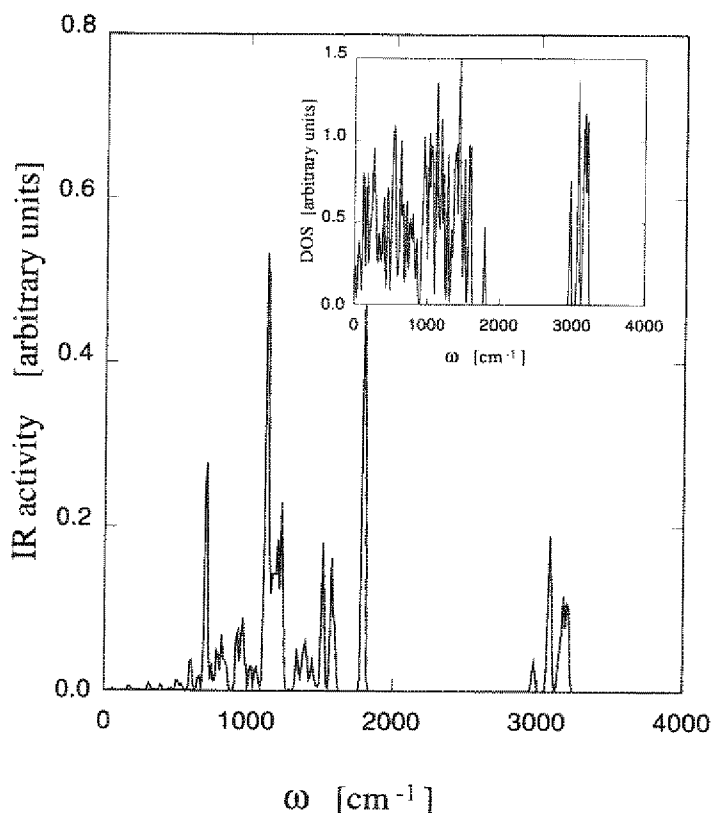


Figure 4.14: The infrared active vibrational spectrum of the isolated cyclic dimer carbonate. The inset shows the total vibrational density of states. Each mode is represented by a Gaussian distribution of width 12 cm^{-1} .

4.3. DFT STUDY OF CYCLIC OLIGOMERS

related to the stretching of the (aromatic C)-H bonds [3146–3216 cm^{-1}] is $\sim 50 \text{ cm}^{-1}$ higher than in DPBC, and a similar shift is observed for the out-of-plane modes of the phenylene rings.

The tetramer geometry is less strained than the dimer structure, and its frequencies generally lie between those of DPBC and of the dimer, and closer to the former. The most informative comparison is between tetramer and dimer, since they have the same relative composition of phenylene, carbonyl and isopropylidene groups. The zero point energy of two dimer molecules is 16.6 kcal/mol higher than that of one tetramer, and contributes significantly to the enhanced stability of the latter.

The most interesting features are due to the different geometry of the molecule around the carbonate group (DPBC and tetramer have a *trans-trans* conformation, while the dimer is *cis-trans*). In the DPBC molecule and in the tetramer, for example, the highest frequency in the spectrum is associated with the (aromatic C)-H stretching modes for the H atoms closest to the carbonyl O19. In the dimer, instead, the highest frequency concerns the H in between C13 and O18. The in-plane bending modes involving O19 are also softer in the dimer (at 718 cm^{-1}) than in either DPBC (844 cm^{-1}) and in the tetramer (846 cm^{-1}), because the *cis-trans* conformation increases the O19–H3 distance. The frequencies of the vibration modes located at the carbonyl group are affected most by the change from the *trans-trans* conformation of DPBC to the *cis-trans* of the dimer, with some frequencies being higher, others lower.

The differences between the isolated molecules and the crystal phase are largest in dimer, where shifts towards higher frequencies are found, for example, for (aromatic C)-H stretching band and for the C=O stretching. The frequencies of the dimer are most affected by the condensation because its crystal structure has the highest density (1.28 g/cm^3) among all crystalline systems considered here. On average, however, vibrational frequencies increase in going from the free molecules to the condensed phase for all these systems, and the zero point energy (per unit cell) is higher in the solid than in the isolated molecules.

4.4 Combined DFT/Classical FF Study

Most of the thermodynamic and mechanical properties of interest for applications involve time and size scales that are outside the reach of our DFT calculations, despite the amazing growth of computer power in recent years. For this reason, we use our DFT results to parametrize a classical force field, which can then be applied for extensive Monte Carlo or molecular dynamics simulations.

Several different force fields have been used to study polycarbonates and similar systems [102]. They can be classified into two groups: (1) very detailed potentials, involving a large number of free parameters, tuned to reproduce all the available information, both from experiments and quantum chemistry computations; (2) “generic” force fields, intended to model a large class of compounds in different aggregation states, relying on a fairly small number of free parameters.

Both approaches have advantages and disadvantages. The description provided by the detailed potentials (1) can be very precise for systems and physical conditions close to those adopted in fitting the potential. However, the determination of a large number of parameters can be problematic, and the reliability of the model often degrades quickly in moving away from the conditions used in the fit. Moreover, the complex functional form of the potential required to reproduce quantitatively the details of the system behaviour can make the simulation very time consuming, thus reducing the advantage of these schemes compared to the parameter-free approaches. The second strategy often provides potentials with a higher degree of “transferability”, and therefore more useful to predict the behaviour of the system under conditions not exploited in the generation of the model. The reason for this reliability is that the large data base and the fairly small number of parameters used to produce “generic” force fields determine the behaviour of the potential under a wider range of geometrical conformations, chemical compositions, and physical conditions. On the other hand, it is difficult to achieve a quantitative and detailed description of any specific system.

In our study, we adopt an intermediate strategy: we assume a simple functional form for the interatomic potential, and we determine the free parameters in order to reproduce the wide data base of information provided by our DFT computations on systems related to BPA-PC, both in the gas phase and in the crystal phase. The only experimental input entering the determination of the potential is the equilibrium volume of the crystal forms considered here.

This strategy is not new, but the size and scope of the DFT study underlying the potential generation is unprecedented, allowing us to rely almost completely on the computational data to test our model.

4.4.1 Tuning the Force Field

From the chemical point of view, polycarbonates are fairly simple materials, with standard covalent intra-molecular bonds and Van der Waals inter-molecular interactions. By extensive DFT computations we have verified that the geometrical parameters characterizing these bonds present a remarkable degree of transferability from one molecule to another. Therefore, these systems appear to be good candidates for a description in terms of classical force fields models. Moreover, polycarbonates are weakly polar, with one of the lowest dielectric constants (equal to 3.17 [93]) among plastic materials. Therefore, a neutral atom model is likely to be adequate, and the exclusion of the long range electrostatic potential, which requires a computationally expensive Ewald summation, greatly simplifies the simulation. On the other hand, in Section 4.1.5 we highlighted several structural features that are related to the quantum mechanical nature of bonding in the molecular unit, and will be difficult to be described by the force field. These details, however, are not very important for the global properties, and we shall not attempt to reproduce them perfectly.

We assume for our force field a functional form similar to that applied in models like Amber [103], Charmm [104], and Tripos [105], widely used for the simulation of organic molecular systems. In all these models, if the atomic charges are negligible, the potential energy of the system is written in terms of Van der Waals non-bonding interactions and several intra-molecular bonding

terms:

$$E = E_{VdW} + E_{str} + E_{bnd} + E_{tor} + E_{op}. \quad (4.2)$$

The meaning and origin of each of these terms is fairly intuitive, and it is discussed in detail in Refs. [103, 104, 105]. Therefore, we limit ourselves to their definitions and to a short description of their role in the determination of the properties of the system. The Van der Waals term accounts for both the inter-molecular cohesion (due to long-range dispersion forces) and the short-range interatomic repulsion. It has the usual Lennard-Jones form:

$$E_{VdW} = \sum_{ij} K_{ij}^{VdW} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (4.3)$$

where r_{ij} is the interatomic distance. In our simulation the sum runs over all the pairs of atoms within a $3\sigma_{ij}$ distance cutoff, excluding pairs of atoms connected by chemical bonds, or belonging to the same functional group (i.e., phenylene, carbonate, and methyl groups).

The bonding interactions are represented by stretching (*str*), bending (*bnd*), torsional (*tor*), and out-of-planarity (*op*) contributions. The meaning of the first two terms is very simple: they specify the equilibrium distances (r_{ij}^0) and angles (θ_{ijk}^0) for the standard covalent bonds, and the energy cost for (slight) deviations from these values is:

$$E_{str} = \sum_{i,j} K_{ij}^{str} [r_{ij} - r_{ij}^0]^2, \quad (4.4)$$

$$E_{bnd} = \sum_{i,j,k} K_{ijk}^{bnd} [\theta_{ijk} - \theta_{ijk}^0]^2. \quad (4.5)$$

The third term plays an equivalent role for the torsional angles:

$$E_{tor} = \sum_{i,j,k,\ell} K_{ijk\ell}^{tor} [1 \pm \cos(\beta \phi_{ijk\ell})]. \quad (4.6)$$

The sign ($\pm$) determines whether $\phi_{ijk\ell}=0$ corresponds to a maximum or a minimum of the potential energy surface. The parameter β defines the period of the function E_{tor} versus the torsional angle $\phi_{ijk\ell}$, which is different for different types of bond. In fact, simple considerations in terms of atomic

4.4. COMBINED DFT/CLASSICAL FF STUDY

orbitals show that this period is 120° in case of sp^3 bonds ($\beta=3$), 180° for sp^2 bonds ($\beta=2$), etc..

The out-of-planarity contribution models the energy cost of breaking the planarity of groups with strong π bonds, like the phenylene or carbonate groups. The plane of the group is defined by the positions of three atoms belonging to it, and the out-of-planarity of any other atom in the group is measured by its coordinate $z_i^\perp$ in the direction perpendicular to this plane. The energy cost is assumed to depend quadratically upon $z_i^\perp$:

$$E_{op} = \sum_i K_i^{op} (z_i^\perp)^2. \quad (4.7)$$

We start our modellization from the parameters of the “Tripos 5.2” force field, which are listed in Ref. [105]. The original Tripos parameters K_{ij}^{Vdw} , σ_{ij} , K_{ij}^{str} , K_{ijk}^{ben} , K_{ijkl}^{tor} , and K_i^{op} had been tuned to reproduce the measured geometries and relative energies for a large set of organic molecules, as it is described in Ref. [105]. We start from these values and compute the ground state geometries and vibrational frequencies for all molecules discussed in Section 4.2. The selected results reported in Table 4.8 for benzene, in Table 4.9 for monophenyl carbonate, and in Table 4.10 for the DPBC molecule show

Table 4.8: Distances ($\text{\AA}$) and vibrational frequencies (cm^{-1}) of the benzene molecule calculated with DFT (PBE functional), the original parametrization of the Tripos 5.2 force field, and with our DFT-based parametrization of the force field (referred to as “new fit”).

Atoms	DFT-PBE	New Fit	Tripos
C-C	1.397	1.398	1.396
C-H	1.093	1.093	1.084
Mode	DFT-PBE	New Fit	Tripos
C-H Stretch	3127	3139	4219
C-C Stretch	1588	1834	2934
C-H Out-of-plane	998	1320	2187

Table 4.9: Distances ($\text{\AA}$) and vibrational frequencies (cm^{-1}) of the monophenyl carbonate molecule calculated with DFT (PBE functional), the original parametrization of the Tripos 5.2 force field, and with our DFT-based parametrization of the force field (referred to as “new fit”).

Atoms	DFT-PBE	New Fit	Tripos
C3-C4	1.393	1.399	1.402
O17-C4	1.413	1.414	1.395
O19-C7-O17	128.0	125.2	121.8
O19-C7-O18	125.4	124.6	121.8
H18-O18-C7	104.5	107.3	112.2
C5-C4-O17-C7	47.9	46.5	48.6
H3 ... O19	2.562	2.54	2.55
Mode	DFT-PBE	New Fit	Tripos
O-H Stretch	3531	3543	5010
C-H Stretch	3153	3139	4219
C-C Stretch	1591	1883	2937
C=O Stretch	1772	1861	2512

that the Tripos 5.2 model describes fairly well the geometrical structures (despite occasional failures), while the vibrational frequencies are overestimated. Also the barriers for the phenylene π -flips in the condensed phases, which are important dynamical features of polycarbonates (see Section 4.2), are significantly overestimated by the Tripos parametrization: the lowest energy barrier for the phenylene π -flip in the “mobile” crystal analog of BPA-PC is predicted to be 21.9 kcal/mol by the model potential, while the DFT computation gives a barrier of 7.7 kcal/mol, and the measured barrier is around 8-9 kcal/mol.

We have devised a simple strategy to tune the parameters to fit the DFT data. First, we refine the equilibrium values r_{ij}^0 and θ_{ijk}^0 for the bond distances and bond angles, respectively. These parameters are already well reproduced by the Tripos model, but, being associated with large force constants, even slight errors in their equilibrium values can lead to a less reliable parametriza-

4.4. COMBINED DFT/CLASSICAL FF STUDY

Table 4.10: Distances ($\text{\AA}$) and vibrational frequencies (cm^{-1}) of the DBPC molecule calculated with DFT (PBE functional), the original parametrization of the Tripos 5.2 force field, and with our DFT-based parametrization of the force field (referred to as “new fit”).

Atoms	DFT-PBE	New Fit	Tripos
C3-C4	1.394	1.401	1.397
C4-O17	1.410	1.415	1.395
C7-O19	1.210	1.209	1.221
C14-C16	1.544	1.546	1.546
H3...O19	2.494	2.46	2.56
C3-C4-O17	123.2	121.1	120.7
O17-C7-O19	128.0	125.6	121.6
O17-C7-O18	105.1	109.3	117.1
C3-C4-O17-C7 (Φ_1)	44.8	47.3	54.7
C9-C8-O18-C7 (Φ_2)	69.3	64.6	73.6
Mode	DFT-PBE	New Fit	Tripos
C-H Stretch (Phenyl)	3166	3140	4219
C-H Stretch (Methyl)	3079	2951	4161
C-C Stretch (Phenyl)	1599	1908	2936
C-C Stretch (Methyl)	1148	1335	2002
C=O Stretch	1775	1839	2501

tion. Equilibrium torsional angles are kept fixed at the original values.

In a second step, we determine the force constants for stretching, bending, torsion and out-of-planarity by fitting the eigenvalues and eigenvectors of some specific vibrational modes, e.g. the C-H, C=O and C-O stretching, some bending modes, and the out-of-planarity modes of the carbonate group.

Finally, the equilibrium volume of the crystal phases and the phenylene π -flip barriers are adjusted by varying the Van der Waals parameters. In this last step, the most important parameters are those referring to pairs of hydrogens, which provide most of the short range inter-molecular repulsion.

The fit is not performed by an automatic procedure, because any global minimization of the difference between the results of the potential and the DFT values tends to give unreliable values of the force constants, as the fit is under-determined. However, the different degrees of freedom are largely independent, and a good fit of the DFT results can be achieved with a reasonably small amount of work. The results obtained with this new parametrization are compared with the Tripos 5.2 and the DFT results in Tables 4.8, 4.9, 4.10, and in Fig. 4.15. The improved agreement with the reliable DFT results, obtained with the present parametrization, is evident. Some parameters, such

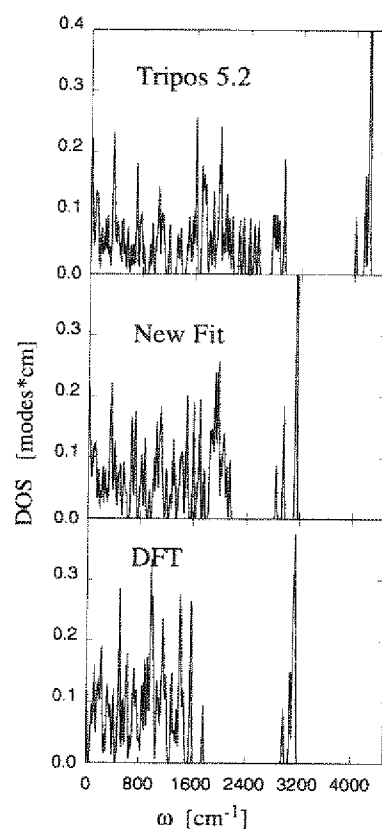


Figure 4.15: Total vibrational density of states of the isolated DPBC molecule obtained with the original parameters of the Tripos 5.2 force field (top panel), with the DFT calculations (bottom panel), and with the force field tuned to reproduce our DFT results (central panel).

as several Van der Waals K_{ij}^{VdW} and σ_{ij} are not well determined, because the structural and dynamical results are not very sensitive to them. However, this insensitivity also suggests that the properties of the system will not be much affected by a lack of refinement in their values.

4.4.2 Details of the Monte Carlo Simulation

The optimized potential described above is now applied in a Monte Carlo (MC) simulation of large polycarbonate samples. The simulation is performed in the isobaric-isothermal (NPT) ensemble, i.e., we fix the number of particles N , the pressure, and the temperature of the system [106, 107]. The probability distribution in the configurational space is then given by:

$$w(\mathbf{q}^N) = \frac{1}{Z} \exp \left(- \frac{U + PV}{kT} \right), \quad (4.8)$$

where U is the potential energy, P is the external pressure, V is the volume of the system, T is the temperature, and k is the Boltzmann constant. The partition function Z is given by:

$$Z = \int \exp \left(- \frac{U + PV}{kT} \right) d\mathbf{q}^N dV, \quad (4.9)$$

and $\mathbf{q}^N = (\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)$ are the configurational variables. The sampling of this probability distribution is performed using the Metropolis algorithm (see Appendix), in which we change the atomic positions and the volume of the system.

The major problem in the simulation of molecular phases is that degrees of freedom characterized by greatly different energy scales coexist in these systems: the stretch of the intra-molecular covalent bonds requires a significantly higher energy than either bending or torsion, and these modes are still much stiffer than rotations of large functional groups (e.g. phenylene rings) or displacements of entire molecular units, which affect only the inter-molecular interactions. As a consequence, the MC algorithm used in simple atomic systems and involving only single atom moves, cannot be applied for molecular systems: the amplitude of the single atom moves is limited by the stiff stretching force constants; if we select the trial displacement in order to achieve a

fairly high acceptance ratio (0.3 – 0.5) for these single atom moves, then the “soft” degrees of freedom are not adequately sampled. This problem is solved by adopting a variety of trial moves, from those involving single atoms, to those involving functional groups and molecular units. Each of these degrees of freedom is sampled using a different strategy and a different length scale for the trial displacement. In our MC implementation we sample: (i) single atom moves; (ii) rotations of functional groups; (iii) rotation of entire molecules; (iv) translation of molecules; (v) volume changes.

The single atom moves are attempted with a small step (typically 0.2 – 0.3 Å), as the stiff intramolecular forces limit drastically the acceptance probability. Although these short moves are ineffective in producing significant global displacements, they are required to equilibrate the structure within each molecule. Larger displacements are obtained by rotating the phenylene rings, the carbonate and the methyl groups. For each of these groups, we identify a rotation axis and attempt a rigid rotation about it. These rotations involve only changes in bending and torsional angles, and are therefore accepted with high probability, although some of the atoms are displaced by distances of the order of 1 Å. The rotation of groups in the molecule is supplemented by rotations of the entire molecule. In this case, the center of rotation is the (instantaneous) molecular center of mass, and the axis is selected at random, with an isotropic probability distribution. Translations of the entire molecule are attempted with relatively large amplitude (~ 1 Å) and are therefore very effective in producing large rearrangements of the system. Both rotations and translations of the entire molecule involve only changes in the inter-molecular part of the potential energy.

Finally, volume changes are attempted by performing a homogeneous expansion or contraction of the simulation cell, whose shape remains unchanged. The different types of moves are attempted in such a way that each of them contributes equally to the sampling of the phase space. More precisely, single particle displacements are the most frequently attempted moves. Less frequent are the rotations of the functional groups, and the rotations and translations of the entire molecule, which are attempted (on average) every

50 single atom moves. The least frequent move is the volume change, which is attempted every few thousand single atom moves. The relative frequency of these attempted moves is such that each atom is displaced with almost equal probability by each of them. The amplitude of the moves has been selected in order to obtain an acceptance probability of ~ 0.3 of the entire number of trials.

4.4.3 Preliminary Monte Carlo Results

We now present preliminary results of some applications of our optimized classical force field to the simulation of a condensed molecular system, closely related to BPA-PC, whose molecular units are DPBC molecules. As explained in Section 4.2, this is a model system extensively investigated in order to clarify properties of the (technologically more important) polycarbonate amorphous materials. The aim of our simulation is two-fold: (i) to investigate the thermal properties of a system that is currently produced in the laboratory for research purposes; (ii) to show what kind of problems can be addressed by the classical simulation method.

Computations for the polymeric systems have been performed in collabo-

Table 4.11: Number of MC steps performed at each temperature for the simulation using a unit cell containing 72 DPBC molecules (4248 atoms). We report also the number of π -flips of the internal and external phenylene rings in the molecules.

T [K]	10^6 MC/steps	N_π inner ring	N_π outer ring
300	194	0	0
400	210	0	0
500	512	0	0
600	720	4	5
700	342	63	69
800	144	51	64
1000	48	51	58

ration with another research group [108], whose preliminary results are also discussed in this section.

I. Thermal properties of crystal and liquid phases of DPBC

The first application of the force field model has been the simulation of the condensed DPBC molecular system at zero pressure and non-zero temperatures in the range [300 – 1000] K. The simulation assumes periodic boundary conditions, and a unit cell containing 72 DPBC molecules (4248 atoms) is used. We start each simulation with the system in the “immobile” crystal form, which is the most stable one in terms of potential energy. Each sample is then equilibrated during a very long sequence of MC steps (Table 4.11 reports the simulation length for each temperature), and average values for the potential energy U , the volume V , and for several structural properties are accumulated during the last 30×10^6 simulation steps.

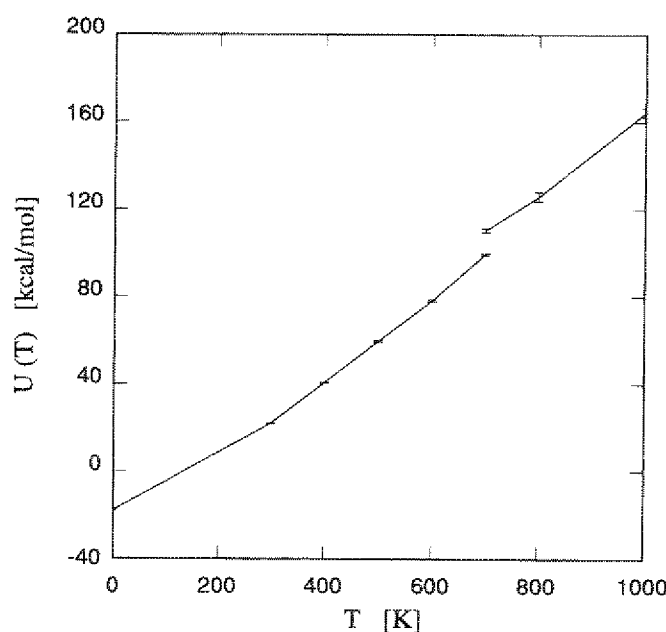


Figure 4.16: Average potential energy as a function of the temperature for a sample of 72 DPBC molecules. The error bars represent the standard deviations of statistically independent sub-averages.

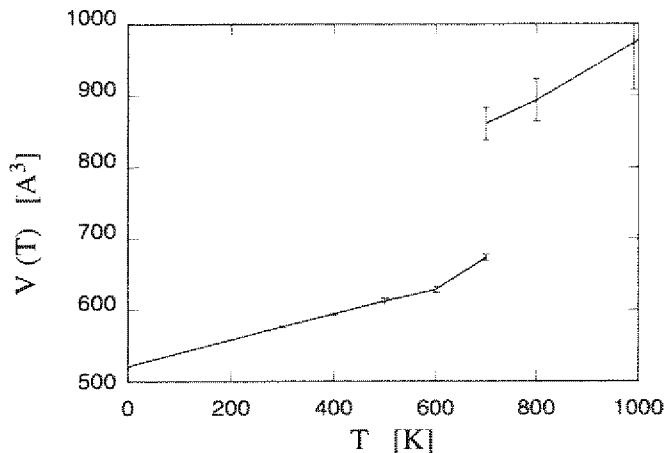
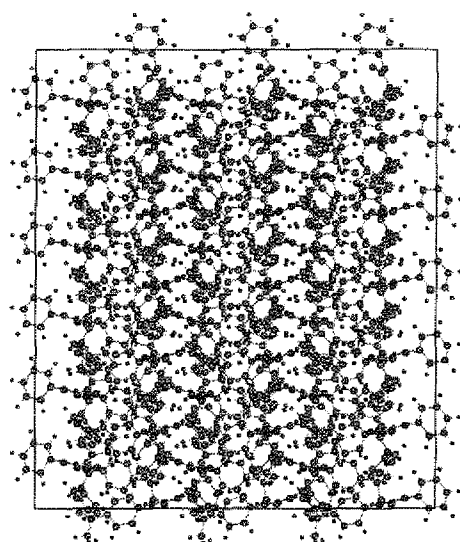


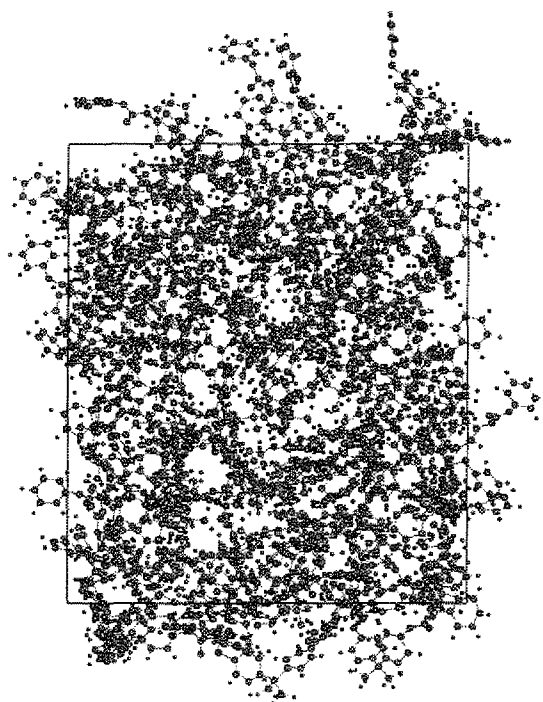
Figure 4.17: Average volume as a function of the temperature for a sample of 72 DPBC molecules. The error bars represent the standard deviations of statistically independent sub-averages.

The plots of U and V as a function of T are reported in Fig. 4.16 and Fig. 4.17, respectively, and show that they increase smoothly with increasing temperature, both at low and high temperatures. At 700 K a discontinuity appears in both plots, indicating a first order transition. The simulation snapshots show that the transition is due to the melting of the system: at $T = 400$ K the system appears clearly in its crystalline phase, despite of the disorder present in any hot solid. At $T = 700$ K the translational order is lost, and the molecules diffuse, slowly but steadily, throughout the simulation cell. At the highest temperature of our simulation (1000 K), the system displays large density fluctuations, and liquid and vapour phase seem to coexist in the system (see Fig. 4.18).

However, the discontinuity at 700 K must not be identified with the melting temperature of the system, as the temperature at which the translational order is lost in heating a crystal during an atomistic simulation represents only an upper bound of the thermodynamic melting temperature T_M . To clarify this point, let us consider the schematic phase diagram in Fig. 4.19. Starting from a state (A) well into the crystal phase and progressively heating the system, we will cross the solid-liquid line at the point (M), defined



$T = 0 \text{ K}$



$T = 1000 \text{ K}$

Figure 4.18: System studied in the MC simulation (72 DPBC molecules, 4248 atoms). We show its “immobile” crystal structure at 0 K, and that equilibrated at 1000 K.

as the thermodynamic state for which the free energy of the two phases is equal. Above this temperature, the free energy of the liquid is lower than that of the solid phase. Nevertheless, the simulated system will not transform to the liquid phase at this point, because this discontinuous process requires the nucleation of the new phase into the old one, and this, in turn, requires to overcome a significant free energy barrier. For this reason, the transformation will occur in the microscopic time of an atomistic simulation only by applying a significant over-heating (see point (B) in Fig. 4.19). In this case the system, which is already in a thermodynamically metastable phase, becomes mechanically unstable, and transforms spontaneously to the new phase.

A precise determination of T_M requires a series of lengthy simulations in order to compute the free energy of the system in the solid and liquid phases, and to find their crossing point. We have not performed this analysis yet, and our simulation determines only an upper bound (between $T = 600$ K and $T = 700$ K) for the melting temperature. Nonetheless, these computations have provided a series of well equilibrated systems in the crystal and liquid phase, and we now present an analysis of their structural properties.

The simplest characterization of the structure of a system at non-zero temperature is given by the so-called *radial distribution functions* $g_{\alpha\beta}(r)$ [109],

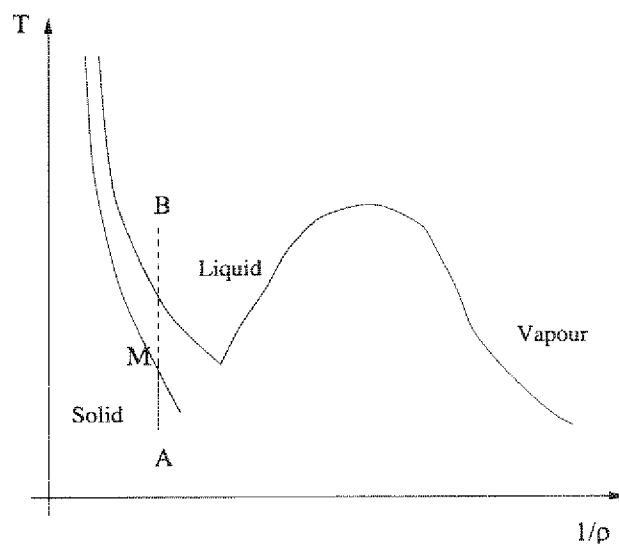


Figure 4.19: Schematic phase diagram in the temperature-volume plane.

where the indexes α and β label the atomic species. These functions describe the average distribution of atoms of type β around an atom of type α . More precisely, if we assume a type α atom as the center of the coordinate system, the average number $dN_{\alpha\beta}$ of β -type atoms found in a volume element $dV = 4\pi r^2 dr$ at a distance r from the origin is given by:

$$\langle dN_{\alpha\beta}(r) \rangle_T = \rho_\beta g_{\alpha\beta}(r) dV, \quad (4.10)$$

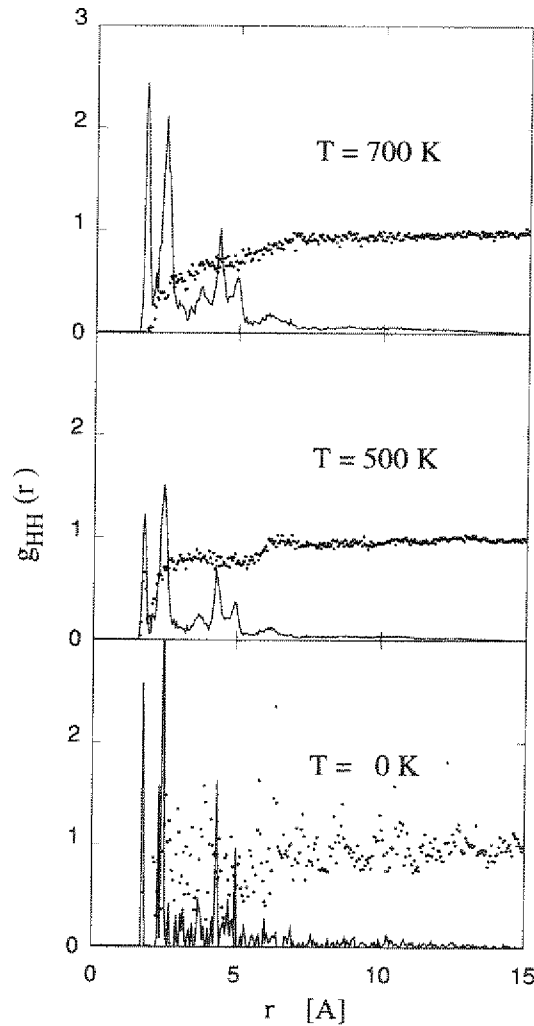


Figure 4.20: Radial distribution function for the H-H pairs at several temperatures. The solid line refers to the *intra*-molecular distances, and the dots to the *inter*-molecular distances.

where ρ_β is the average density of atoms β , and the $\langle \dots \rangle_T$ brackets indicate thermal averaging at temperature T .

In Fig. 4.20 and Fig. 4.21 we display the radial distribution functions for the hydrogen-hydrogen and carbon-carbon pairs, respectively, at three different temperatures. In these figures we distinguish the intra-molecular contribution (full line) from the inter-molecular one (dots). The behaviour illustrated in the two figures is typical of organic molecular solids. In each case, the radial distri-

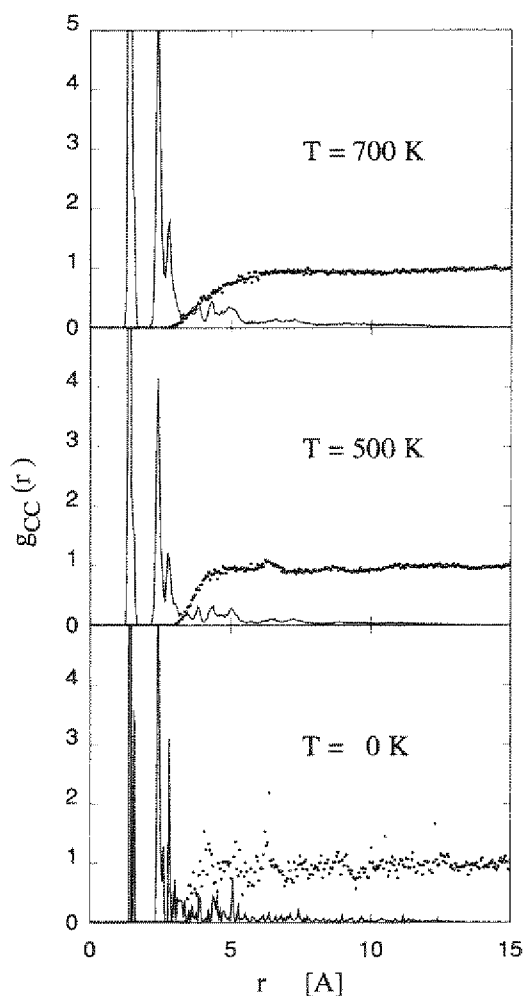


Figure 4.21: Radial distribution function for the C-C pairs at several temperatures. The solid line refers to the *intra*-molecular distances, and the dots to the *inter*-molecular distances.

bution function at $T=0$ is simply given by a series of delta functions (slightly broadened in our figures), corresponding to the homogeneity of the interatomic distances in the crystal. Since these molecular crystals are rather complex, the sequence of discrete distances becomes fairly dense with increasing r , almost approaching a continuous distribution. Of course, the intra-molecular part is short range, because of the finite diameter of each molecular unit. The inter-molecular component tends to unity for large values of r , corresponding to the loss of correlation in the distribution of the β component with increasing distance from the central atom. At short distance every radial distribution function must vanish, because of the short range repulsion of the interatomic potentials. With increasing temperature, the discrete structure of the radial distribution functions is lost rapidly. At $T = 500$ K, i.e., in the hot solid, there is some residual correlation in the atomic positions, which is apparent from the shape of the inter-molecular component of $g_{\alpha\beta}(r)$ around 5–7 Å. In the liquid phase at $T=700$ K this component of radial distribution function is smoother, and approaches monotonically the asymptotic value. As expected, the intra-molecular part of $g_{\alpha\beta}(r)$ is much less sensitive to the temperature than the inter-molecular contribution, as it is determined by the interatomic distances and angles given by the intra-molecular covalent bonds and by the short range repulsion, whose energy scale far exceeds thermal energies.

Another important characterization of the system structure is provided by the probability distribution of bending and torsional angles. For the system considered in our MC simulation we show in Fig. 4.22 the probability distribution $P(\Phi)$ for the Φ_1 and Φ_2 torsional angles – defined in Chart 4.4 – which is of special interest, as it describes the equilibrium correlation in the orientation of the phenylene rings.

Also in this case, the probability distribution is the sum of a series of delta functions at $T=0$. The distribution broadens quickly with increasing temperature, because the potential and the free energy required to rotate the rings is rather low, as it was described in Sect. 4.2. With further increase of the temperature (beyond $T = 500$ K), the probability distribution is no longer sensitive to the temperature, and does not show dramatic changes upon melt-

ing. This observation suggests that the system makes a transition to a state characterized by rotational disorder already in the solid phase, and the residual angular correlation is determined by strong, short range inter-molecular interactions, which do not change much upon melting. These preliminary results are not sufficient to ensure that this rotational disordering corresponds to a phase transition, as it could simply be the result of the gradual and continuous increase of orientational disorder. Further investigations of this point are in progress.

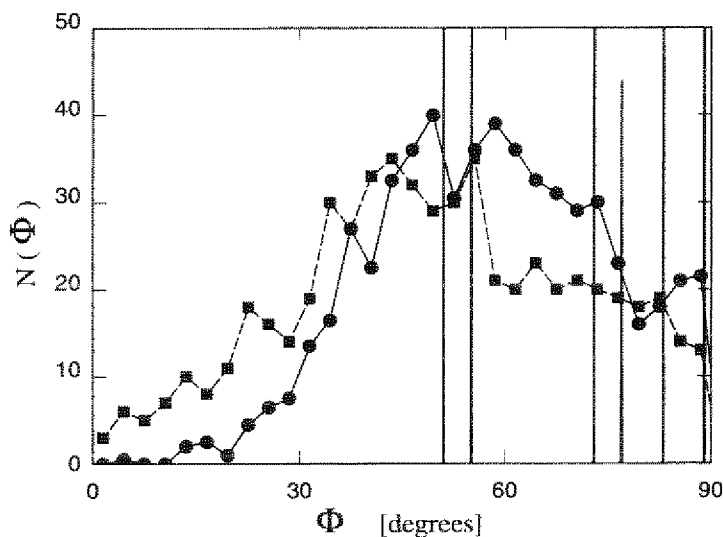


Figure 4.22: Distribution of the $\Phi_{1,2}$ angles at 0 K (vertical lines), 500 K (dotted solid line), and 700 K (broken line with squares).

II. An estimate of the time scale of our simulation

The system evolution during a MC simulation has no direct relation to the true system dynamics. Nevertheless, we may estimate the order of magnitude of the averaging time equivalent to our Monte Carlo sampling by counting how many times (N_r) a rare (i.e., activated) event occurs in the simulation. The rate ν at which these events are expected in real time is given by the

standard Arrhenius expression:

$$\nu = \nu_0 \exp(-\Delta/kT), \quad (4.11)$$

where ν_0 is a characteristic frequency scale, and Δ is the free energy barrier for the activated state. Then, we may estimate the time scale of the simulation by setting:

$$\tau = N_r/\nu. \quad (4.12)$$

In the case of BPA-PC, there is indeed a kind of natural clock, provided by the π -flip of the phenylene rings. The process is activated ($\Delta = 8$ kcal/mol), it can be detected easily in NMR experiments, and it occurs on a mesoscopic time scale (from nanoseconds in the liquid state to microseconds in the solid at room temperature).

In our simulation of a 72 molecules sample at 700 K, we observe, on average, a number of flips of the order of one flip per ring. The frequency scale ν_0 is given by the frequency of the vibrational modes corresponding to rotations of the phenylene rings. These modes occur at rather low frequency, because of the substantial momentum of inertia of the ring. From the vibrational spectra that we have computed, we may estimate this frequency to be around 400 cm^{-1} , i.e., 10^{10} Hz . Therefore we have:

$$\tau = 1/(10^{10} \times \exp(-\Delta/kT)) = 32 \text{ ns}. \quad (4.13)$$

We underline that this identification is not rigorous, and we use this relation only on an intuitive basis to estimate the time scale of our simulation. It is nevertheless apparent the enormous advantage offered by classical potential model with respect to a parameter-free DFT-based simulation. At present, the latter technique allows us to simulate systems of up to ~ 200 atoms for a few ps at most, using the most powerful parallel computers that are available. The force-field simulation of 72 DPBC molecules (4248 atoms) instead, as been simulated for a time of the order of 30 ns using a single CPU workstation, at a cost that is orders of magnitude lower than the one required by the DFT computations.

III. Surface properties of amorphous DPBC

The high computational efficiency of the classical simulation scheme allows us to address the problem of the surface properties of amorphous DPBC samples, which is currently well outside the reach of DFT computations.

We start our simulation from the liquid sample described in Paragraph I of this section, equilibrated at $T = 700$ K, and we remove the periodic boundary conditions in the z direction, while keeping the system periodic in the xy plane (the choice of the x , y and z directions is immaterial, since the liquid sample is isotropic). We create in this way a slab with two parallel surfaces perpendicular to the z axis (sample AS). The system is quenched discontinuously to 0 K, and relaxed during 10^7 MC steps, during which also the periodicity in the xy plane is allowed to change. This relaxation stage is required to remove most of the strain introduced in the system by the discontinuous change of the boundary conditions and temperature.

The final configuration is an amorphous slab, whose central simulation cell is almost cubic, with a side of ~ 40 Å. To isolate the effect of the surface

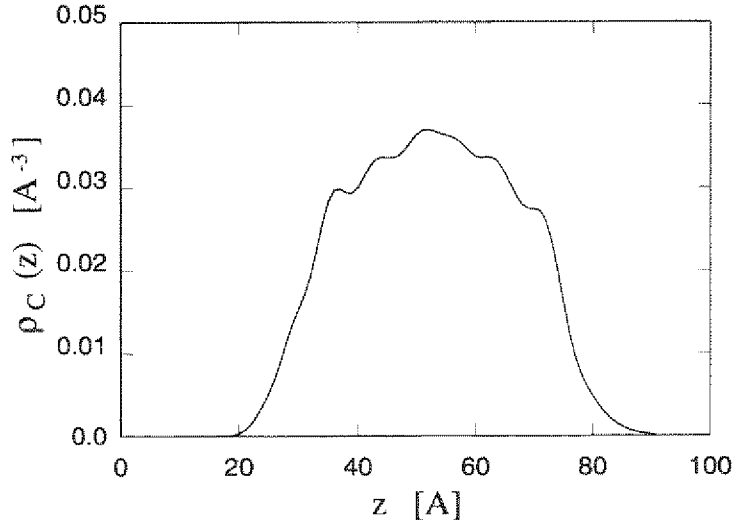


Figure 4.23: Average density of C atoms across an amorphous slab of DPBC molecules.

discontinuity from the effect of the quenched disorder, we prepared another sample by quenching the $T = 700$ K liquid without changing the periodic boundary conditions (sample AB). Also this sample is relaxed during 10^7 MC steps.

The first property we analyse is the surface energy. Since sample (AS) and sample (AB) have been prepared by the same thermal cycle, the difference in their potential energy can be attributed to the formation of the two parallel surfaces of sample (AS). By dividing this energy difference (equal to 146 kcal/mol) by the sum of their areas, we estimate the low temperature surface energy of amorphous DPBC to be 18 erg/cm^2 , which is in the typical range of surface energies for polymeric materials [110].

The structure has been characterized by looking at the density profile across the surface, and by analysing the surface topography. The density

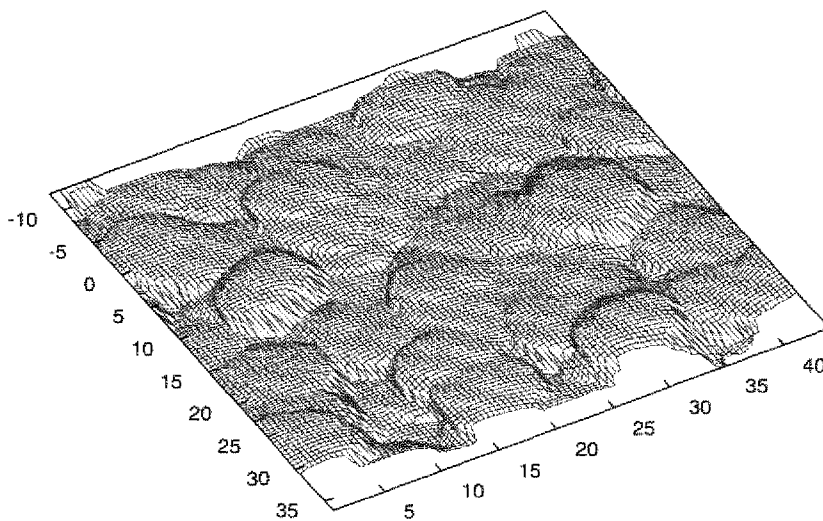


Figure 4.24: Example of an application of the MC simulation for studying surface properties. AFM image of a free surface of the amorphous DPBC.

profile $\rho_\alpha(z)$ is the density of atoms of species α averaged over the xy plane at height z . In the case of non-zero temperature, $\rho_\alpha(z)$ contains also a thermal average. The result for $\rho_C(z)$ at $T = 0$ is reported in Fig. 4.23. We see that the surface region (defined as the region where the density changes from 10 % to 90 % of the bulk value) is broad, having a width of ~ 10 Å.

The surface topography is the property that is probed by scanning tunneling and atomic force microscopy (STM and AFM, respectively) [111]. In our simulation, we mimic the AFM exploration of the surface by moving an additional atom above the sample surface (in our study we used an hydrogen atom), and by drawing the surfaces of constant potential energy or constant force on the “external” atom. The “external” atom in our simulation represents an oversimplified model of the AFM tip. More realistic atomistic models could be simulated with only a minor increase in the computational cost and complexity. In Fig. 4.24 we report the surface of zero force measured on the (AS) sample. This is defined as the surface dividing the attractive from the repulsion region in the surface potential energy and it is sometimes measured in AFM experiments. In the simulated measurements, we see that the surface is fairly regular, and we can distinguish the structure of the phenylene rings, which tend to be oriented parallel to the surface.

IV. A molecular dynamics investigation of the BPA-PC polymer

The final aim of the force field modellization is the simulation of the technologically relevant amorphous BPA-PC, i.e., of the disordered polymeric material with chains composed by $\sim 10^2$ monomers. Preliminary computations for this system have been performed in collaboration with a research group at the Max-Planck Institut for Polymer Research in Mainz [108]. A system consisting of 80 chains, each consisting of 16 chemical repeat units, (corresponding to approximately 30000 atoms) has been simulated by Molecular Dynamics (MD), using the force field parametrized as described above. The simulation was performed using a cubic box with a lattice parameter of 70 Å, and equilibrated at 570 K for a time interval of 100 ps. The resulting structure has been characterized in terms of the coherent structure factor $S(q)$, as a func-

tion of the wave vector q in the reciprocal space. $S(q)$ is the quantity directly accessible by the measurements. More precisely, if the system is composed by a set of n atoms, the j -th atom having a scattering length ℓ_j (dependent on the isotopic species), the coherent structure factor is defined by:

$$S(q) = \left| \sum_j \ell_j \exp(i\mathbf{q} \cdot \mathbf{r}_j) \right|^2. \quad (4.14)$$

The contribution of the different atom types can be identified by changing the isotopic composition of the sample, thus altering the corresponding scattering length. In the case of organic molecules, one of the most common substitutions is the sample enrichment in deuterium. The comparison of the computed and measured $S(q)$ is carried out in Fig. 4.25 for a sample of normal isotopic composition, and in Fig. 4.26 for a deuterated sample. We see that the agreement is only qualitative: the position of the main peak is correctly reproduced, and the correspondence in high- q region is also fairly good. However, the shape of the main peak is not well reproduced by the computations and the low- q region (describing the long wave length correlations) is also rather different. The discrepancies may be due to several reasons: (i) the length of the simulated

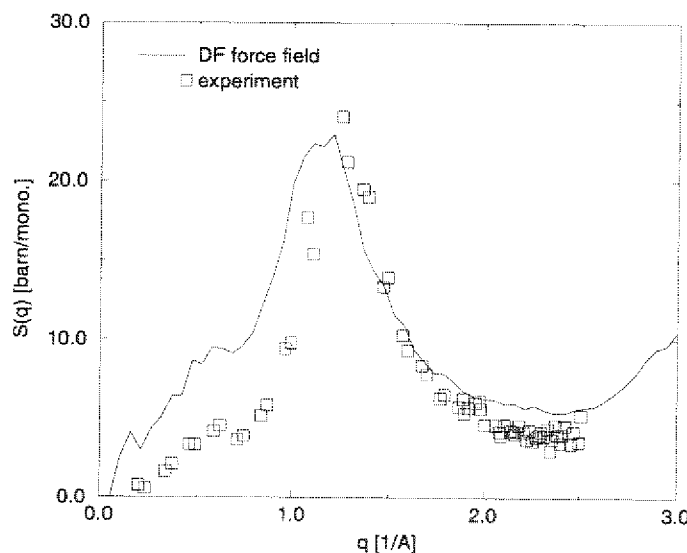


Figure 4.25: Static coherent structure factor $S(q)$ of undeuterated BPA-PC as function of the wave vector q .

chains is shorter than in the experiment; (ii) all the chains in the simulation have the same length, while in the experiment they are distributed according to a given probability law; (iii) the time spanned by the simulation may still be too short to fully equilibrate the system, and this would especially affect the long wave-length properties; (iv) finally, the experimental sample may have inhomogeneities on the mesoscopic scale, which also would modify the low- q part of the structure factor. Despite the partial disagreement, however, it is encouraging to be able to reproduce qualitatively the properties of such a complex system on the basis of combined DFT/FF computations.

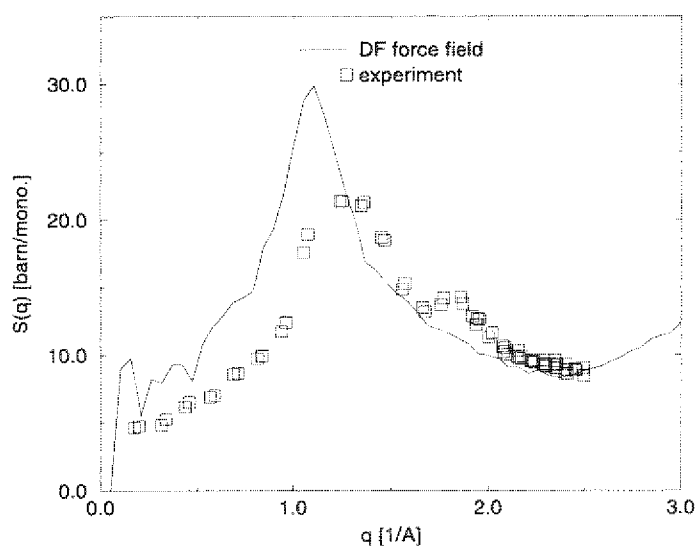


Figure 4.26: Static coherent structure factor $S(q)$ of methyl-deuterated BPA-PC as function of the wave vector q .

Conclusions

We have applied the density functional theory (DFT) to the study of *isotactic* polypropylene (*it*-PP), polyethylene (PE), and systems closely related to bisphenol-A polycarbonate (BPA-PC). Our investigation has focused on their structural, electronic, vibrational, and dynamical properties both in the isolated configuration and crystalline phases.

The first important result of this work is that present-day powerful computers, together with efficient programming techniques, allow calculations on very complex systems – with up to several hundred atoms – to be performed without adjustable parameters.

As described in Chapter 1, the reliability of the DFT results depends on the quality of the approximation to the exchange-correlation energy used in the computation. In our study we have tested three different approximations, namely the local spin-density (LSD) functional and the generalized-gradient approximations (GGA) of Becke and Perdew (BP) and of Perdew, Burke, and Ernzerhof (PBE). All three approximations provide very reliable *intra*-molecular structural parameters for all systems studied here, but they differ dramatically in the description of the weak *inter*-molecular interactions. In particular, the LSD approximation overestimates the strength of the intermolecular bonds in both PE and in a crystalline analog of BPA-PC, i.e., it leads to smaller volumes than those found experimentally. On the other hand, the gradient-corrected BP functional leads to *no binding* between the PE chains and to a very weak bond in the polycarbonate. The PBE functional provides a much better description of these interactions, although also in this case the intermolecular attraction is underestimated and the measured equi-

librium volumes are overestimated. These results are consistent with previous tests on much simpler systems reported in the literature, and indicate that a sophisticated, fully non-local treatment of the exchange-correlation energy is required to reproduce all the structural properties of molecular crystals.

Nevertheless, all three functionals reproduce the measured geometries very well if the unit cell is *constrained* to have the experimental dimensions. It is often difficult to measure the precise location of the atoms in the unit cell of complex systems, and the quality of our structural results shows that DFT calculations can play a valuable role in complementing and refining the experimental structural information for such systems.

The calculations of the vibrational frequencies and of the corresponding eigenvectors contribute to the identification of the interactions responsible for the structural features of the systems, and are an important help for the experimental analysis of the vibration spectra, because enable us to determine the nature of the vibration associated with the individual frequencies.

For both *isotactic* polypropylene and BPA-PC polymer chains, we have performed calculations on smaller molecules that correspond to isolated fragments of the chains. In particular, we have investigated propane, several conformers of isopentane, and 2,4,6-trimethyl heptane, which correspond to segments of the infinite chain of *it*-PP. Among the systems related to BPA-PC, we have studied segments of the infinite chain up to the DPBC molecule, whose experimentally determined crystal structure is analogous to the crystalline BPA-PC, and also the cyclic dimer and tetramer carbonates. The results show that much structural information is *transferable* from the molecular segments to larger systems. This enables us to isolate the effects of *sub*-molecular interactions on both the structural and vibrational properties, and justifies the use of the present data for the parametrization of force fields that are applied for the study of much larger systems (see below).

For PE, DPBC, and the cyclic dimer and tetramer carbonates, the comparison of the results obtained for the gas and crystal phases allows us to identify the influence of the *inter*-molecular interactions. In particular, this analysis lead to two important conclusions for the polycarbonate systems: First, the

CONCLUSIONS

computation of the activation barriers for the rotation of functional groups in the DPBC molecule, both in the isolated and crystalline phases, allows us to understand whether the hindrance to these motions arises from interactions *within* the molecule, or to close packing of the molecules. Furthermore, we have found that the phenylene rings rotate freely in the isolated molecule, but the corresponding motion in the crystalline phase is hindered by the neighbouring molecules. These results, which are in good agreement with experiment, allow us to identify to which ring in the molecule the measured barrier refers. Second, we have found that the most stable conformation around the carbonate group for segments of the BPA-PC chain is generally *trans-trans*, although the energies of the *cis-trans* conformations are only slightly higher. Strain in cyclic dimer is sufficient to favour the latter conformation. Both conformations are present in amorphous BPA-PC, and previous work – supported now by the present results – suggests that the less favoured conformation is stabilized by interchain forces.

The DFT, free of adjustable parameters, retains the quantum nature of the electrons, and therefore has many advantages over the methods based on modelled and parametrized force laws. For example, DFT calculations can describe structural features due to peculiarities of the local electronic distribution, and can be used to study chemical reactions. However, very large systems, not yet addressable by a parameter-free method, are needed for specific applications in polymer science. In this case, DFT can still play an important role providing an extended, homogeneous, and flexible data base for designing a reliable force field (FF) applicable for the study of such systems. We have used this combined approach to study a polycarbonate system containing several thousand atoms. The DFT results served two distinct goals: (i) to identify which interatomic interactions determine the structural and dynamical properties of these systems; (ii) to tune the parameters of the modelled potential until it reproduced the DFT structures, vibration frequencies, and rotation energy barriers calculated in this work.

Preliminary results of a Monte Carlo simulation based on this force field concern bulk and surface structural properties of an amorphous systems, and

its melting transition. These results are encouraging, and show that the combination of DFT and FF simulation should be a powerful tool for addressing a wide range of relevant problems.

Acknowledgments

First, I want to thank Dr. Robert O. Jones for his constant support and presence during these three years, and for having shared with me part of his vast knowledge and experience. For his constant care, self-discipline, and passion for his work he is an example that I will always keep in mind.

I am grateful to Prof. Gert Eilenberger for his stimulating questions, for his exemplary vivid and open-minded interest in many areas of physics, and for the friendly atmosphere he has created in the Theory I group of the IFF.

Special thanks are devoted to Prof. Pietro Ballone, for his generous help, enlightening answers and discussions, for supporting me with his advice, and for having taught me a correct attitude towards scientific questions. Thanks to his enthusiasm for science and sense of humor, working with him has always been exciting and pleasant.

I thank all the Theory I group, in particular Silke Biermann, with whom I shared much more than just the office. With her never-ending optimism, she has been an important support not only for scientific problems. Thanks also to Dr. Angela Borrmann, with whom I have enjoyed our collaboration.

I want to thank all the friends I met here in Jülich. In particular, Jung-hsing Lin and Tomas Sintes for interesting and amusing discussions, Xia Feng and Oliver Pfaffenzeller, Michael Krenzlin, Kiaresh Mussawisade, Karl-Heinz Herrmann and K. Sumithra. All my house-mates were for me a great company after work: Roberta Lantier is a sister more than a friend, and we have really grown together; the true friendship with Alessandra will always be with me; thanks also to Max, Alberto, Cristina, Ute, and Theo. Among the people with whom I enjoyed life in Germany Andreas, Fulvia, Boris, Lothar, Valerio, Ralf,

ACKNOWLEDGMENTS

Carla, Rossano, Jochen, Volker, Frank, Uli, Ugo and Flavio, deserve special mention.

The distance did not affect my precious friendship with Alice and Marco, who were with me “on line” day by day. A special thank also to Valdis and Fabio, and to my old friends Elisa, Barbara, and Paolo.

My brother Marco and Rita were for me an important support. Finally, I thank my parents for their immense love, and for trusting me for all the important decisions of my life.

For the CPU time on the Cray T916/12512, T3E-600/512 and T3E-900/256 I thank the Forschungszentrum Jülich and the German Supercomputer Centre (HLRZ).

This work has been supported by the MaTech Program of the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie, Bonn. I thank all the participants in this program for the helpful discussions.

Appendix

Monte Carlo Method

The Monte Carlo (MC) method is a computational technique for estimating the values of many-dimensional integrals [34], and it is widely applied in the field of classical statistical mechanics, where the basic problem is indeed the evaluation of such integrals.

To illustrate this point, let us consider, for instance, an N -dimensional system, in the canonical ensemble, described by the Hamiltonian $\mathcal{H}$. The average of any observable $\mathcal{A}$ of this system is given by the integral:

$$\langle \mathcal{A} \rangle = \int \mathcal{A}(\mathbf{q}^N) w(\mathbf{q}^N) d\mathbf{q}^N, \quad (\text{A.1})$$

where

$$w(\mathbf{q}^N) = \frac{e^{-\beta \mathcal{H}}}{\int e^{-\beta \mathcal{H}} d\mathbf{q}^N}. \quad (\text{A.2})$$

$\mathbf{q}^N = (\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)$ are the configurational variables, $\beta = 1/kT$, and k is the Boltzmann constant. The normalization integral in Eq. (A.2) is the canonical partition function. The straightforward way to estimate $\mathcal{A}$ would be to sample the configurational space with a configuration of random points uniformly distributed in the volume of the system, and then calculate $\mathcal{A}(\mathbf{q}^N)$ and $w(\mathbf{q}^N)$ for such configuration. The average of $\mathcal{A}(\mathbf{q}^N)w(\mathbf{q}^N)$ over many of these configurations gives an estimate for $\langle \mathcal{A} \rangle$. Unfortunately, this strategy is not feasible, mainly because we cannot compute the canonical partition function $\int e^{-\beta \mathcal{H}} d\mathbf{q}^N$, as it is a high-dimensional integral and contains the rapidly varying Boltzmann factor $e^{-\beta \mathcal{H}}$.

This problem is circumvented in the MC technique, where the successive sample configurations, rather than being independent, are chosen as elements of a so-called *Markov chain* [112]. In this way, this algorithm never needs to compute the canonical partition function, but it is only necessary to evaluate the *ratios* of $w(\mathbf{q}^N)$ for successive configurations. This is easy to do since the denominators $\int e^{-\beta\mathcal{H}} d\mathbf{q}^N$ cancel.

The standard method used to construct the Markov chain, which was originally proposed by Metropolis *et al.* [113], is exploited in the following way:

- (1) start from a likely initial configuration,
- (2) choose at random a configurational variable $\mathbf{q}_i$ (or a set of such variables) and attempt a trial “move” in which the variable assumes a new value, usually distributed uniformly in a cube of fixed size centred at the old value,
- (3) calculate the change in energy ΔE due to this trial move. If the energy is decreased the move is accepted. If the energy is increased the move is accepted with probability $e^{-\beta\Delta E}$ and rejected with probability $1 - e^{-\beta\Delta E}$.

This process is repeated to form a sequence of configurations that are the realization of a Markov chain.

Having constructed the sequence of sampling configurations in this way, and under the condition that each configuration in the Markov chain can be reached from every other configuration in the chain (*ergodicity* condition), it can be proved [114] that the distribution of the sampled configurations approaches the Boltzmann distribution as the length of the Markov chain approaches infinity. In this way one is sampling on the Boltzmann distribution itself, and the average of $\mathcal{A}$ over the sampled configurations will itself give the canonical average of Eq. (A.1).

This presentation of the Monte Carlo method has been limited to the basic ideas. See Refs. [115, 116, 117, 36] for further reading.

Bibliography

- [1] R. Colle and A. Curioni, J. Am. Chem. Soc. **120**, 4832 (1998).
- [2] E.J. Bylaska, P.R. Taylor, R. Kawai, and J.H. Weare, J. Phys. Chem. **100**, 6966 (1996).
- [3] A. Borrmann and R.O. Jones, Chem. Phys. Lett. **252**, 1 (1996).
- [4] S. Hirata and S. Iwata, J. Chem. Phys. **108**, 7901 (1998).
- [5] M. Boero, M. Parrinello, and K. Terakura, J. Am. Chem. Soc. **120**, 2746 (1998).
- [6] J. Baker, M. Muir, and J. Andzelm, J. Chem. Phys. **102**, 2063 (1995).
- [7] M. Born and R. Oppenheimer, Ann. Phys. **84**, 457 (1927).
- [8] P. Hohenberg, W. Kohn, Phys. Rev. **136**, B864 (1964).
- [9] A. Nagy, Physics Reports **298**, 2 (1998).
- [10] R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).
- [11] H. Eschrig, *"The Fundamentals of Density Functional Theory"* (Teubner, Stuttgart - Leipzig, 1996).
- [12] R.G. Parr and W. Yang, *"Density-Functional Theory of Atoms and Molecules"* (Oxford University Press, New York, 1989).
- [13] W. Kohn, L.J. Sham, Phys. Rev. **140**, A1133 (1965).
- [14] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

- [15] G. Ortiz and P. Ballone, Phys. Rev. B **50**, 1391 (1994).
- [16] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [17] O. Gunnarsson and B.I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
- [18] C. Lee, D. Vanderbilt, K. Laasonen, R. Car, and M. Parrinello, Phys. Rev. B **47**, 4863 (1993).
- [19] J.M. Pérez-Jordá and A.D. Becke, Chem. Phys. Lett. **233**, 134 (1995).
- [20] E.J. Meijer and M. Sprik, J. Chem. Phys. **105**, 8684 (1996).
- [21] See, for example, A.D. Becke, J. Chem. Phys. **96**, 2155 (1992).
- [22] A. Dal Corso, A. Pasquarello, and A. Baldereschi, Phys. Rev. B **53**, 1180 (1996).
- [23] D.R. Hamann, Phys. Rev. B **55**, R10157 (1997).
- [24] K. Laasonen, F. Csajka, and M. Parrinello, Chem. Phys. Lett. **194**, 172 (1992).
- [25] A.D. Becke, Phys. Rev. A **38**, 3098 (1988).
- [26] J.P. Perdew, Phys. Rev. B **33**, 8822 (1986).
- [27] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [28] G.P. Srivastava and D. Weaire, Adv. Phys. **36**, 463 (1987).
- [29] J.C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959); F. Bassani and V. Celli, J. Phys. Chem. Solids **20**, 64 (1961); for further references see F. Bassani and G. Pastori Parravicini, *“Electronic States and Optical Transitions in Solids”*, edited by R.A. Ballinger (Pergamon Press, Oxford, 1975).
- [30] D.R. Hamann, M. Schlüter, C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

BIBLIOGRAPHY

- [31] M.L. Cohen, T.K. Bergstresser, Phys. Rev. **141**, 789 (1966); V. Heine, I. Abarenkov, Phyl. Mag. bf 9, 451 (1964); A.O.E. Animalu, Phyl. Mag. **11**, 379 (1965); I. Abarenkov, V. heine, Phyl. Mag. **12**, 529 (1965).
- [32] G.B.Bachelet, D.R. Hamann, M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
- [33] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).
- [34] H.W. Press, P.B. Flannery, S.A. Teukolsky, and W.T. Vetterling, "*Numerical Recipes*" (Cambridge University Press, 1986).
- [35] I. Štich, R. Car, M. Parrinello, and S. Baroni, Phys. Rev. B **39**, 4997 (1989).
- [36] See, for instance, M.P. Allen and D.J. Tildesley, "*Computer Simulations of Liquids*" (Clarendon, Oxford, 1987); G. Ciccotti and G. Hoover, "*Molecular Dynamics Simulation in Statistical Mechanical Systems*" (North Olland, 1986).
- [37] P. Ehrenfest, Z. Phys. **45**, 455 (1927); R.P. Feynman, Phys. Rev. **56**, 340 (1939); see also B.M. Deb, Rev. Mod. Phys. **43**, 22 (1973).
- [38] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
- [39] R. Car and M. Parrinello, "*Simple Molecular Systems at Very High Density*", edited by A. Polian, L. Loubeyre, and N. Boccara, p. 455 (Plenum Press, New York, 1988).
- [40] G. Galli and M. Parrinello, "*Computer Simulations in Material Science*", edited by M. Meyer and V. Pontikis, p. 283 (Plenum Press, New York, 1991); G. Galli and A. Pasquarello, "*Computer Simulations in Chemical Physics*", p. 261 (Kluwer, Netherlands, 1993).
- [41] T. Oguchi and T. Sasaki, Progr. Theoret. Phys. Suppl. **103**, 93 (1991).
- [42] M.C. Payne, M.P. Teter, D.C. Allen, T.A. Arias, and J.D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

- [43] D.K. Remler and P. Madden, *Mol. Phys.* **70**, 921 (1990).
- [44] R.O. Jones, "*Density-functional Methods in Chemistry and Material Science*", edited by M. Springborg (John Wiley & Sons Ltd, 1997); "*Density Functional Theory*", edited by E.K.U. Gross and R.M. Dreizler, p. 273 (Plenum Press, New York, 1995); "*Computational Approaches to Novel Condensed Matter Systems*", edited by D. Neilson and M.P. Das, p. 37 (Plenum Press, New York, 1995).
- [45] S. Kirkpatrick, C.D. Gelatt, and M.P. Vecchi, *Science* **220**, 671 (1983).
- [46] N. Binggeli, J.L. Martins, and J.R. Chelikowsky, *Phys. Rev. Lett.* **68**, 1992 (1992).
- [47] L. Schäfer, K. Siam, J.D. Ewbank, and E. Ogawa, *J. Mol. Struct. (Theochem)* **139**, 125 (1986).
- [48] L. Schäfer, K. Siam, and J.D. Ewbank, *J. Mol. Struct. (Theochem)* **188**, 111 (1989).
- [49] Thanks to S. Baroni and S. de Gironcoli for providing the program used for these calculations.
- [50] G. Natta and P. Corradini, *Nuovo Cimento Suppl.* **15**, 40 (1960).
- [51] For a description of the special points technique see, for example, D.J. Chadi and M.L. Cohen, *Phys. Rev. B* **8**, 5747 (1973); H.J. Monkhorst and J.D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [52] DGauss program from the UniChem package of Cray Research, Inc.
- [53] R.M. Dickson and A.D. Becke, *J. Chem. Phys.* **99**, 3898 (1993).
- [54] D.R. Beckett, J.M. Chalmers, M.W. Mackenzie, H.A. Willis, H.G.M. Edwards, J.S. Lees, and D.A. Long, *Eur. Polym. J.* **21**, 849 (1985).
- [55] A. Bunn, M.E.A. Cudby, R.K. Harris, K.J. Packer, and B.J. Say, *Polymer* **23**, 694 (1982).

BIBLIOGRAPHY

- [56] I. Flamant, D.H. Mosley, M. Deleuze, J.M. Andre, and J. Delhalle, *Int. J. Quantum Chem. Symposium* **28**, 469 (1994).
- [57] A. Immirzi and P. Iannelli, *Macromolecules* **21**, 768 (1988).
- [58] D.J. Lacks and G.C. Rutledge, *Chem. Eng. Sci.* **49**, 2881 (1994).
- [59] D.R. Ferro, S. Brückner, S.V. Meille, and M. Ragazzi, *Macromolecules* **25**, 5231 (1992).
- [60] C.W. Bunn, *Trans. Farad. Soc.* **35**, 482 (1939).
- [61] H.M.M. Shearer and V. Vand, *Acta Cryst.* **9**, 379 (1956).
- [62] P.W. Teare, *Acta Cryst.* **12**, 294 (1959).
- [63] S. Kavesh and J.M. Schultz, *J. Polym. Sci. Part A-2* **8**, 243 (1970).
- [64] G. Avitabile, R. Napolitano, B. Pirozzi, K.D. Rouse, M.W. Thomas, and B.T.M. Willis, *Polym. Lett. Ed.* **13**, 351 (1975).
- [65] G. König and G. Stollhoff, *J. Chem. Phys.* **91**, 2993 (1989).
- [66] B. Champagne, J.G. Fripiat, J.M. André, *Physica Mag.* **14**, 123 (1992).
- [67] M.S. Miao, P.E. Van Camp, V.E. Van Doren, J.J. Ladik, and J.W. Mintmire, *Phys. Rev. B* **54**, 10430 (1996); PZ denotes the exchange-correlation functional of Ref. [16]; XO denotes the exchange-only LSD approximation.
- [68] K. Seki, N. Ueno, U.O. Karlsson, R. Engelhardt, and E.E. Koch, *Chem. Phys.* **105**, 247 (1986); H. Fujimoto, T. Mori, H Inokuchi, N. Ueno, K. Sugita, and K. Seki, *Chem. Phys. Lett.* **141**, 485 (1987).
- [69] M. Springborg and M. Lev, *Phys. Rev. B* **40**, 3333 (1989).
- [70] K.J. Less and E.G. Wilson, *J. Phys. C: Solid State Phys.* **6**, 3110 (1973).
- [71] J.F. Dobson, *Int. J. Quantum Chem.* **69**, 615 (1998).

-
- [72] Y. Andersson, E. Hult, P. Apell, D.C. Langreth, and B.I. Lundqvist, Solid State Comm. **106**, 235 (1998); see also Y. Andersson, D.C. Langreth, and B.I. Lundqvist, Phys. Rev. Lett. **76**, 102 (1996).
- [73] W. Kohn, Y. Meir, and D.E. Makarov, Phys. Rev. Lett. **80**, 4153 (1998).
- [74] D.C. Patton, D.V. Porezag, and M.R. Pedersen, Phys. Rev. B **55** 7454 (1997); D.C. Patton and M.R. Pedersen, Phys. Rev. A **56**, R2495 (1997) [rare gas dimers].
- [75] I.-H. Lee and R.M. Martin, Phys. Rev. B **56**, 7197 (1997).
- [76] B. Montanari, P. Ballone, and R.O. Jones, submitted for publication (October 16, 1998).
- [77] CPMD program version 3.0, J. Hutter *et al.*, MPI für Festkörperforschung and IBM Research 1990-98.
- [78] See, for instance, G.D. Hawkins, C.J. Cramer, and D.G. Truhlar, J. Chim. Phys. (Paris) **94**, 1448 (1997) for a discussion of electrostatic charges derived from quantum chemistry computations.
- [79] G. Herzberg, *"Infrared and Raman Spectra"*, p.259 ff (Van Nostrand Reinhold, New York, 1945).
- [80] L. Goodman, A.G. Ozkabak, and S.N. Thakur, J. Phys. Chem **95**, 9044 (1991).
- [81] *"CRC Handbook of Chemistry and Physics, 76th Edition"*, edited by D.R. Lide, p. 9-25 (CRC Press, Boca Raton, 1995).
- [82] BLYP: exchange functional of A.D. Becke (see Ref. [25]); correlation functional of C. Lee, W. Yang, and R.G. Parr, Phys. Rev. B. **37**, 785 (1988) (LYP). B3LYP: exchange approximation of A.D. Becke, J. Chem. Phys. **98**, 1372 (1993); correlation functional of LYP.
- [83] H. Sun, S.J. Mumby, J.R. Maple, and A.T. Hagler, J. Phys. Chem. **99**, 5873 (1995).

BIBLIOGRAPHY

- [84] I. Mayer, Chem. Phys. Lett. **97**, 270 (1983).
- [85] H. Sun, S.J. Mumby, J.R. Maple, and A.T. Hagler, J. Am. Chem. Soc. **116**, 2978 (1994).
- [86] P. Schmidt, J. Dybal, E. Turska, and A. Kulczycki, Polymer **32**, 1862 (1991).
- [87] U.C. Singh and P.A. Kollman, J. Comp. Chem. **4**, 129 (1984); L.E. Chirlian and M.M. Francl, J. Comp. Chem. **8**, 894 (1987); B.H. Besler, K.M. Merz, and P.A. Kollman, J. Comp. Chem. **11**, 431 (1990); C.M. Breneman and K.B. Wiberg, J. Comp. Chem. **11**, 361 (1990).
- [88] A. Prietzschk, Kolloid Z. **8**, 156 (1957).
- [89] S. Perez and R. P. Scaringe, Macromolecules **20**, 68 (1987) ["immobile" form].
- [90] P.M. Henrichs and H.R. Luss, Macromolecules **21**, 860 (1988).
- [91] P.M. Henrichs, H.R. Luss, and R.P. Scaringe, Macromolecules **22**, 2731 (1989) ["mobile" form].
- [92] See, for example, F.T. Gentile and U.W. Suter in "*Material Science and Technology*" Vol. 12, edited by R.W. Cahn, P. Haasen, and E.J. Kramer, p. 57 (VCH, Weinheim, 1993).
- [93] J.A. Brydson, "*Plastics Materials*", p. 511 (Butterworth, London, 1982).
- [94] B. Montanari, P. Ballone, and R.O. Jones, Macromolecules **31**, xxxx (1998) (to appear 3 November).
- [95] J. Bicerano and H.A. Clark, Macromolecules **21**, 585 (1988).
- [96] P.M. Henrichs and V.A. Nicely, Macromolecules **24**, 2506 (1991).
- [97] M. Hutnik, A.S. Argon, and U.W. Suter, Macromolecules **24**, 5970 (1991).

- [98] J.H. Walton, M.J. Lizak, M.S. Conradi, T. Gullion, and J. Schaefer, *Macromolecules* **23**, 416 (1990).
- [99] C.F. Fan, T. Çagin, W. Shi, and K.A. Smith, *Macromol. Theory simul.* **6**, 83 (1997). See also C.F. Fan, T. Çagin, Z.M. Chen, and K.A. Smith *Macromolecules* **27**, 2383 (1994).
- [100] D.J. Brunelle and M.F. Garbaskas, *Macromolecules* **26**, 2742 (1993).
- [101] D.J. Brunelle, "*Ring-Opening Polymerization: Mechanisms, Catalysis, Structure, Utility*", edited by D.J. Brunelle (Hanser, München, 1993).
- [102] H. Sun, S. J. Mumby, J. R. Maple, and A. T. Hagler, *J. Am. Chem. Soc.* **116**, 2978 (1994); C. F. Fan, T. Cagin, Z. M. Chen and K. A. Smith, *Macromolecules* **27**, 2383 (1994); J. H. Shih, and C. L. Chen, *Macromolecules* **28**, 4509 (1995); C. F. Fan, T. Cagin, W. Shi, *Macromol. Theory Simul.* **6**, 83 (1997); D. R. Whitney, and R. Yaris, *Macromolecules* **30**, 1741 (1997).
- [103] W.D. Cornell, P. Cieplak, C.I. Bayly, I.R. Gould, K.M. Merz Jr., D.M. Ferguson, D.C. Spellmeyer, T. Fox, J.W. Caldwell, and P. Kollman, *J. Am. Chem. Soc.* **117**, 5179 (1995).
- [104] B. Brooks, R. Bruccoleri, B. Olafson, D. States, S. Swaminathan, and M. Karplus, *J. Comp. Chem.* **4**, 187 (1983).
- [105] M. Clark, R.D. Cramer III, and N. Van Opdenbosh, *J. Comp. Chem* **10**, 982 (1989).
- [106] H.C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).
- [107] M. Parrinello and A. Rahman, *Phys. Rev. Lett.* **45**, 1196 (1980).
- [108] O. Hahn, MPI für Polymerforschung, Mainz (Germany).
- [109] J.P. Hansen and I.R. Mc Donald, "*Theory of Simple Liquids*" (Academic Press, London – New York, 1976).

BIBLIOGRAPHY

- [110] G.T. Dee and B.B. Sauer, Adv. Phys. **47**, 161 (1998).
- [111] H. Lüth, "*Surfaces and interfaces of solids*", second edition (Springer-Verlag, Heidelberg, 1993).
- [112] L. Takacs, "*Stochastic Processes*" (Methuen, London, 1962).
- [113] N. Metropolis, A.W. Metropolis, M.N. Rosenbluth, A.H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
- [114] K.L. Chung, "*Markov Chains with Stationary Transition Probabilities*", Part I (Springer-Verlag, Berlin, 1960).
- [115] J.M. Hammersley and D.C. Handscomb, "*Monte Carlo Methods*" (Methuen, London, 1964).
- [116] D. Frenkel, "*Computer Modelling of Fluids, Polymers and Solids*", edited by C.R.A. Catlow *et al.*, pp. 83-123 (Kluwer Academic Publishers, 1990).
- [117] J.P. Valleau and S.G. Whittington, "*Modern Theoretical Chemistry, 5: Statistical Mechanics, Part A: Equilibrium Techniques*", edited by B.J. Berne, pp. 137-168 (Plenum Press, New York, 1977).

List of Publications

Publications about this work:

- A. Borrmann, B. Montanari, and R. O. Jones: “*Density functional study of polypropylene and its submolecules*”, J. Chem. Phys. **106**, 8545 (1997).
- B. Montanari and R. O. Jones: “*Density functional study of crystalline polyethylene*”, Chem. Phys. Lett. **272**, 347 (1997).
- B. Montanari, P. Ballone, and R. O. Jones: “*Density functional study of molecular crystals: polyethylene and a crystalline analog of bisphenol-A polycarbonate*”, J. Chem. Phys. **108**, 6947 (1998).
- B. Montanari, P. Ballone, and R. O. Jones: “*Density functional study of crystalline analogs of polycarbonates*”, Macromolecules **31**, 7784 (1998).
- B. Montanari, P. Ballone, and R.O. Jones: “*Density functional study of polycarbonate. 2. Crystalline analogs, cyclic oligomers, and their fragments*”, submitted for publication (October 16, 1998).



Forschungszentrum Jülich

J01-3624
January 1999
ISSN 0944-2952