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Multiscale simulations of critical interfacial failure in carbon nanotube-polymer composites.

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Abstract

Functionalised carbon nanotube/polymer composites (CNPC) have received significant interest as promising structural materials with applications in the most demanding areas of industry such as ballistic protection. However, the current generation of CNPCs falls short of their theoretical limit for mechanical properties and improvement is desirable. Quality of the interface between CNTs and polymers are a key factor affecting the reinforcement in CNPCs and developing a fundamental understanding of critical failure at the interface is essential to optimise the properties of this class of materials.

Computer simulations are instrumental in improving our understanding CNPC interfacial failure but their execution can be challenging; the bond-breaking processes at the polymer-CNT attachment point that initiate failure are quantum-mechanical (QM) in nature, yet the mechanisms by which stresses are transferred through the disordered polymer occur on length-scales far in excess of anything that can be simulated quantum-mechanically. In this work, we address this issue with a novel, adaptive quantum mechanics/molecular mechanics (QM/MM) simulation method where the majority of the system is simulated with a classical forcefield, while areas of particular interest are identified on-the-fly and simulated quantum-mechanically. We demonstrate that this method's results are in excellent agreement with fully-QM benchmark simulations and offer qualitative insights missing from classical simulations.

Using this approach, we investigate the effects of interfacial chemistry on the ISS in CNPCs by simulating carbon nanotube pull-out from a crosslinked polyethylene matrix. We find that the choice of the functional group linking the polymer matrix to the nanotube determines the effective interfacial shear strength (ISS), which can be increased up to the limit dictated by the strength of the polymer backbone by choosing groups with higher interfacial binding energy. We rank the functional groups based on the strength of the resulting interface and suggest broad guidelines for the rational design of nanotube functionalisation for CNPCs.

Statement of Originality

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Publications

I have contributed to two publications during the course of my PhD:

1. Golebiowski, J. R., Kermode, J. R., Mostofi, A. A., and Haynes, P. D. (2018). Multiscale simulations of critical interfacial failure in carbon nanotube-polymer composites. *The Journal of Chemical Physics*, 149(22), 224102. <https://doi.org/10.1063/1.5035508>
2. Golebiowski, J. R., Kermode, J. R., and Haynes, P. D. and Mostofi, A. A. Atomistic QM/MM simulations of the strength of covalent interfaces in carbon nanotube-polymer composites. *Submitted to Physical Chemistry Chemical Physics*

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Nomenclature

Carbon nanotubes

$\mathbf{a}_x$ Graphene lattice vector $\mathbf{x}$.

$\mathbf{C}_h$ Chiral vector of the CNT.

k Index used to define CNT chiral vector using graphene lattice vectors.

l Index used to define CNT chiral vector using graphene lattice vectors.

Composite theory

γ Shear strain inside the matrix.

r_f Radius of the fibre in shear lag theory.

ν_x Poisson ratio of $\mathbf{x}$.

$\bar{\sigma}_x$ Average stress on $\mathbf{x}$.

ρ Distance from the center of the fibre in shear lag theory.

σ_x Stress on $\mathbf{x}$.

τ_i Shear stress at the fibre/matrix interface.

$\tau_m(\rho)$ Shear stress inside the matrix at distance ρ from the centre of the fibre.

Υ Empirically chosen measure of reinforcement geometry in the Halpin-Tsai model.

ε_x Strain field of $\mathbf{x}$.

E_x	Elastic modulus of x.
F_{shear}	Shear force.
G_x	shear modulus of x.
l_c	Critical length of the fibres reinforcing a composite.
P_x	Load carried by x.
u_x	Displacement at point x.
V_x	Volume fraction of x.
w	Dimensionless constant used in shear lag theory derivation.
X_c	Subscript corresponding to composite properties.
X_f	Subscript corresponding to fibre properties.
X_i	Subscript corresponding to the fibre/matrix interface.
X_m	Subscript corresponding to matrix properties.
$X_{y,crit}$	Critical value of quantity X of element y.

Classical simulation methods

ι	Time constant in Berendsen thermostat.
κ	Viscosity coefficient in Langevin thermostat.
θ	Free parameters in a classical forcefield.
$\mathbf{F}_i$	Force on particle i .
$\mathbf{p}_i$	Momentum of particle i defined as $\mathbf{p}_i = m\dot{\mathbf{r}}_i$.
$\mathbf{r}_i$	Position of particle i .
$\mathcal{H}$	Hamiltonian.

ζ_{coll}	Characteristic time of collisions in Langevin thermostat.
E	Total energy.
f_{R}	Random force drawn from a Gaussian distribution with zero mean and variance given by the Einstein-Stokes fluctuation-dissipation theorem.
K	Kinetic energy.
k_B	Boltzmann's constant.
m_i	Mass of particle i , total mass of particles if without index.
N	Number of particles in a system.
r	Position.
T	Temperature.
t	Time.
U	Potential energy.
U_{angle}	Energy of three body interactions (angles) in a classical forcefield.
U_{bonded}	Energy of bonded interactions in a classical forcefield.
U_{bond}	Energy of two body interactions (bonds) in a classical forcefield.
U_{coul}	Electrostatic coulomb energy term.
$U_{\text{non-bonded}}$	Energy of non-bonded interactions in a classical forcefield.
U_{torsion}	Energy of four body interactions (dihedral torsion) in a classical forcefield.
U_{vdW}	Van der Waals energy term.
V	Volume.

Quantum simulation methods

δn	Electronic density fluctuation in density functional tight binding.
$E_{BS}[n^0]$	Band structure energy term in density functional tight binding.
$E_{rep}[n^0]$	Repulsive energy term in density functional tight binding.
U_{rep}^{IJ}	Repulsive potential between atoms I and J in density functional tight binding.
χ	Electronegativity.
$\delta \hat{n}_I$	Electronic density profile.
Δq_I	Contribution to the density fluctuation from atom I.
$\mathcal{V}_I$	Volume related to atom I.
ε_a	Lagrange multipliers used in the variational energy minimisation in density functional tight binding.
φ	Atomic orbitals from the minimal basis set.
$\xi(r)$	Analytical function used to approximate electronic density fluctuations in density functional tight binding.
c	Coefficients used to express single particle states in terms of atomic orbitals.
$E_H[n]$	Hartree electron-electron energy functional.
$E_{II}[n]$	Ion-ion interaction energy functional.
$E_{XC}[n]$	Exchange and correlation energy functional.
$E_{sc}[n^0 + \delta n]$	Charge fluctuation energy term in density functional tight binding.
$E[n]$	Total energy functional in density functional theory based methods.
$F_{HK}[n]$	Unique Hohenberg and Kohn energy functional.
f_a	Occupation of single particle state ψ_a .
H	Hamiltonian, H^0 corresponds to $H[n^0]$.

$K_S[n]$	Kinetic energy of non-interacting particles functional.
n^0	Reference electronic density in density functional tight binding.
n	Electronic density in density functional theory based methods.
q_I^0	Reference charge density for atom I given by the number of valence electrons in its neutral state.
q_I	Charge density for atom I.
$U_H[n]$	Hartree electron-electron potential.
$U_{II}[n]$	Ion-ion interaction potential.
$U_{XC}[n]$	Exchange and correlation potential.
U_{ext}	External potential in density functional theory based methods.
U^H	Hubbard parameter.

Hybrid simulation methods

$\mathbf{r}_i$	Position of atom i .
ϵ_i	Energy contribution from atom i in a hybrid simulation approach.
λ	Free parameter used for interpolation between QM and MM forces.
$\mathbf{F}_{\text{MM}}^i$	Atomic force on atom i computed with classical method.
$\mathbf{F}_{\text{QM}}^i$	Atomic force on atom i computed with quantum method.
$\mathbf{F}^i$	Force on i -th atom.
$E_{\text{buffer}}^{(x)}$	Energy of the buffer region of area X.
$E_{\text{inner}}^{(x)}$	Energy of the inner region of area X.
$E_{\text{total}}^{(x)}$	Total energy of area X.

$E_{MM}(X)$ Classical energy of region X.

$E_{QM}(X)$ Quantum mechanical energy of region X.

E_{tot} Total energy of a system.

E_{QMMM}^I Energy of interactions across the QM/MM boundary.

T Temperature.

X_{buff} Buffer region of area X.

Result sections

α Free parameter used to compute the dispersion correction for atomic forces.

η Free parameter used to define energy threshold in Chapter 4.

a Free parameter used to define energy threshold in Chapter 5.

b Free parameter used to define energy threshold in Chapter 5.

d_{CNT} Diameter of a carbon nanotube.

E_{mean}^i Mean energy of atom i during the burnout period.

E_{std}^i Standard deviation of energy of atom i during the burnout period.

E_{thresh}^i Energy threshold for atom i to enter/exit quantum mechanical region.

F^i Force on atoms i .

F_{LJ}^i F on atoms i from the Lennard-Jones (LJ) term of the generalised Amber force-field.

F_{QM}^i Quantum mechanical force on atoms i .

F_{max} Maximum recorded force in pull-out experiment.

Other Symbols

F_u Force of the universal Hamiltonian in LoTF scheme.

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Chapter 1

Introduction

1.1 Motivation and Objectives

Composites, defined as a mixture of two separate materials that exhibit superior properties as compared to the sum of the individual components, have accompanied human civilisation for thousands of years. The oldest records show ancient Egyptian engineers, developing a method of mixing clay and straws to create bricks taking advantage of the tensile strength of straw fibres and the compressive strength of clay. Nowadays, the clay-straw combination is no longer at the cutting edge of technology. However, the general principle of combining two different materials to create one greater than the sum of its parts continues to be applied.

Nowadays, a lot of the focus has shifted to reinforced polymers, most notably the widely used carbon fibre polymeric composites (CFPC) which exhibit better structural characteristics than most conventional materials. The improvement is twofold, they usually offer similar mechanical properties at reduced weight and can be tailored to exhibit functional properties such as improved heat transport [8, 22, 146, 168]. As a result, CFPs are widely applied in the most demanding areas such as aerospace, for instance in the newly developed Boeing 787 which offers unparalleled fuel economy due to its lightweight construction based on CFPs [216].

The excellent mechanical properties of carbon fibre-polymer composites make them remark-

able and well-established structural materials. Despite their success, CFPCs may be improved by using alternative reinforcement such as carbon nanotubes (CNTs), which offer similar advantages to carbon fibres but their better mechanical properties translate to enhanced structural and functional characteristics of the composite [49, 89, 146, 172]. Current applications of carbon nanotube-polymer composites (CNPCs) involve mostly lab-based experimental systems [21, 130, 229, 255]. However, increased understanding and availability could make them an industrially feasible choice, replacing CFPCs in demanding applications such as ballistic protection [130] or aerospace, where high-strength yet lightweight components are needed.

The impact of reinforcement on mechanical properties of a composite is more complicated than it may seem at first glance. In a simplistic view, Young's modulus of a composite material could be obtained using a rule of mixtures; however, in reality, the properties of such structures are worse than predicted by the mean weighted by volume fraction [49, 168]. The primary mechanism causing the polymer strengthening is based on the load transfer between the matrix and reinforcing fibres [50] allowing fibres with high elastic modulus to take the majority of the load. The impact of this mechanism is dependent on dispersion [49, 120, 152, 155, 248] and alignment of the fibres [49, 248], as well as the quality of the CNT-polymer interface [8, 29, 39, 147, 152, 153, 191]. Given the high surface area to weight ratio of CNTs [49], the last factor is considered to be especially important [8, 49, 140, 152] when CNPCs are considered. Developing a fundamental understanding of failure mechanisms at the interface is essential to making better materials suited to a broader range of applications [37, 49, 128, 147, 153, 177, 234].

In order to improve the Interfacial Shear Strength (ISS) representing the yield shear stress of the interface, it is necessary to enable a better connection between the polymer chains and the CNT surface; a solution is offered by CNT functionalisation. Introduction of functional groups grafted to the CNT surface and covalently bonded to both CNTs and the polymer matrix was shown to increase the ISS substantially [76, 88, 128, 138, 153, 168, 235]. In order to optimise the properties of this class of interfaces, it is imperative to understand how load is transferred between the two components as the nature of this process as well as the mechanism of critical failure remain open questions. An investigation into this matter will help in determining the key factors affecting the ISS.

CNT-polymer interfacial load transfer has been investigated experimentally using Raman spectroscopy of CNPCs [29, 127, 153, 162, 197, 252] and by conducting pull out tests with an atomic-force microscope [10–12, 42, 51, 81, 169, 235]. Although experimental investigations can be instrumental when evaluating the interfacial strength, consistent measurements of a single CNT-polymer interface, let alone a single attachment can be challenging due to the nanometre diameter of the CNTs; as a result, the reported values exhibit wide variations [235]. The mechanism of interfacial load transfer is believed to depend on the local atomic structure [138, 153, 244, 249] so the molecular resolution offered by computational investigations can provide complementary insight into the underlying processes. Precise studies carried out with computer simulations can help answer specific questions about the failure mechanism and therefore streamline the design of new high-performance composites.

Computational methods have been used to investigate the bonded CNT-polymer interface by simulating pull-out tests using Molecular Dynamics with classical [9, 44], or more sophisticated bond order [76, 168] and reactive [138] forcefields, capable of describing bond breaking. The simulations show a substantial increase in the ISS when compared to the non-bonded interface as predicted by experimental studies [88, 127, 128, 153] and provide insight into the mechanism of load transfer through the CNT-polymer bonded interface. While the results are illuminating more work is required to fully understand the nature of the interfacial failure. Showcased studies were limited to investigating the interfacial properties of a two composite system based on amorphous [76, 138, 168] and crystalline [44, 76] polyethylene (PE) reinforced with CNTs with the interface composed of PE chains grafted to the CNT surface. A comprehensive study involving varied interfacial systems would provide a more complete description of interfacial strength and aid the understanding of the mechanism of load transfer in other, less studied systems.

The key issues that need to be addressed include investigating the impact of changes in CNT functionalisation as well as polymer chemistry on properties of the bonded interface. As reported by Ma *et al.* [153] and Lachman *et al.* [128], using different functional groups as covalently bonded links between CNTs and polymer chains influences the ISS and studies performed on systems based on various polymers yield distinct values of the ISS [12, 29, 52, 153, 197, 235].

Varying the chemistry of the functional groups and the polymer matrix can have a strong influence on the properties of CNT-polymer interface and the dynamics of interfacial shearing. Identifying the relations between them will help to answer open questions about the properties of the CNT-polymer connection such as which element of the interface, attachment or the matrix, should be improved to optimise the ISS.

CNT surface modification can have a tremendous influence on the quality of dispersion of the fibres in the polymer matrix [120, 152] and preventing CNT bundling and/or aggregation has, in turn, a high impact on the properties of resulting composite [49, 120, 152, 155, 248]. The effectiveness of such measures is highly dependent on the chemistry of the functional groups and the polymer matrix and as a result, when various CNT functionalisation strategies are discussed, the issue of improving dispersion is often prioritised. I believe that the changes in mechanical properties of the interface, composed mostly of CNT surface modifications, should not be overlooked as they play a key part in composite reinforcement.

Additionally, the dynamics of interfacial shearing needs to be analysed – according to some studies, covalent links between the CNT and polymer do not share the load transferred through the interface but tear one by one [44, 76, 138]. However, some experimental studies report a peak pull-out force necessary to extract the CNT which would indicate brittle-like interfacial shearing [12]. It is also unclear whether, in the case of critical interfacial failure, the polymer chain would detach from the surface of the CNT, break at the interface or tether inside the polymer bulk.

Before advancing with the study of covalently bonded interfaces, it is important to address one methodological difficulty. Investigating the critical failure problem using computational simulations is challenging because the mechanisms are inherently multi-scale: failure is a macroscopic phenomenon yet it originates from local changes in chemical bonding that occur at the nanoscale. The bond-breaking processes at the polymer-CNT attachment point that initiate failure are quantum-mechanical in nature, yet the mechanisms by which stresses are transferred through the disordered polymer occur on length-scales far in excess of anything that can be simulated quantum-mechanically. As a result, it is preferable to use an approach that is in-

expensive to model the polymer matrix and locally accurate to describe interactions at the attachment point.

The most common approach involves using reactive forcefields such as ReaxFF [237], which are capable of modelling bonding and debonding through a very complex formulation of the interaction potential. The scope of those methods is limited to bond breaking and formation, and they rely on using a large number of parametrised functions to accurately capture the energy landscape of those effects [3, 38, 95, 207]. Due to the large number of parameters, fitting the reactive potential can be a very challenging task and is usually done to match the results of *ab initio* DFT calculations for specific system configurations, one at a time [3, 38, 95, 207]; as a result, it can be difficult to investigate systems with new or uncommon interactions.

A different solution to those problems could be offered by the quantum mechanics (QM) / molecular mechanics (MM) hybrid methods such as ‘Learn on the Fly’ (LotF) [55]. In this approach, molecular dynamics (MD) based on a classical forcefield is used to simulate the majority of the system under strain, while regions of particular interest, such as the functional groups where changes in electronic structure are likely to occur, are simulated using QM methods resulting in an accurate description of bond-breaking processes. In CNPCs, effects that would benefit from a QM description, such as changes in bonding, are present only at points where interfacial failure is initiated while the behaviour of the surrounding environment can be well-described by a less accurate, classical model. As such, using a single universal method is not a necessity and the multi-scale nature of the problem can be addressed using a hybrid approach that concurrently combines an accurate QM Hamiltonian with an inexpensive classical forcefield. Similar simulation techniques have been successfully applied in the past: QM/MM methods have been used to study crack propagation in a silicon crystal, resulting in an accurate treatment of atomic-scale effects and the prediction of the stability of crack propagation through various cleavage planes [55, 117, 118] in agreement with experimental results for the first time; atomistic QM/MM methods have also been used to study CNTs with the ONIOM approach [46], successfully predicting elastic properties of defective CNTs [119] and interactions of CNTs with non-covalently bonded molecules [103, 202]. Investigation of CNT-polymer interfaces, however, has been mostly limited to classical molecular dynamics [44, 76, 76, 138, 168]

and atomistic-continuum hybrid approaches [94, 133, 236] studying the properties of CNPC structures of 100 nm and larger, with some exceptions presented in Chapter 2. In this work, I investigate interfacial interactions on a smaller length scale, studying a simplified model of the CNT-polymer interface consisting of the fundamental building-block of the interface, namely the attachment of a single CNT and polymer chain. In our method, I supplement the fully atomistic, classical approach with a quantum mechanical description of chemical bonding.

The methodology has not been used to study this class of materials before, and as such, a significant effort must be directed at validating and fine-tuning the approach. Before advancing to a large-scale simulation of a representative volume element of a CNPC, the QM/MM technique is studied extensively on simplified systems including a single, defective CNT and a single carbon nanotube functionalised with a single polymer chain. Both investigations provide validation of the method and demonstrate that an accurate description of QM effects such as bond breaking is essential when simulating critical failure in CNPCs. Such effects govern the initial evolution of the failure process and an accurate description of the surrounding electronic structure is required to simulate them correctly. Initial simulations demonstrate that the need to include QM description in the large-scale MD simulation can be successfully addressed by employing a quantum/classical hybrid simulation technique. In our work, such method is shown to produce similar results when compared to a fully QM technique for problems of critical failure in CNT and polymer-based systems.

Additionally, the study of a single CNT-functional group system is used to answer some of questions regarding the effect of attachment chemistry on the interfacial strength. In fact, due to the simplicity of the structure, it is much easier to isolate individual contributions. Initial simulations are used to investigate various polymer grafting strategies and the results indicate that the chemistry at the attachment point significantly contributes to the effective ISS of the interface and using a carefully chosen attachment can lead to increasing the ISS to the limit dictated by the strength of the polymer used in the composite.

After successful application of the hybrid simulation method, it was deployed to investigate a large-scale model of carbon nanotube reinforced polymer by conducting a simulated CNT

pull-out test. The candidate structure contains a single CNT embedded in a matrix of a thermosetting polymer with functional groups acting as covalent links between the two components. This study confirms the findings of the first one and helps understand the mechanism of interfacial failure by investigating the dynamics of the process. Results are expected to answer some questions presented in this introduction and help guide further studies of CNT-polymeric interfaces.

In order to cover the subject of CNT-polymer interfaces, several topics must be introduced; most notably the structure of functionalised CNTs and the properties of CNPCs. The Second chapter provides a brief literature review of those topics; the review starts with a description of functionalised CNTs, continues with a discussion about polymer systems and concludes with a description of composite reinforcement and CNPCs in particular. The third chapter, three computational methods are characterised: Molecular Dynamics commonly applied to study nanoscale composite elements, Density-Functional Tight Binding used to simulate functionalised CNT systems and a novel hybrid technique which is hoped to provide an accurate description of the interactions at a CNT-polymer interface. The fourth and fifth chapters are concerned with a dynamical study of a mechanism of load transfer at the CNT-polymer interface. Initially, a novel hybrid concurrent approach is presented and simplified system of functionalised CNT is studied to validate the new method. The subsequent chapter is focused on simulating a single functionalised carbon nanotube pullout from a crosslinked polyethylene matrix to determine how chemistry at the interface affects its critical failure. The thesis ends with the conclusions and potential future outlook of studies in this area.

Chapter 2

Carbon Nanotube Polymer Composites

Polymers are a widely used material, however, their mechanical performance is not competitive with traditional structural materials and can be lacking when compared to functional ones. Their properties can be significantly improved by reinforcements; introducing nanoscale particles such as carbon nanotubes into existing polymer materials can lead to the development of composites that exhibit structural [49, 114, 146], thermal [96, 161] and electrical [144, 167] properties overshadowing the pristine materials they are based on. The development of such materials sidesteps standard limitations and trade-offs taking advantage of characteristics of both components and unique synergies between them. This section is devoted to exploring the background information about polymer composite materials and introducing their advantages and disadvantages.

2.1 Polymers

Polymers are large molecules, composed of a multitude of repeated sub-units, so-called monomers. In the process of polymerisation, single monomers are joined together into much larger structures with the topology of chains, rings or networks. Physical properties of polymers are often very different from the characteristics of a single monomer and vary based on the number of repeater units bound into a molecule. A property known as the degree of polymerisation de-

scribing the number of individual subunits in a single chain can be as important as chemical composition when determining polymeric properties.

Polymeric materials, both synthetic and natural, have found numerous applications in both everyday life and cutting edge technology. Examples include rubber, Nylon or more recently conductive polymers for battery usage [165] or solar cells [136, 175].

In general, polymers can be classified into three broad families: thermoplastics composed of individual entangled chains, thermosets characterised as rigid networks of crosslinks polymer strands and elastomers that lay between the two with only a few chemical crosslinks between entangled chains. The first two polymeric types are most commonly used to produce nanocomposites with both advantages and disadvantages.

2.1.1 Thermoplastic polymers

Thermoplastic polymers are composed of individual, entangled chains deriving their mechanical properties from the characteristics of monomers and high molecular weight. High degree of polymerisation ensures an abundance of molecular entanglements which bind the network of chains together forming a solid material and in case of crystalline and semi-crystalline polymers, favours molecular ordering and alignment. Both of those composition are portrayed in Figure 2.1.

At high temperatures, the thermoplastic polymer melt is a viscous liquid with chains forming irregular and entangled coils. Below the melting point, some polymeric materials such as nylon or polymethyl methacrylate (PMMA) mostly retain the disordered nature forming amorphous solids while others, such as polyethylene or polystyrene, are found to rearrange the local structure of the chains during solidification forming a solid with highly ordered regions. The degree of crystallinity in polymers is usually between 10 and 80% making all of them effectively semi-crystalline materials. Upon further cooling, thermoplastic polymers undergo a transition into a glassy state (glass transition), turning into brittle solids. The process of melting and solidifying can be repeated numerous times without any change in properties and is often used in various

processing techniques. In methods such as moulding and extrusion, initially, solid polymers are melted, formed into appropriate shapes and finally cooled down to solidify again.

Once prepared, thermoplastic polymers have high temperature and chemical resistance. They usually exhibit lower strengths and lower elastic modulus than their thermosetting counterparts [105] but are significantly more flexible with a failure strain up to two orders of magnitude higher than crosslinked polymers; comparison of some of their properties can be found in Table 2.1. High ductility makes thermoplastics a desirable choice for composite matrices as they can be reinforced with large amounts of fillers before becoming brittle; examples include polyethylene with 70% w.f. of CNTs [257] or Polyethyleneimine with 75% w.f. of CNTs [164].

On the other hand, processing of nanocomposites based on a thermoplastic polymer can be challenging due to the high viscosity of the melt. It is often difficult to impregnate a fine array of fibres using the amorphous liquid and various adjustments need to be made. Potential methods include applying substantial pressure over long times or shortening flow distances by manually weaving thin layers of melt and reinforcing fibres.

2.1.2 Thermoset polymers

In thermoset polymers, the liquid resin composed of separate chains is converted into the hard rigid solid material by introducing chemical crosslinks between individual polymer strands; the resulting material is a tightly bound, solid, three-dimensional network which is schematically shown in Figure 2.1c. The transformation from a liquid resin to a solid thermoset, also known as curing, is caused by heat or radiation and is often promoted by increased pressure or the presence of a catalyst.

Mechanical properties of thermosetting polymers depend on molecular units composing the initial chains as well as the structure and density of crosslinks. The former can be specified by choosing an appropriate resin while the latter is determined mostly by choice of curing catalyst and the crosslinking process.

In general, thermosetting polymers can be characterised by high elastic modulus and strength

Table 2.1: Mechanical properties of selected polymers, data reproduced from Ref. [105].

Matrix	Density [g/cm ³]	Young's modulus [GPa]	Tensile strength [GPa]	Failure strain [%]
Thermosets				
Epoxy rasins	1.1 - 1.4	3 - 6	0.035 - 0.1	1 - 6
Polyesters	1.2-1.5	2.0 - 4.5	0.04 - 0.09	2
Thermoplastics				
Nylon 6.6	1.14	1.4 - 2.8	0.06 - 0.07	40 - 80
polypropylene	0.90	1.0 - 1.4	0.02 - 0.04	300
PEEK	1.26 - 1.32	3.6	0.17	50

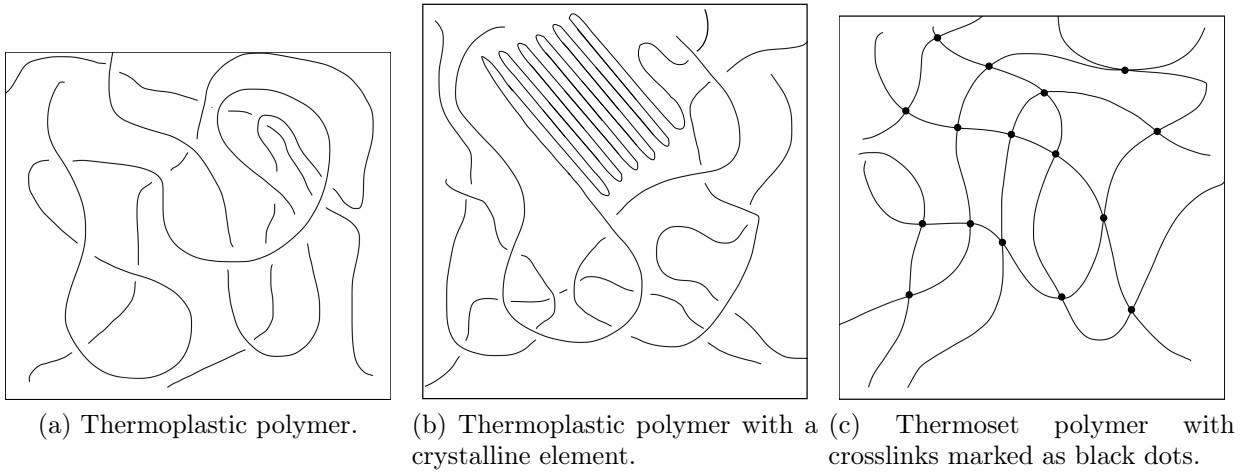


Figure 2.1: Schematic representation of different polymer networks.

but are usually more brittle than thermoplastic materials [105]. Even though their lower strain to failure means they are usually reinforced with less filler material than thermoplastic polymers, the naturally superior mechanical properties make thermoset matrixes a prime candidate for high-performance composites. It is important to note that there are considerable differences between different types of thermoset, i.e. epoxies, unsaturated polymers and vinyl esters; some of their properties can be found in Table 2.1.

2.2 Carbon Nanotubes

Carbon nanotubes (CNT), first synthesised in the early 1990s [106] are a fascinating material, exhibiting excellent thermal, structural and electronic properties [15, 131]. Initially, CNT applications involved mostly experimental nanodevices [21, 130, 204, 229, 255], however, improved

production methods and lower costs make them an attractive choice for industrial applications in areas such as aerospace [130] or ballistic protection[172]. The following section will provide a brief description of the structure of CNTs; more information can be found in [73].

2.2.1 Structure of carbon nanotubes

The structure of carbon nanotubes can easily be described as a rolled sheet of graphene. In this approach, the CNT's circumferential vector can be expressed as a chiral vector in terms of graphene lattice vectors $\mathbf{C}_h = k\mathbf{a}_1 + l\mathbf{a}_2$, as portrayed in Figure 2.2. The circumferential vector defined in this way connects two crystallographically equivalent sites on the nanotube and therefore the exact structure of the CNT can be specified by two indexes (k, l) . It is useful to define three classes of CNTs: armchair nanotubes with indexes (k, k) , zigzag nanotubes with indexes $(k, 0)$ and chiral nanotubes where $k \neq l$; examples can be found in Figure 2.3.

Nanotubes described above, composed from a single rolled-up sheet of graphene are known as single wall carbon nanotubes (SWCNT). This type of nanotubes is most interesting for experimental purposes as their properties strongly depend on chirality (see Section 2.2.1.1), but SWCNT manufacturing is difficult and expensive limiting industrial applications. More common multi-walled carbon nanotubes (MWCNT) consist of multiple concentric tubes of graphene, usually arranged in the Russian Doll structure with smaller SWCNTs within larger SWCNTs and the inter-tube distance close to the inter-layer distance in graphite.

2.2.1.1 Bonding in carbon nanotubes

In order to describe the electronic structure of the CNTs, it is instructive to start with bonding in a graphene sheet. In a graphene structure, carbon atoms are located in the vertices of a honeycomb lattice forming connections with three nearest neighbours. Three orbitals, referred to as sp^2 hybridised, form strong σ bonds with adjacent carbons while the last, unhybridised p_z orbital is used to create π bonds with adjacent particles; this is schematically shown in the top panel of Figure 2.4. The π bonding network spans throughout the whole CNT surface forming

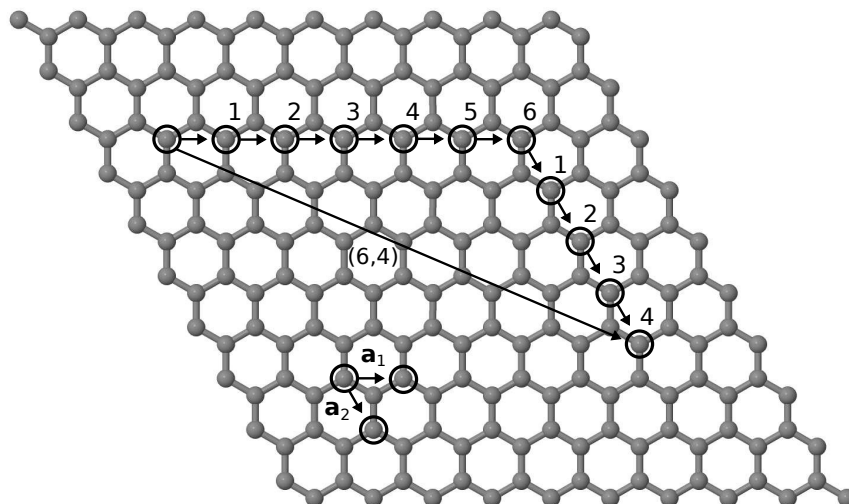
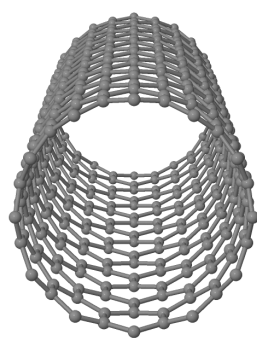
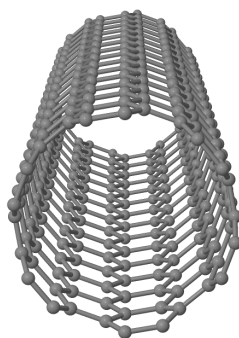


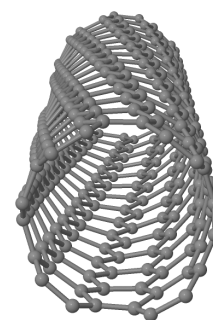
Figure 2.2: Graphene sheet with lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ as well as a selected chiral vector $\mathbf{C}_h = 6\mathbf{a}_1 + 4\mathbf{a}_2$. A CNT resulting from folding a graphene sheet according to this vector can be seen on Figure 2.3c. Figure created with JMOL v14.8.



(a) (12,0) zigzag CNT



(b) (6,6) armchair CNT



(c) (6,4) chiral CNT

Figure 2.3: Three CNT subclasses. Figure created with JMOL v14.8.

a conjugated structure.

The bonding mechanism in graphene is representative of what can be observed in a carbon nanotube. The electronic structure of CNTs can be approximated by the one of a graphene sheet with an additional boundary condition: due to the cylindrical nature of CNTs, wavefunctions on the nanotube's surface have to obey the equivalent of Bloch's theorem [121] around the circumference. This can be used to define the CNT band structure as a superposition of graphene bands with wavevectors meeting the constraints defined by the boundary conditions. Knowing the band structure, it is reasonably simple to determine the band gap (and conductivity) of a nanotube given its chirality defined in terms of the (k, l) indexes. Following this, it can be stated that CNTs defined by

$$k - l = 3s \quad \text{where } s \in \mathbb{Z} \quad \text{are metallic,} \quad (2.1)$$

$$k - l = 3s \pm 1 \quad \text{where } s \in \mathbb{Z} \quad \text{are semiconducting.} \quad (2.2)$$

This approximation is only exact for CNTs with an infinite diameter; for smaller nanotubes, the curvature causes the unhybridised p_z orbitals to not be parallel with respect to each other and the σ bonds to mix with π bonds. Applying these effects leads to small changes in the description of the CNT electronic structure which are insignificant unless a detailed analysis is desired [5]; the impact of curvature effects along with more in-depth information can be found in the textbook by Foa Torres *et al.* [73].

2.2.2 Functionalisation

Apart from their excellent thermal, structural and electronic properties [15, 131], pristine CNTs exhibit high mechanical and chemical stability. While the chemical inertness of the nanotubes can be advantageous in some applications, it affects their performance as a reinforcing fibre by weakening the CNT-matrix interface.

The issue of the low reactivity of CNTs can be tackled by surface modifications in the process

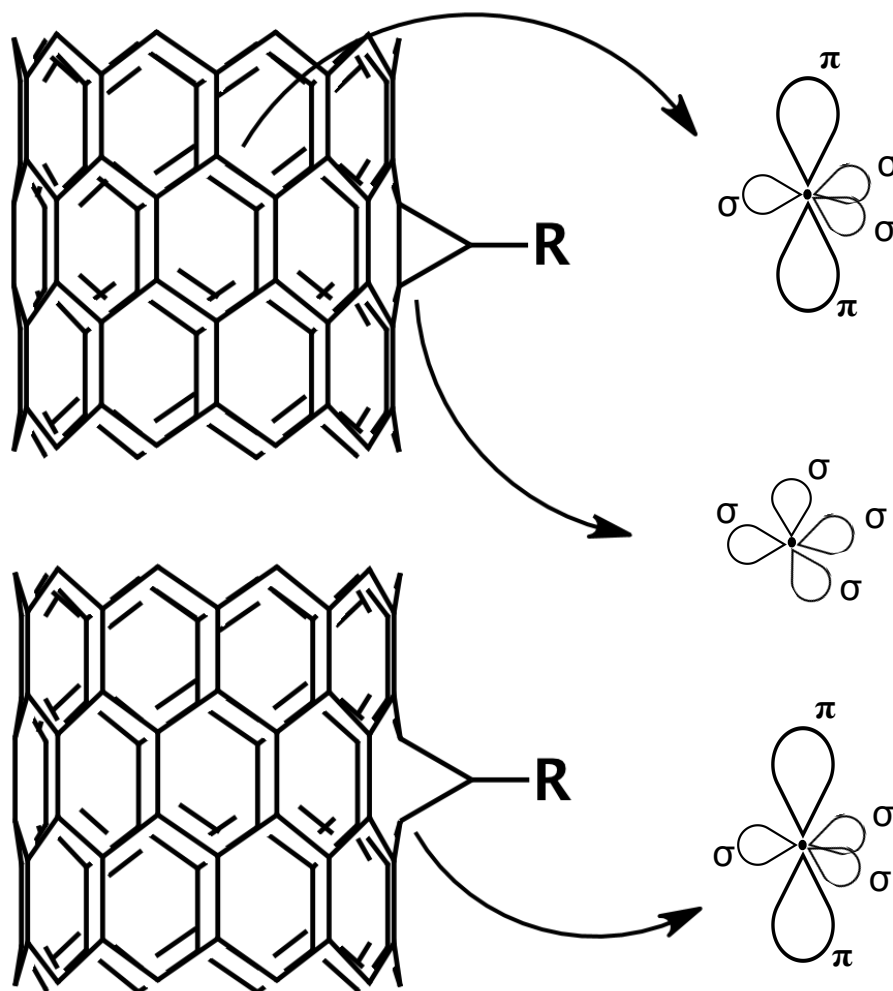


Figure 2.4: Schematic representation of bonding in carbon nanotube. Top panel shows bonding in a pristine CNT where surface atoms are connected to their three nearest neighbours by σ bonds between orbitals referred to as sp^2 hybridised and π bonds between the remaining, unhybridised p_z orbitals. The middle panel schematically shows bonding at the point of CNT functional attachment where formation of the fourth bond makes the resulting sp^3 state more energetically favourable thus breaking the π bonds with adjacent CNT atoms in favour of an additional σ bond. Finally the bottom panel shows the original bonding being restored upon cleaving the bond between two carbon atoms anchoring the functional group.

of functionalisation. This approach aims to add new features or capabilities to the material by changing its surface chemistry through attaching selected chemical groups to SWCNTs or the outer layer of MWCNTs. The method can be used not only to increase CNT reactivity for structural applications [240] but also to tailor their electronic structure for the production of nanodevices [99].

Attaching external molecules to the surface of a pristine CNT can be approached in two manners: covalent bonding between the addend and atoms within the CNT or linking the two objects by long-range interactions such as van der Waals forces. The former is known as covalent functionalisation while the latter is described as non-covalent.

Covalent functionalisation can disrupt the previously described electronic structure of the CNTs; functional groups can be attached to the surface of the nanotube by forming covalent bonds with either one or two carbon atoms from the carbon nanotube's surface. In a pristine CNT, surface atoms are connected to their three nearest neighbours by σ bonds between orbitals referred to as sp^2 hybridised and π bonds between the remaining, unhybridised p_z orbitals. Formation of the fourth bond makes the resulting sp^3 state more energetically favourable thus breaking the π bonds with adjacent CNT atoms as shown in the middle panel of Figure 2.4. As a result, the π bonding network spanning through the whole CNT surface is disrupted. In some cases, the functional group bonds to two CNT surface atoms and the original sp^2 hybridisation is restored by cleavage of the bond between the two anchoring carbon atoms in the CNT; this is schematically shown in the bottom panel of Figure 2.4.

Functionalisation altering the bonding structure of the CNT can have a significant effect on its mechanical properties [83, 200]. It is often vital to carefully consider the benefit of improved reactivity against the cost of deteriorated mechanical performance. In the case of composites reinforced with carbon nanotubes, the advantage of the former usually outweighs the latter.

2.2.3 Mechanical properties of carbon nanotubes

Since their discovery, carbon nanotubes were expected to exhibit mechanical properties superior to any other material. Structure composed of carbon atoms connected by sp^2 bonds, stronger than sp^3 bonds found in diamond, was predicted to put CNTs in their own class when strength and stiffness were concerned and the forecasts were grounded in multiple theoretical studies reporting CNT Young modulus on the order of 1 TPa [150, 176]. Experimental results provided by Wong *et al.* [245] confirmed the predictions by a stress-strain measurement with an atomic force microscope (AFM) finding the Young's modulus of CNTs to reach 1.28 TPa and their bending strength to be as high as 14 GPa, making them one of the resilient materials on Earth. Additionally, more detailed measurements of Yu *et al.* investigating the stress-strain behaviour of a single MWCNT under electron microscope were used to quantify the strength of multi-wall carbon nanotubes as 11 – 63 GPa and confirm the Young's modulus to be in the range of 0.27 - 0.95 TPa [254]. Additional studies conducted on SWCNTs were consistent with MWCNT results, reporting the Young's modulus at 1 TPa [201].

2.3 Polymer fibre reinforcement

Efficient composite reinforcement is mainly dependent on an effective mechanism of transferring external load from the matrix to reinforcing fibres, allowing the latter to take a major share of the load [8, 29, 39, 145, 147, 152, 153, 191]. In the case where load transfer is non-existent, the matrix would strain and break according to its properties, and the fibres would be nothing more than fillers, reducing the volume of matrix resin used in the composite.

Under a simplifying assumption of perfect bonding between fibres and matrix leading to uniform strain within the composite, the ratio of the load carried by the fibres to the load carried by the matrix is given by [2]

$$\frac{P_f}{P_m} = \frac{E_f}{E_m} \frac{V_f}{(1 - V_f)}. \quad (2.3)$$

In case of CNT-polymer composites where $E_f \gg E_m$ this demonstrates that reinforcing fibres

take the majority of the load; this issue is explored further in Section 2.3.1.1.

This mechanism relies on three major factors: good dispersion [49, 120, 152, 155, 248] and alignment of the fibres [49, 248] as well as the quality of interfacial load transfer through CNT-polymer interface [8, 29, 39, 49, 147, 152, 153, 191].

An ideal composite is built out of well-dispersed fibres each fully coated with the matrix material minimising direct interactions between individual reinforcements. Agglomeration of reinforcing material can reduce the effective surface area of the nanotube network necessary for load transfer as well as lead to stress concentration centres additionally limiting composite strength and modulus [211].

Promoting alignment of the fibres can further help optimise composite strength and stiffness [49, 211, 248]. However, improving composite properties by lining up the fibres is often a trade-off as boosting strength or stiffness in one direction can weaken them in others leading to highly anisotropic characteristics. In applications where the anisotropy is not problematic, such as composite beams, improving fibre alignment can be a very effective way to maximise reinforcement.

Finally, the capacity of the interface to transfer stress is not unlimited. At a certain point, stress reaches a critical value, known as the Interfacial Shear Strength (ISS), which causes the bonding between the matrix and fibre to break, leading to slippage. The ISS is a crucial parameter as strain mismatch at the interface means the primary mechanism of composite reinforcement is not present, and external load cannot be efficiently transferred to the fibres. Lack of load-sharing can lead to the mechanical properties of the composite being reduced to those of pure matrix which defeats the purpose of reinforcement.

2.3.1 Theory of composite reinforcement

The primary focus of this project is CNT-polymer composites. The properties of those materials can be most efficiently and clearly described within the framework of fibre reinforced composites.

A great deal of theoretical work has been devoted to the task of an analytical description of the mechanical properties of fibre composites. The three, arguably, most influential models used for modelling composite properties are the rule of mixtures, the Halpin-Tsai model [93] and the Shear Lag theory [53]. In the simplest views of the rule of mixtures, the composite can be portrayed as an isotropic matrix with uniformly distributed, aligned fibres. When stress is applied to such idealised material, both components are equally strained, sharing the external load. This behaviour results in the composite stress of [105]

$$\sigma_c = V_f \bar{\sigma}_f + (1 - V_f) \bar{\sigma}_m. \quad (2.4)$$

The composite modulus can then be recovered as

$$E_c = V_f E_f + (1 - V_f) E_m. \quad (2.5)$$

This model, while reproducing some data surprisingly well, relies on strong approximations of perfect load transfer (no interfacial sliding) between the matrix and aligned fibres that span the whole length of the sample with stress being applied in the fibre alignment direction.

An improvement was introduced by Halpin and Tsai in 1976 [93] in their semi-empirical model aiming to interpolate between the upper and lower bound of composite properties by

$$E_c = E_m \frac{1 + V_f z \Upsilon}{1 - V_f z} \quad (2.6)$$

where

$$z = \frac{E_f - E_m}{E_f - \Upsilon E_m}. \quad (2.7)$$

The parameter Υ is an empirically chosen measure of reinforcement geometry calculated based on fibre geometry, packing geometry and loading conditions. Setting Υ to 0 gives the lower bound of the properties while $\Upsilon \rightarrow \infty$ recovers the upper bound given by Equation 2.5. Improvements introduced in the Halpin-Tsai equations make the approach extremely effective in reproducing experimental data but using an empirical parameter can make it difficult to use

when predictions are important. In order to change focus to a realistic description from reproducing results, the load transfer between fibres and matrix should not be neglected; the model that explicitly takes it into account is the shear lag theory developed by Cox in 1952 [53].

2.3.1.1 Shear Lag theory

A realistic composite material is not constructed from aligned fibres that span the length of the sample. In the case of short fillers, the reinforcement mechanism relies on an efficient method of transferring tensile stress from the matrix to fibres via interfacial shear stress. The model of composite mechanical properties, taking into account stress transfer at the interface, was proposed by Cox *et al.* [53] and centres around the load transfer from the matrix to short fibres via interfacial stress. A schematic representation of a reinforcing fibre in a composite element under stress can be found in Figure 2.5. We first observe that the shear force inside the matrix at a given cylinder of height dx and radius ρ , located around the centre of the fibre at any value of x is given as

$$dF_{\text{shear}} = 2\pi\rho\tau_m(\rho)dx. \quad (2.8)$$

The forces in the system must be balanced, therefore we can equate the force on two cylinders with different radii, specifically one with an unspecified radius ρ and one with radius r_f , located at the fibre/matrix interface

$$2\pi r_f \tau_i dx = 2\pi \rho \tau_m(\rho) dx. \quad (2.9)$$

Using this formula, it is possible to recover the shear stress inside the matrix in terms of the shear stress at the interface and the distance from the center of the fibre as

$$\tau_m(\rho) = \tau_i \left(\frac{r_f}{\rho} \right). \quad (2.10)$$

Having found the stress, it is now possible to write the shear strain inside the matrix γ in terms of shear modulus of the matrix G_m as

$$\gamma = \frac{\tau_m}{G_m}, \quad (2.11)$$

which can in turn be used to find the shear displacement of the matrix u relative to its equilibrium position. The incremental displacement du as a result of moving away from the fibre is given as

$$\frac{du}{d\rho} = \gamma = \frac{\tau_m(\rho)}{G_m} = \frac{\tau_i}{G_m} \left(\frac{r_f}{\rho} \right), \quad (2.12)$$

and can be used to calculate the displacement at some distant location R in terms of the displacement at the interface. Definite integral of the rightmost element in Equation 2.12 leads to

$$\int_{u_i}^{u_R} du = \frac{\tau_i r_f}{G_m} \int_{r_f}^R d\rho/\rho \quad (2.13)$$

$$(u_R - u_i) = \frac{\tau_i r_f}{G_m} \ln(R/r_f). \quad (2.14)$$

Here, the radius R represents some distant location in the composite which can be approximated by the distance between neighbouring fibres; as a result the value of R/r_f can be further approximated by the fibre volume fraction V_f as $r/R \approx V_f$. The exact relation between V_f and R/r_f is dependant on the orientation and dispersion of the fibres but the term only appears inside a logarithm therefore the final result is not very sensitive to small deviations of this value [105] and our approximation can be considered appropriate.

Having discussed the matrix, it is possible to focus on the reinforcing fibre presented in the rightmost panel of Figure 2.5. Force balance on the highlighted fibre element requires

$$2\pi r dx \tau_i = -\pi r_f^2 d\sigma_f \quad (2.15)$$

leading to

$$\frac{d\sigma_f}{dx} = -\frac{2\tau_i}{r_f}. \quad (2.16)$$

Here it is necessary to find the formula for interfacial shear stress τ_i which can be recovered from Equation 2.14. Assuming the matrix is isotropic and $G_m = \frac{E_m}{2(1+\nu_m)}$, this can be written as

$$\tau_i = \frac{2E_m (u_R - u_i)}{(1 + \nu_m) r_f^2 \ln(1/V_f)} \quad (2.17)$$

where u_i and u_R are still unknown. Assuming the adhesion between fibre and the matrix is perfect, displacement of the matrix at the interface is equal to the displacement of the fibre and $u_i = u_f$. The latter term u_R can be found by assuming the strain field of the matrix far away from the fibre can be equated with the strain field of the composite material ε_c resulting in

$$\frac{du_R}{dx} \approx \varepsilon_m \sim \varepsilon_c. \quad (2.18)$$

The two assumptions of perfect, no-slip interface and far-field matrix strain being equal to composite strain are not necessarily rigorous but are reasonable approximations of the composite behaviour; see Ref. [105] for more details.

Finally, we differentiate Equation 2.16 w.r.t. x substituting Equation 2.17 as the interfacial shear stress. $\frac{du_R}{dx}$ can be found from Equation 2.18 while $\frac{du_i}{dx}$ is given by the previous assumption of $u_i = u_f$ followed by analysis of elastic properties of the fibre:

$$\frac{du_f}{dx} = \varepsilon_f = \frac{\sigma_f}{E_f}. \quad (2.19)$$

It is now possible to write the equation as

$$\frac{d^2\sigma_f}{dx^2} = \frac{w^2}{r_f^2} (\sigma_f - E_f \varepsilon_c) \quad (2.20)$$

where

$$w = \left[\frac{2E_m}{E_f (1 + \nu_m) \ln(1/V_f)} \right]^{1/2} \quad (2.21)$$

is a dimensionless constant. Equation 2.20 can be solved by applying boundary conditions of $\sigma_f = 0$ at $x = \pm \frac{1}{2}L$ where L is the length of the fibre to obtain

$$\sigma_f = E_f \varepsilon_c [1 - \cosh(wx/r_f) \operatorname{sech}(wL/r_f)]. \quad (2.22)$$

Interfacial shear stress can be recovered by substituting Equation 2.22 into 2.16 leading to

$$\tau_i = \frac{n\varepsilon_c}{2} E_f \sinh\left(\frac{wx}{r_f}\right) \operatorname{sech}(wL/r_f). \quad (2.23)$$

Those results can be used to find the composite stress from the rule of mixtures in Equation 2.4 where the stress of the fibre is obtained by integrating Equation 2.22

$$\bar{\sigma}_f = \frac{E_f \varepsilon_c}{L} \int_0^L \left[1 - \frac{\cosh(wx/r_f)}{\cosh(wL/r_f)} \right] dx = E_f \varepsilon_c \left(1 - \frac{\tanh(wL/r_f)}{wL/r_f} \right) \quad (2.24)$$

leading to the strain-stress relationship for the composite

$$\sigma_c = \varepsilon_c \left[V_f E_f \left(1 - \frac{\tanh(wL/r_f)}{wL/r_f} \right) + (1 - V_f) E_m \right]. \quad (2.25)$$

One of the key assumptions necessary for the original shear lag theory is that of a perfect interface. Equation 2.25 will only hold for finite composite strain as increasing ε_c over a certain threshold will elevate the shear stress at the interface above the ISS (Equation 2.23) causing slippage between fibre and matrix. Knowing the value of interfacial shear strength, it is possible to evaluate the critical strain. The beginning of interfacial sliding is predicted to occur at the fibre ends, where the shear stress is at its maximum. Substituting x with the fibre length L in Equation 2.23 we obtain

$$\varepsilon_{c,crit} = \frac{2\tau_{i,crit} \coth(wL/r_f)}{wE_f}, \quad (2.26)$$

which can be further converted using Equation 2.25 to find out the critical stress $\sigma_{c,crit}$

$$\sigma_{c,crit} = \frac{2\tau_{i,crit}}{wE_f} \left[[V_f E_f + (1 - V_f) E_m] \coth(wL/r_f) - \frac{V_f E_f}{wL/r_f} \right]. \quad (2.27)$$

The value of $\sigma_{c,crit}$ marks the point where the strain-stress curve departs from linear shape and composite properties deteriorate due to the onset of the interface slippage. It is evident that increasing the ISS is necessary to retain efficient load transfer, essential to keeping composite mechanical properties at a high level. While the description provided by the outlined models is simplified and relies on some assumptions, it provides necessary insights into characteristics of short fibre composites underlying the importance of efficient load transfer and the presence of strong interface.

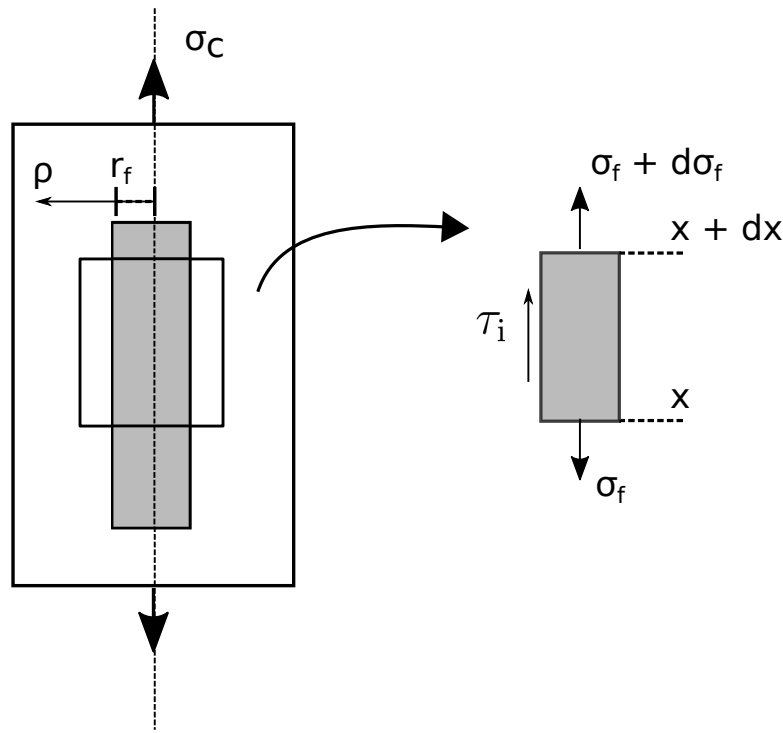


Figure 2.5: Schematic illustration of the basic elements used to derive the shear lag model.

Summary In polymeric composites, the soft matrix is reinforced by transferring a disproportionately large part of the external load to the stiff fibres embedded within. This mechanism lets composite materials rely on exceptional characteristics of the fibres for their mechanical properties such as stiffness and strength while maintaining the flexibility and light weight of the matrix.

It is clear that attention must be paid to the geometry of the composite; the success of the Halpin-Tsai equations over the rule of mixtures in reproducing experimental data is mostly due to the accurate treatment of dispersion and alignment of the fibres via the empirical term Υ . Geometrical factors are considered in the most successful composite models which strongly points to their importance. This is largely because a sub-optimal distribution of the reinforcing agents can severely reduce the capacity of a composite for matrix-fibre load transfer leading to sub-par performance.

As discussed above, efficient load sharing is accomplished via stress transfer at the interface between two constituents of the composite. This is only possible within the limits of interfacial strength as extensive stress can cause debonding between the two materials and subsequent

displacement at the interface. As a result, the quality and critical limit (ISS) of that transfer are some of the most important properties of the composite. We conclude that developing a fundamental understanding of the interaction between reinforcing fibres and the matrix is essential to making better materials suited to a broader range of applications.

2.4 Interfacial Properties of CNT-Polymer Composites

As discussed in earlier sections, the quality of the interface between the polymer matrix and carbon nanotube fibres is an important factor governing composite reinforcement, and its improvement can go a long way towards optimising the properties of CNPCs. Although significant efforts were devoted to studying the CNT-polymer interface, there are still unanswered questions necessitating further research.

The interface region can be divided into two areas, the surface of contact between the CNT and the matrix which will be referred to as the interface whereas the polymer material in the vicinity of the carbon nanotube is known as the interphase. A number of studies suggest that interactions between the polymer in the interphase region and the CNTs can affect its morphology making it noticeably different from the polymer bulk [40, 49, 192]. The altered structure in the vicinity of the fibres can have a significant influence on the properties of the interface, and it is instructive to address this mechanism before studying CNT-polymer bonding.

Introduction of carbon nanotubes into the matrix can affect the polymer in two ways, locally altering the orientation of the chains and promoting crystallisation. The former has been observed experimentally in the form of polymer chains wrapping CNTs inside the CNPC, leading to an aligned orientation of the chains [159, 243] and theoretical work was devoted to showing how this process is energetically favourable for purely geometric reasons [48]. Additionally, carbon nanotubes embedded in polymeric material can act as nucleating agents, promoting crystallisation in the vicinity of the fibres [6, 61, 135, 154, 203]. This process has been shown to create a layer of material with high shear strength coating the nanotubes, increasing the ISS by facilitating improved CNT-polymer bonding and reducing the probability of shear failure of

the matrix around the fibres [61, 154]. This process can benefit composite properties further as the highly ordered polymer coating is expected to have better mechanical properties than the matrix bulk resulting in increased average strength and elastic modulus of the polymer leading to an improvement in composite properties.

Interactions between CNTs and the polymer can have a significant impact on the morphology of the matrix in the vicinity of the interface and by extension affect the mechanics of load transfer from the matrix to the fibres, most notably, modifying the ISS [61, 154]. Improving control over the formation of the highly ordered interphase region is a promising pathway to improving the mechanical reinforcement process and one that should be explored further. However, for the purpose of this project, we focus on investigating the bonding between CNTs and the polymer at the interface itself. The following section will cover various potential interfaces between CNTs and polymer matrix namely those composed of long-range interactions and chemical bonds. Additionally, the methods of investigating interactions between two material will be studied.

2.4.1 Experimental measurements of interfacial strength

It is rather difficult to reason about a physical system without experimental observation, and to that end, a substantial body of work has been devoted to empirical studies of CNT-polymer interfaces. Selected studies are outlined in Table 2.2.

The most intuitive method of measuring interfacial properties is a single fibre pullout where an isolated fibre is extracted from the matrix using a dynamometer recording the applied force that can later be used to calculate shear stress at the interface. In case of CNPCs, the matrix is reinforced using carbon nanotubes with a diameter of tens of nanometres necessitating an extremely delicate treatment; the desired precision is usually achieved with an Atomic Force Microscope (AMF) tip as the dynamometer. Such apparatus has been successfully used to study the properties of multiple composites [10, 10–12, 41, 42, 51, 81, 127, 128, 156, 169, 197, 235] with tremendous success. While this method is quite simple conceptually, the size of studied elements makes it difficult for measurements to be precise often leading to a scatter between consecutive tests.

Table 2.2: Experimental Studies of CNT-polymer Interfacial Shear Strength

Polymer ^a	CNT	Interface	Method	ISS (MPa)	Other findings	Ref.
Epon 828 Epoxy	MWCNT	Silane functionalisation	Raman spectroscopy	NA	G' peak shift of -25.8 cm ⁻¹ / % untill interface fracture	[153]
Epon 828 Epoxy	MWCNT	Modified amine functionalisation	Raman spectroscopy	NA	G' peak shift of -38 cm ⁻¹ / % in the first phase, later -20 cm ⁻¹ / % and finally -3 cm ⁻¹ / % after interface fracture	[153]
Epoxy	MWCNT	Carboxyl functionalisation	AMF pullout	150		[10]
DGEBA Epoxy	MWCNT	Carboxyl functionalisation	Fracture test	NA	Pullout lengths of 200nm	[128]
PVA	MWCNT	Carboxyl functionalisation	Raman spectroscopy	NA	G' peak shift of -5.56 cm ⁻¹ / %	[127]
PVA	MWCNT	Carboxyl functionalization	Raman spectroscopy	160	G' peak of -15 cm ⁻¹ / %	[197]
Epon 828 Epoxy	MWCNT	None	AMF pullout	245		[41]
Epoxy	MWCNT	None	AMF pullout	30		[10]
Epon 828 Epoxy	MWCNT	None	AMF pullout	6.24 ± 3.6		[81]
Epoxy	MWCNT	None	AMF pullout	170		[156]
PMMA	MWCNT	None	AMF pullout	85 - 372		[42]
Epoxy	MWCNT	None	AMF pullout	38 - 360		[51]
polyethylene-butene	MWCNT	None	AMF pullout	20 - 80		[11]
PEEK	MWCNT	None	AMF pullout	5,2		[235]
polyethylene-butene	MWCNT	None	AMF pullout	47		[12]
PMMA + PS 5:1 Ratio	MWCNT	None	Sideways AMF pullout	48		[169]
DGEBA Epoxy	MWCNT	None	Fracture test	NA	Pullout lengths of 500nm	[128]
DGEBA Epoxy	MWCNT	None	Fracture test	NA	Pullout lengths of 200nm	[128]
PMMA	SWCNT	None	Raman spectroscopy	NA	G' peak shift of -7.5 cm ⁻¹ / %. At higher strains, interface slippage is seen	[162]
PVA	MWCNT	None	Raman spectroscopy	NA	G' peak shift of -3.58 cm ⁻¹ / %	[127]
Bisphenol-A Epoxy	MWCNT	None	Raman spectroscopy	16.75 ± 5	G' peak shift of -4.55 cm ⁻¹ / %	[252]
Epon 828 Epoxy	MWCNT	None	Raman spectroscopy	NA	G' peak shift of -0.34 cm ⁻¹ / %	[153]
Epoxy	MWCNT	None, potential carboxyl functionalisation	Microdroplet test	14,4		[262]

^aPMMA: Polymethyl methacrylate, PE: Polyethylene, PE-C: Crystalline polyethylene, PE-A: Amorphous polyethylene, PS: polystyrene, PVA: polyvinyl alcohol, PEEK: Polyether ether ketone.

The AFM pull-out test is quite challenging to execute and often a simpler alternative is desired. The solution can be offered by a fracture test, where a composite sample is fractured, and the resulting surface is analysed using an electron microscope to measure the diameter and length of any nanotubes pulled out from the matrix [128]. The CNT pull-out length can be treated as a lower bound for the half of critical length of the fibre with diameter d given by the Kelly-Tyson model [115] as $l_c = \frac{E_f d}{2\tau_i}$. Having the approximate value of the fibres' critical length, the ISS can be recovered from this equation.

The load transfer from the polymer matrix to the CNT can also be investigated non destructively using Raman spectroscopy. The position of the Raman G' band (also known as D*) at approximately 2662 cm^{-1} is sensitive to the stress of the nanotube and shifts down in frequency when the tube is under tension. In the elastic regime, the magnitude of the shift is proportional to the stress acting on the nanotube and as such, can be used to quantify the stress applied to the CNT through the interface as a result of composite strain. Studies using this approach [127, 153, 162, 197, 252] can be extremely useful in determining and quantifying load transfer to the CNT and can be used to highlight differences between various interfaces.

Experimental investigation of nanocomposite interfaces can often be troublesome: the small scale of the problem makes it difficult to reproduce the exact conditions between measurements. Parameters such as CNT embedded length and diameter and in case of functionalised nanotubes, the density and distribution of modifications often vary and considerable statistical power is necessary in order to ensure consistent results. The issues are even more prominent when separate studies are compared. Experimental apparatus is rarely identical and there are often discrepancies in CNT and polymer characteristics coming from various suppliers and slightly different preparation methods.

Additionally, it is often hard to reason about the mechanism of load transfer and critical failure at the nanocomposite interface as characterisation methods with molecular resolution are only available on samples before or after fracture, while the dynamics of the failure can only be inferred and not directly observed.

2.4.1.1 Non-covalent interfaces

As previously mentioned, load transfer between the soft matrix and the stiff CNTs is the cornerstone of CNPC reinforcement and the strength of the polymer/nanotube interface directly affects the characteristics of a composite. In conventional composites, pristine CNTs are embedded in the polymer matrix relying on non-bonded interactions such as van der Waals forces for stress transfer.

The primary quality of the interface that needs to be determined is the ability to transfer stress from the matrix to reinforcing fibres. In the case of CNPCs, this can be achieved using a previously discussed method based on spectroscopic analysis of carbon nanotubes (see the discussion on Raman spectroscopy in the previous section). Studies conducted on various combinations of CNT/polymer, outlined in Table 2.2 all report a negative slope of the G' peak shift / composite strain curve which means that CNTs embedded in a composite are strained while the composite sample is strained. While there are some discrepancies between the numerical values, the qualitative conclusions are consistent between studies proving that stress can effectively be transfer through the non-bonded interface.

More directed studies, including pull-out and fracture tests discussed in Section 2.4.1, have been performed to quantify the strength of non-bonded CNT-polymer interfaces. Most reported values of the ISS fall within one order of magnitude between 30 MPa and 300 MPa (see Table 2.2), but some outliers are present.

Although experimental investigations can be instrumental when evaluating the interfacial strength, such studies are rarely performed identically. The details of reagents used can vary depending on suppliers and the experimental setups are rarely indistinguishable; additionally, measuring some properties of a CNT-polymer interface such as the area of CNTs (diameter and length [51]) can be challenging due to the nanometre scale of the nanotubes. As a consequence, numerical results show large discrepancies: more than an order of magnitude difference can be observed between results from single study as in Chen *et al.*[42] or two experiments using the same method on a similar system as in Chen *et al.*[41] and Ganesan *et al.*[81] with groups reporting

the ISS of 245 MPa and 6.24 ± 3.6 MPa respectively for MWCNT pull-out out from Epon 828 epoxy matrix. The significant variance in reported results makes it difficult to investigate trends; while there is an abundance of data regarding the strength of interfaces between CNTs and various polymers in multiple settings, noise is often stronger than any signal as seen by scattered values reported in Table 2.2.

2.4.1.2 Covalent interfaces

The quality of the CNT-polymer interface directly affects the characteristics of a CNPC which may result in low strengthening in conventional composites based on pristine carbon nanotubes. The surface of pure CNTs is chemically inert so the major binding force between nanotubes and polymer chains comes from van der Waals interactions which are known to be weaker than chemical bonding. In order to improve the interfacial shear strength, it is necessary to enable a better connection between the polymer chains and the CNT surface, ideally in the form of covalent crosslinks between nanotubes and the matrix.

While direct bonding between the polymer chain and CNT surface can be difficult to achieve, a reasonable solution can be obtained with the help of CNT functionalisation. Selected functional groups attached to the surface of the nanotubes [64, 120, 152] bond with the polymer chain linking the two together and providing a very efficient way of transferring load between the two materials. Two main strategies for forming covalent interfaces involve “grafting from” and “grafting to”. The former is a two-step process that starts with attaching the functional groups to the surface of the CNT and is completed by *in situ* polymerisation of appropriate monomers to form polymeric molecules already bonded to the functionalised nanotube. This method can be used to achieve high grafting density, however, it is extremely delicate and strict control over the process is necessary. The latter, “grafting to” approach requires pre-functionalised polymer chains as well as functionalised carbon nanotubes for the process and relies on the functional groups from both CNTs and polymers reacting together to form covalent bonds. This method can often be advantageous as both materials can be obtained from external suppliers. Disadvantages include low grafting density and necessity of using polymers with

reactive functional groups.

Experimental studies relying on Raman spectroscopy have been used to quantify the quality of load transfer through the covalently bonded interface. Results show that introducing chemical crosslinks between the matrix and reinforcing fibres consistently improves stress transfer to the nanotubes. Lachman *et al.*[127] analysed the changes in MWCNT Raman spectra as a proxy for composite strain for CNPCs reinforced with pristine and carboxylated nanotubes. The group found that the G' peak shift to composite strain slope in the former case was approximately $3.59 \text{ cm}^{-1}/\%$ while in the latter $5.58 \text{ cm}^{-1}/\%$ indicating that carboxylated CNTs are much more sensitive to strain applied to a composite sample. Similar results have been observed by Ma *et al.*[153] for amine and silane functionalisations and Roy *et al.*[197] for carboxyl attachments with all both groups confirming that more stress is transferred via covalent interfaces.

Similar conclusions can be drawn from both AMF pullout studies and fracture tests investigating ISS improvement as a result of CNT functionalisation. Barber *et al.*[10] showed that carboxyl functionalisation induced crosslinking between polymer and nanotubes has resulted in an increase of ISS from 40 MPa to 150 MPa which is consistent with fracture tests of Lachman *et al.*[128] in which functionalised CNTs have been found to exhibit significantly shorter critical lengths.

All studies presented in Table 2.2 agree on the qualitative trend of the covalently bonded interface being significantly stronger than the non-covalent counterpart. However, there is little information pointing to which type of crosslinked interface could offer the best properties. Apart from one investigation of Ma *et al.*[153], most studies treat only one kind of CNT-polymer connection and significant variations between results from different sources make it difficult to perform a meta-analysis comparing various interface chemistries.

The effect of CNT functionalisation on properties of CNPCs has been studied from the perspective of nanotube dispersion. Various surface attachments can be used to prevent CNT agglomeration in the polymer resin which leads to improved composite properties [64, 120, 152]. A large body of work has been devoted to quantifying the effect that various functionalisation strategies have on CNT dispersion with multiple reviews highlighting promising candidates.

However, the impact of varying the CNT functional attachment on interfacial strength remains an open question. An investigation exploring this problem could offer valuable insight complementing existing knowledge and the combined expertise could accelerate the design of new high-performance composites.

2.4.2 Computational measurements of interfacial strength

Experimental studies of CNT-polymer interfaces were conducted alongside a significant number of computational investigations. *In silico* methods can often offer greater control over the studied systems and allow for a more detailed analysis of results compared to experimental studies which make them an excellent tool to complement empirical investigations. Selected studies are outlined in Table 2.3.

The most common method for studying CNT-polymer interfacial properties with computational simulations involves reproducing the AFM pull-out experiments using Molecular Dynamics [9, 44, 75, 76, 88, 137, 140, 168, 210, 246, 249, 259, 260] discussed in Section 3.1. Such investigations are run on a representative volume element (RVE) composed of a carbon nanotube with lengths varying from 10 nm [88] to 500 nm [9] embedded in a polymeric box, large enough to ensure the boundary effects can be dismissed. However, the lengths of studied nanotubes are usually much smaller than an experimentally observed micron long embedded CNTs which can make verifying quantitative results difficult. Once the RVE is prepared, an external force or velocity is applied to one of the CNT ends, the dynamical evolution of the system is recorded, and later, analysed. This type of simulation can be slightly modified by simulating CNT pull-out quasi-statically [91] instead of fully dynamically. The former method relies on an iterative approach when each step consists of displacing the nanotube and relaxing the resulting system. The method effectively simulates CNT a pull-out test with infinitely small pull-out speed.

Molecular Dynamics could also be used to measure load transfer through the interface by monitoring the elastic response of a carbon nanotube inside a composite sample under strain, following the experimental method relying on Raman spectroscopy discussed in Section 2.4.1. Changes in CNT C-C bond lengths, experimentally inferred by analysing the shifts in the

Table 2.3: Computational Studies of CNT-polymer Interfacial Shear Strength

Polymer ^a	CNT	Interface	Method	ISS (MPa)	Other findings	Ref.
PMMA	SWCNT	CNT functionalised with benzene rings not linked to polymer	CNT pullout	400		[259]
PE	SWCNT	CNT functionalised with benzene rings not linked to polymer	CNT pullout	600		[259]
PE-C	SWCNT	c-c crosslinks	CNT pullout	250-300	ISS depending on matrix density	[44]
PE	SWCNT	c-c crosslinks	CNT pullout	1000		[168]
PE-A	SWCNT	c-c crosslinks	CNT pullout	30		[76]
PE-C	SWCNT	c-c crosslinks	CNT pullout	110		[76]
LY556 Epoxy	MWCNT	CNT functionalised with amine groups non linked to polymer	CNT pullout	40-90	ISS depending on functionalisation density	[210]
PMMA	SWCNT	None	CNT pullout	20		[259]
PE	SWCNT	None	CNT pullout	20		[259]
PE	SWCNT	None	CNT pullout	100-140	value depending on CNT diameter	[137]
PMMA	SWCNT	None	CNT pullout	30		[260]
PMMA	SWCNT	None	CNT pullout	0,77		[9]
PMMA	SWCNT	Pristine CNT defects	CNT pullout	3,5	Defects in CNT improve the ISS	[9]
PS	SWCNT	None	CNT pullout	160		[140]
DGEBA Epoxy	SWCNT	None	CNT pullout	~50		[249]
PE	SWCNT	None	CNT pullout	12,5		[168]
PE	SWCNT	None	CNT pullout	2,8		[76]
PE-C	SWCNT	None	CNT pullout	NA		[75]
Epon 862 Epoxy	SWCNT	None	CNT pullout	75		[88]
PS	MWCNT	None	CNT pullout	138		[246]
Epoxy	MWCNT	None	CNT pullout	186		[246]
PE	SWCNT	None	Quasi-static CNT pullout	141		[91]

^aPMMA: Polymethyl methacrylate, PE: Polyethylene, PE-C: Crystalline polyethylene, PE-A: Amorphous polyethylene, PS: polystyrene, PVA: polyvinyl alcohol, PEEK: Polyether ether ketone.

position of G' peak, can be directly extracted from the simulation and the load transferred to the nanotube can be found using the methods devised for post-processing experimental data. This approach is, however, not very common and the simulated pull-out test is more widespread.

Interactions between polymers and CNTs do not need to be studied by simulating an entire composite sample, in some cases, it can be helpful to focus on a simpler model such as a single nanotube interacting with one polymer chain to extract specific information. Similar successful studies are used to investigate polymer wrapping and the strength of non-covalent bonding between CNTs and polymers [228, 250, 253, 256, 261] as well as the strength of covalent interfaces [87]. The former results are achieved by analysing system's geometries during an MD relaxation [213, 256], as well as comparing the energies of two components separately with the energy of the combined system. The latter can be found with a simplified fracture simulations [87]. A focused study conducted on a system of limited size has an additional benefit of enabling more accurate simulation methods. Bonding between CNTs and a single polymer chain has been successfully studied using DFT [213] or potentially other quantum mechanical methods [87], while an investigation of whole composite samples with such methods would be prohibitively expensive.

As discussed in Section 3.1, the time evolution algorithm is only one of the elements of a successful Molecular Dynamics simulation as a large part of complexity is contained in the method for computing total energy and forces of the system. While this can, in principle, include fully *ab initio* methods [91], composite simulations usually rely on parametrised forcefields such as COMPASS [91, 137, 210, 259, 260], AMBER [44], DREIDING [9], PCFF [249] or MM+ [140, 250].

In some cases, such as interaction strength measurements for interfaces with complex CNT-polymer bonding, simulations can involve a variety of quantum mechanical effects including bond breaking, formation or interactions between electronic states of the attachments and the CNT [87, 91]. Various QM effects often play an important role in interactions at the CNT-polymer interface, and in order to perform successful simulations, it is necessary to use a method capable of accurately describing them. The prime example of this class of problems is

the critical failure of covalently bonded CNT-polymer interface where the rupture of chemical crosslinks plays a crucial part in the process. Simple empirical simulation techniques such as classical forcefields are not well equipped to describe such phenomena and more detailed methods are needed to obtain correct results. The most common approach involves using reactive forcefields such as ReaxFF [237] or bond-order potentials such as REBO [26], AIREBO [219] and the original Tersoff-Brenner potential [25, 230] which are capable of modelling bonding and debonding through a large array of parametrised functions with a special descriptor of the atomic environment. The scope of those methods is limited to bond breaking and formation, and they rely on using a large number of parametrised functions to accurately capture the energy landscape of those effects [3, 38, 95, 207]. While large number of parameters makes the reactive potentials very descriptive, inferring their correct values can be extremely challenging due to the complexity of the problem. It is usually done to match the *ab initio* DFT description of specific system configurations [3, 38, 95, 207] which the forcefield learns to reproduce well. However, this makes them less powerful in situations where uncommon or previously unseen interactions are studied. Still, reactive forcefields and bond order potentials have been successfully used to simulate CNT pullout (REBO) [168], (AIREBO) [9], (Brenner) [76], (ReaxFF) [256] achieving promising results as their main shortcoming can be mitigated by studying common, carbon-based structures.

The alternative to empirical simulation methods can be offered by semi-empirical or *ab initio* modelling techniques. Approaches such as density functional tight binding (DFTB) or density functional theory (DFT) can serve as a base for very accurate studies of the most complex systems; however, the computational cost of those methods is much higher than classical approaches. Simulations of a composite element require a proper description of the stress transfer through a disordered polymer which can only be captured by studying large systems over an extended period of time. In this setting, the high cost of quantum mechanical methods can be prohibitive and the excessive accuracy is not needed in the majority of the system where basic morphology of the polymer bulk is studied.

The primary motivation for studying the bonding between CNTs and polymer is improving our understanding of the critical failure mechanism at the interface between the polymer matrix

and reinforcing fibres. In its essence, failure is a multiscale phenomenon that originates from local changes in chemical bonding that occur at the nanoscale and need to be studied rigorously but propagates by stress transfer over micrometre lengths and timescales not accessible to simulations driven by accurate methods. Computational studies such as that require an approach that is inexpensive when applied to the bulk of the system but can offer a precise description in selected local areas of interest. Potential solutions to this issue could be provided by a QM/MM hybrid method presented in Section 3.4 that combines the benefits of classical and quantum simulation methods. In this setting, the bulk of the system is treated with a simple classical forcefield while selected areas of interest are investigated with a more accurate QM method. An approach such as that has been successfully used to investigate a brittle crack in a silicon crystal [118] taking advantage of the multiscale nature of the phenomenon in a similar manner as discussed here. This indicates that QM/MM methods can be used to solve this class of problems and as such, could provide a good way of investigating polymeric nanocomposites, most notably, the failure at the covalently bonded interface, which at the moment lacks an accurate description.

2.4.2.1 Non-Covalent interfaces

Following experiments, multiple computational studies were devoted to measuring the strength of a non-covalent CNT-polymer interface. The results, summarised in Table 2.3 fall within a similar range as experimental observations with most groups reporting the ISS between 12 MPa and 170 MPa. The discrepancies between various studies are also present for this class of investigations with the most likely causes being differences in force evaluation methods as well as the differences in sizes of studied systems; both issues are discussed in more detail in previous parts of this section. On the other hand, results presented within individual studies are usually consistent.

The increased control available in computational studies was used for a more detailed analysis of various factors affecting the strength of CNT-polymer interfaces, most notably, different methods of improving the bonding between two materials. Both Zheng *et al.*[259] and Sharma *et*

al.[210] have found CNT functionalisation can have a positive impact on the bonding strength even in cases when no covalent bonds are formed between nanotubes and the matrix. Introducing functional groups to the surface of the CNT was reported to improve the strength of the interface four times when amide functionalisation is used [210] and up to an order of magnitude when benzene rings are attached to the CNT surface [259]. Furthermore, Bagchi *et al.*[9] have found that an increase of ISS by five times can be achieved by introducing defects in the CNT, which indicates that any effect disrupting the perfect, inert, honeycomb structure of the CNTs can have a beneficial effect on interfacial strength.

2.4.2.2 Covalent interfaces

The results of computational investigation of critical failure at CNT-polymer interface show a noticeable improvement in ISS when covalent crosslinks between two materials are present; see Table 2.3. However, methodological issues, discussed in previous parts of this section, make it difficult to study complex systems with varied chemical structure. As a result, work has been mostly aimed at investigating the fundamental properties of simple carbon-based systems with carbene attachments linking CNTs with a polyethylene matrix. While providing insight into the dynamics of interfacial failure, those studies are focused on one composite system. A more varied study involving other commonly used interfacial systems could help broaden our understanding of critical failure and provide a more robust description of key factors affecting the ISS.

2.5 Conclusions

Reinforcement in CNT-polymer composites relies on an efficient way of transferring external load from the soft polymer matrix to stiff reinforcing fibres. The capacity for the load transfer is in turn determined by the quality of the CNT-polymer interface making a robust connection between the two materials a requirement for efficient composite reinforcement. Special emphasis is placed on the strength of the matrix-fibre bonding as critical failure at the interface can greatly

diminish composite properties.

In the case of CNPCs, two types of interface can be characterised, one relying on non-bonded interactions for interfacial load transfer and other using covalent crosslinks. Composites build from pristine nanotubes and relying on the former strategy of non-covalent interactions at the interface have been proven to exhibit excellent properties. However, the introduction of bonded crosslinks between CNTs and the polymer matrix has been shown to improve the ISS significantly and as such, lead to CNPCs with improved performance.

One of the most common ways of achieving crosslinks between the matrix and the CNTs is via nanotube fictionalisation. Functional groups attached to the surface of the CNT bond with the polymer and act as chains, linking the two mediums together, creating a strong interface. The impact of varying the functionalisation on the ISS is difficult to determine due to high variance in experimental results and limited information from computational studies. However, attaching functional groups to the surface of the CNT has been studied extensively in the context of improving dispersion of the nanotubes in the composite. Complementing that knowledge by information on how varying the functional attachments can affect the strength of the interface can accelerate the design of new high-performance composites.

Studying those effects *in silico* requires a new approach, taking advantage of the multiscale character of interfacial failure. QM/MM methods, presented in Section 3.4 can combine a very accurate description of bond breaking phenomena at the interface and an inexpensive way of modelling polymer bulk allowing for simulations spanning the required length and timescales.

Chapter 3

Methodology

3.1 Molecular Dynamics

Molecular dynamics (MD) is a computer simulation technique that predicts the motion of individual atoms in a system of interacting particles by numerically integrating Newton's equations. Due to an approximate, usually classical, formulation of the interaction potentials, the method is capable of modelling a large number of particles over timescales up to micro[79] or even milliseconds [143]. The outcome of a successful simulation contains the trajectories and velocities of all particles in the studied system, which can be used to compute various structural and thermodynamical properties making MD an extremely versatile and powerful tool. In this section, a brief introduction to the molecular dynamics method is provided while a more detailed description can be found in References [80, 92, 194].

3.1.1 Time evolution

In a closed system of N particles labelled $i = 1 \dots N$ with masses $\{m_i\}$, the sum of kinetic and potential energies of all molecules is conserved and the two contributions can be used to define the Hamiltonian as

$$\mathcal{H} = K(\{\mathbf{p}_i\}) + U(\{\mathbf{r}_i\}). \quad (3.1)$$

The kinetic energy in above equation is given as

$$K(\{\mathbf{p}_i\}) = \frac{1}{2m} \sum_i \mathbf{p}_i^2 \quad (3.2)$$

while the potential energy results from interactions between atoms. Assuming U is only dependant on atomic positions, the molecular dynamics algorithm presented here is independent of the formulation of the potential energy and any reasonable approach can be used. Classical forcefields presented in Section 3.1.4 are the most common method for computing atomic interactions, but any model such as the fully *ab initio* treatment, more approximate DFTB technique presented in Section 3.3 or a hybrid method discussed in Section 3.4 can be employed. While various forms of the potential energy function are appropriate, the choice has a significant impact on the resulting molecular dynamics simulation.

Using the Lagrangian formulation of dynamics, the Hamiltonian can be used to derive Hamilton's equation of motion for each particle as

$$\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -\dot{\mathbf{p}}_i, \quad (3.3)$$

where using H specified in Equation 3.1 and the definition of mechanical momentum leads to more familiar Newtonian equations of motion

$$m\ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} \quad (3.4)$$

for each particle i . It is important to note that the result of presented here can also be reached considering Newton's third equation of motion alongside the conservation of force in the form of $\mathbf{F}_i = -\partial U / \partial \mathbf{r}_i$.

3.1.2 Integrating equations of motion

A molecular dynamics simulation aims to simulate the time evolution of a given system by numerically integrating Equation 3.4 with a finite-difference method. The basic approach to

this task relies on a Taylor expansion of the trajectories around t , forward

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \frac{d\mathbf{r}(t)}{dt}\Delta t + \frac{1}{2}\frac{d^2\mathbf{r}(t)}{dt^2}\Delta t^2 + \frac{1}{3!}\frac{d^3\mathbf{r}(t)}{dt^3}\Delta t^3 + O(\Delta t^4) \quad (3.5)$$

and backward

$$\mathbf{r}(t - \Delta t) = \mathbf{r}(t) - \frac{d\mathbf{r}(t)}{dt}\Delta t + \frac{1}{2}\frac{d^2\mathbf{r}(t)}{dt^2}\Delta t^2 - \frac{1}{3!}\frac{d^3\mathbf{r}(t)}{dt^3}\Delta t^3 + O(\Delta t^4). \quad (3.6)$$

Summing the two expansions together results in elimination of all of the odd terms to form a widely used Verlet algorithm [239]

$$\mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \frac{d^2\mathbf{r}(t)}{dt^2}\Delta t^2 + O(\Delta t^4) \quad (3.7)$$

where $d^2\mathbf{r}(t)/dt^2$ can be found using Equation 3.4. The presented scheme, while simple, is extremely powerful as it provides third order accuracy without having any third order terms and has time reversal symmetry ensuring excellent numerical stability even for large timesteps.

The integrator presented by Verlet primarily deals with particle trajectories, leaving the calculation of the velocities to a finite difference method. In the original work, they were computed with the first order central difference method as

$$\mathbf{v}(t) = \frac{\mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t)}{2\Delta t} + O(\Delta t^2). \quad (3.8)$$

Although velocity errors are not accumulated over time, this approach is not very accurate as velocities are only approximated to second order. An improvement can be achieved with a related, and much more popular approach related to the Leapfrog method, known as Velocity Verlet [226]. This scheme follows a similar procedure as the original approach presented by Verlet but the velocities are treated explicitly rather than *post hoc*, leading to the following

equations

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \dot{\mathbf{r}}(t)\Delta t + \frac{1}{2}\ddot{\mathbf{r}}(t)\Delta t^2 + O(\Delta t^4) \quad (3.9)$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2}[\ddot{\mathbf{r}}(t) + \ddot{\mathbf{r}}(t + \Delta t)]\Delta t + O(\Delta t^4). \quad (3.10)$$

The Velocity Verlet algorithm is the most widely used method for integrating the equations of motion thanks to its third order accuracy without any explicit third order terms and numerical stability due to time reversal symmetry. Additionally, in case acceleration of the particles results from the changes in potential energy in a conserved Hamiltonian system, the total energy will be conserved, oscillating around the initial value with second order error.

3.1.3 Ensembles and Thermostats

The standard formulation of molecular dynamics aims to mimic nature by evolving an isolated system in time according to Newtonian equations of motion where the number of particles, the volume of the system and the total energy are conserved. Assuming we can equate MD time averages with ensemble averages, results of a conventional MD simulation can be used to compute an average in a microcanonical, NVE ensemble. In this context, the temperature of the system can be specified by setting initial atomic velocities to appropriate values and allowing the system to settle at the desired temperature. This setting, however, is not representative of real experimental conditions where studied systems are hardly isolated and usually coupled to a heat bath keeping their temperature T fixed, resulting in an NVT canonical ensemble. For a system of sufficient size, nearing the thermodynamic limit, temperature fluctuations tend to be small and simulation in an NVE ensemble with carefully scaled initial velocities is effectively equivalent to one with fixed T . However, for microscopic structures the oscillations can be much higher and including a thermostat that simulates coupling the system to an external heat bath is necessary to model the equilibrium behaviour of the canonical ensemble.

In some cases, control over the temperature of the system is not sufficient, and pressure must be regulated to recreate desired conditions. Fixing the number of particles, temperature and

pressure P leads to an NPT, isothermal-isobaric ensemble, enforced by an appropriate barostat. In this thesis, only the thermostats will be covered in detail, but plenty of information about constant pressure simulations can be found in excellent reviews [80, 92, 194].

3.1.3.1 Andersen thermostat

One of the first practical implementations of the constant temperature simulation method was an algorithm proposed by Andersen [4] in which the desired temperature is enforced by coupling the system to a heat bath. The coupling is represented as a series of stochastic collisions of random particles with the heat bath, each carried out by reassigning the velocity of a particle to one drawn from a Maxwell-Boltzmann distribution for the requested temperature. This scheme, while capable of reproducing a canonical ensemble given sufficient time, is not widely used as the spikes in atomic velocities significantly affect the dynamics of the system.

3.1.3.2 Berendsen thermostat

A simpler alternative developed by Berendsen [16] operates by weakly coupling the system to a heat bath through gradually rescaling atomic velocities. The temperature is controlled in a manner that reduces its deviation from the target value T_0 exponentially with the time constant ι , according to

$$\frac{dT}{dt} = \frac{T_0 - T}{\iota} \quad (3.11)$$

until the kinetic energy (given by atomic velocities) of the system corresponds to the desired temperature. The clear advantages of this algorithm are its simplicity and efficiency, but it does not generate a correct canonical ensemble as the energy fluctuations are not captured properly. In the limit of large systems, this formulation yields approximately correct results, but it is rarely used in any rigorous simulations.

3.1.3.3 Langevin thermostat

Stochastic coupling with the heat bath, first introduced by Andersen can also be implemented within the framework of Langevin dynamics [1]. In this approach, the explicitly modelled central system is submerged in a bath of fictitious solvent particles in constant motion due to thermal agitation. The solvent particles are assumed to be of significantly smaller masses than the atoms of the main system resulting in much faster-changing trajectories that are difficult to track. Fortunately, the detailed motion of the fictitious particles is not of particular interest and they can be simulated implicitly via viscous damping and random forces representing collisions with the atoms of the explicit system. As a result of this latent solvent, the motion of the i -th particle of the main system at time greatly larger than the characteristic time of collisions can be described by

$$m\dot{v}_i = -\nabla_i U - m\kappa v_i + f_{Ri} \quad (3.12)$$

where f_R is a random force drawn from a Gaussian distribution with zero mean and variance σ , given by the Einstein-Stokes fluctuation-dissipation theorem:

$$\sigma^2 = 2m\kappa k_B T. \quad (3.13)$$

The viscosity parameter κ can be related to the collision time ζ_{coll} which represents the characteristic timescale of the thermostat as $\zeta_{coll} = 1/\kappa$.

Care must be exercised when using the Langevin thermostat to ensure a constant temperature in molecular dynamics simulation. While the method reproduces the canonical ensemble and offers quick temperature convergence, a large value of the viscosity coefficient can lead to an overdamped Langevin dynamics where the simulation is equivalent to Monte Carlo as transition between states becomes stochastic and no dynamics can be observed. Usually, the aim is to find the lowest value of κ that keeps the temperature constant ensuring the smallest possible disruption to the dynamics.

3.1.3.4 Nosé-Hoover thermostat

Finally, one of the most popular approaches for generating correct NVT statistics is a thermostat originally developed by Nosé [173] and later improved by Hoover [101] to form the currently used scheme. In this method, the dynamics of the heat bath are explicitly modelled by introducing an additional degree of freedom in the Hamiltonian. The combination of the initial system and the heat bath, known as the extended system, is simulated together in an NVE ensemble and the exchange of kinetic energy between the two ensures the main system stays at the desired temperature generating correct canonical statistics.

The Nosé-Hoover thermostat, similarly to the solution proposed by Berendsen, is deterministic as no random variables are involved. While the latter relies upon damping the temperature explicitly by velocity rescaling, the former implements true coupling between the heat bath and the system resulting in slowly decaying temperature oscillations and long thermalisation times. In practice, the thermostat developed by Nosé and Hoover drives the system to the desired temperature much more softly than the counterpart proposed by Berendsen.

3.1.4 Interaction potential

The time evolution according to the equations of motion presented in Eq 3.4 cannot be performed without computing the potential energy of the system $U(\{\mathbf{r}_i\})$ and resulting forces; finding them is the most important and time consuming part of the Molecular Dynamics simulation. The method employed for this task defines the nature of the simulation as time integration is relatively precise and inexpensive.

The most accurate approach of finding the potential energy relies on *ab initio* calculation such as Density-Functional theory or semi-empirical methods. The former is discussed briefly in Section 3.2 and serves as a base for one of the most accurate simulations in the Car-Parrinello implementation [35] or more recently with the Born-Oppenheimer QM-MD while the latter, discussed in Section 3.3 sacrifices the precision and transferability for efficiency and has been used by a variety of large-scale specialised packages [33]. Quantum mechanical energies can be

a base for very accurate and complex studies; however, due to the computational costs the size of the system is very limited. As a result, the most common approach to Molecular Dynamics relies on empirical methods where the potential energy is computed with a carefully selected functional form with free parameters fitted to reproduce experimental or *ab initio* properties. Due to the simplicity of this functional form, it is possible to scale up the MD simulation to extremely large systems; tens or hundreds of thousands of atoms can be simulated when using a polymeric forcefield, while in crystalline systems, where only pairwise interactions are necessary, this number can go as high as hundreds of millions [60].

3.1.4.1 Classical Forcefields

One of the most efficient descriptions of the potential energy of a system of atoms relies on a set of functions with empirically chosen parameters. The exact formulation of those functions, along with a set of parameters define a force-field which provides a detailed description of the interactions between particles in a system and is used to derive forces on individual atoms.

In this view, the energy is usually decomposed in a sum of one, two, three and up to N body terms with the one-body component representing the external potential and all others interactions between atoms. The description can be made arbitrarily accurate by including a significant number of multi-body terms, but as computational efficiency is one of the main goals of this approach, the accuracy is rarely prioritised to ensure the complexity is kept low. This is often achieved by limiting the total number of distinct contributions to the energy and removing the N -body terms with $N > 4$ and only keeping a small fraction of the 4-body terms, e.g. those that define bond torsion.

Modern forcefields make the computation of the energy more efficient by making use of a system's topology information, decomposing the potential energy further into non-bonded and bonded terms. The former, long-range interactions are tallied for all pairs of particles in the system, and the latter are computed only for atoms connected by chemical bonds and include terms with order higher than two. In practice, most standard forcefields implement the non-

bonded interactions as

$$U_{\text{non-bonded}}(\{\mathbf{r}_i\}) = \sum_{i=1}^{N-1} \sum_{j>i}^N U_{\text{vdW}}(i, j, \mathbf{r}_i, \mathbf{r}_j) + \sum_{i=1}^{N-1} \sum_{j>i}^N U_{\text{coul}}(i, j, \mathbf{r}_i, \mathbf{r}_j), \quad (3.14)$$

where the van der Waals energy U_{vdW} term is represented by a Lennard-Jones potential and the second term U_{coul} representing electrostatic interactions is given by a standard Coulombic formula. The major contribution to the bonded interactions comes from deviations of bond lengths and angles away from the equilibrium as well as the torsion of dihedrals. The most common approach is to represent the bonding energy as a sum of those three quantities in the form of

$$U_{\text{bonded}}(\{\mathbf{r}_i\}) = \sum_i^{N_{\text{bond}}} U_{\text{bond}}(i, \mathbf{r}_a, \mathbf{r}_b) + \sum_i^{N_{\text{angle}}} U_{\text{angle}}(i, \mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c) + \sum_i^{N_{\text{torsion}}} U_{\text{torsion}}(i, \mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d), \quad (3.15)$$

where the bonding and angular terms are described by harmonic potentials while the dihedral term is a periodic function represented as a Fourier series. Combining energy contributions from both classes of interactions enables the formulation of a system wide interaction potential.

The general form of the individual terms of the interaction potential is straightforward, however, it can be used to perform realistic simulations by adjusting the parameters and details of the formulations to match the results of *ab initio* simulations [108, 111, 223] or experiments [242]. There is a variety of different forcefields available including the implementations of the fundamental interactions described in this section such as OPLS-AA [108, 111] or GAFF [242] which rely on the robust formulation for transferability and efficiency. Slightly more complex forcefields known as class-two, include additional cross-terms representing interactions between separate bonds or angles and are implemented in the PCFF [223] or COMPASS [224] packages. The most advanced approach involves “reactive force fields” (e.g. ReaxFF [237], REBO [27]) which are designed to capture the interactions in bond breaking and forming events, but at the expense of many more parameters.

3.1.5 Applications and limitations

There are plenty of computational experiments performed using MD as the framework encompassing all the modelling methods that rely on Newtonian description of dynamics at a molecular level; depending on the method for computing atomic interactions, a broad range of problems can be investigated. The all-atom simulations based on a quantum-mechanical description can provide the most accurate results, necessary for some investigations [36, 104, 124, 233], but at a small scale [13, 212] while in the empirical realm, optimised forcefields would allow us to look into systems of hundreds of thousands or millions of atoms or higher, depending on the simplicity of the interactions; the latter approach has been used in virtually all scientific fields and will most likely remain as a staple method [59, 80, 92, 102, 183, 194]. More extensive simulations could be performed if one were to move away from all-atom simulations, different techniques such as the united atom model, where hydrogen and carbon ions are combined into single particles, are available and can be used to scale the simulations up to even larger systems.

In general, the accuracy of a molecular dynamics simulation can always be traded for computational efficiency by choosing a different model for potential energy. There is, unfortunately, no free lunch as available methods either lack precision, speed or transferability.

3.2 Density-Functional theory

Density-Functional theory (DFT) is a theory forming the basis for quantum mechanical modelling methods used to investigate the electronic structure of a many-body system. Ever since its initial formulation in the 1960s, it has had a growing influence on the fields of solid state Physics and Chemistry, with the original papers reaching 20 000 citations each. In a conventional framework, finding the properties of a system of interacting atoms requires the solution of a many-body Schrödinger equation describing all the electrons and ions involved. The groundbreaking work of Hohenberg and Kohn [100] allowed the problem to be reformulated in terms of

the ground state electronic density which can be found by minimising the total energy functional

$$E[n] = F_{\text{HK}}[n] + \int U_{\text{ext}}(\mathbf{r})n d^3\mathbf{r}. \quad (3.16)$$

The functional $F_{\text{HK}}[n]$ has the same form for all N -electron systems, therefore the total energy functional and the ground state density are completely defined by the number of electrons N and the external potential. Variational minimisation of $E[n]$ results in the ground state density $n_0(\mathbf{r})$ and the ground state energy $E_0 = E[n_0(\mathbf{r})]$.

The practical functional and the recipe for finding its minimum was derived by Kohn and Sham [122] and relies on mapping the system of interacting electrons to a system of fictitious non-interacting particles. We rewrite the density in form of single-particle states $|\psi_a\rangle$

$$n = \sum_{a=1}^N \langle \psi_a | \psi_a \rangle \quad (3.17)$$

and expand the functional $F_{\text{HK}}[n]$ into a sum of three contributions

$$F[n] = K_{\text{S}}[n] + E_{\text{H}}[n] + E_{\text{XC}}[n], \quad (3.18)$$

where

$$K_{\text{S}}[n] = \sum_{a=1}^N \langle \psi_a | -\frac{1}{2} \nabla^2 | \psi_a \rangle \quad (3.19)$$

is the kinetic energy of non-interacting particles,

$$E_{\text{H}}[n] = \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' = \sum_{a=1}^N \langle \psi_a | \frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' | \psi_a \rangle \quad (3.20)$$

is the Hartree electron-electron energy and the $E_{\text{XC}}[n]$ is the exchange and correlation energy which constitutes other effects that are too complex to compute directly; it is given in an approximate form such as the Local Density Approximation (LDA) or the Generalised Gradient

Approximation (GGA). Combining all the terms together results in the total energy functional.

$$E[n] = \sum_{a=1}^N \left\langle \psi_a \left| \left(-\frac{1}{2} \nabla^2 + U_{\text{ext}} + \frac{1}{2} \int \frac{n(\mathbf{r}') d^3 r'}{|\mathbf{r}' - \mathbf{r}|} \right) \right| \psi_a \right\rangle + E_{xc}[n] \quad (3.21)$$

Finding the ground state in this scheme is achieved by minimising Equation 3.21 with respect to each of the single particle states. This requires the solution of a system of N equations (Kohn-Sham equations) which are not explicitly coupled but necessitate a self-consistent approach to finding the electronic density. This scheme has proven to be a major simplification from the original many body Schrödinger problem.

The theory formulated by Hohenberg, Kohn and Sham is exact in principle; however, it is impossible to use in that form. In order to facilitate computations, a variety of approximations have been developed, both conceptual such as the Born-Oppenheimer approximation and introduction of the exchange and correlation potential as well as numerical such as pseudopotentials, representation of the wave function in an incomplete basis set and the discrete Brillouin zone sampling. Even though the method is not exact, the results that it yields can be extremely accurate and provides useful insight into the electronic structure of investigated systems. Due to a resulting favourable balance of accuracy vs computational efficiency, Density-Functional Theory is one of the most commonly used simulation techniques and is very well perceived within the scientific community [180].

It is important to note that for the structures this project is concerned with such as CNTs and simple polymers, the standard formulation of DFT performs very accurately except for long-range van der Waals interactions [17] which are not included in the basic exchange-correlation (XC) functionals. There are, however, more specialised methods, such as DFT-D that can help to tackle that shortcoming [17, 90, 151].

3.3 Density-Functional Tight-Binding

The density-functional theory presented in the previous section is an invaluable tool. However, even with a sustained increase in available computational power, some problems are infeasible to treat with DFT. Classical forcefields on the other hand, while designed to drive large scale simulations, can often lack the desired accuracy due to missing quantum effects and limited availability of high precision parametrisations. Tight-binding (TB) methods such as Density-Functional tight binding (DFTB) [68, 186] sit in between two of those approaches being up to three orders of magnitude faster than DFT and significantly slower than classical potentials. They require some fitted parameters but much fewer than parametrised forcefields, and those necessary have a solid theoretical basis making them more transferable. Finally, TB methods can model most quantum effects available to DFT at lower cost, making them a worthwhile alternative in many cases where a qualitative understanding of a large-scale process is desired. The DFTB method itself couples the benefits of the TB formulation with relatively robust parametrisation making it a popular choice for many studies [77, 78] including large biomolecules[45, 65, 67], nanostructures [149] or organic systems [241].

3.3.1 Description

The DFTB formalism is derived from DFT equations; although only a brief summary is included in this section a more thorough presentation can be found in the following references [68, 69, 74, 123, 205]. We begin by presenting a Taylor expansion of the KS-DFT total energy functional [122] given in Equation 3.21, with an explicit ion-ion term, around the reference density which forms the base of the DFTB formulation [69, 123]. We first state the full formula and partition it into three contributions which are discussed individually in Sections 3.3.1.1, 3.3.1.2, 3.3.1.3 concluding with a recipe for finding the ground state energy in Section 3.3.1.4.

For a given system of particles, a reference density $n_0(\mathbf{r})$ represents an approximation to the ground state density that can be easily defined, for instance as the superposition of atomic densities as if all particles were neutral and isolated. The reference density does not minimise

the Kohn-Sham total energy functional $E[n]$ [122] but is assumed to lie close to the minimising density so that only a small perturbation $\delta n(\mathbf{r})$ is needed to find the ground state energy and therefore the perturbative analysis is valid. The third order Taylor expansion of the KS functional, including the expanded exchange and correlation functional reads

$$\begin{aligned}
E[n^0 + \delta n] = & \sum_a f_a \left\langle \psi_a \left| -\frac{1}{2} \nabla^2 + U_{\text{ext}} + U_H[n_0] + U_{\text{xc}}[n_0] \right| \psi_a \right\rangle \\
& - \frac{1}{2} \int U_H[n_0](\mathbf{r}) n_0(\mathbf{r}) d^3r + E_{\text{xc}}[n_0] - \int U_{\text{xc}}[n_0](\mathbf{r}) n_0(\mathbf{r}) d^3r + E_{\text{II}} \\
& + \frac{1}{2} \iint \left(\frac{\delta^2 E_{\text{xc}}[n_0]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} + \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \delta n(\mathbf{r}) \delta n(\mathbf{r}') d^3r d^3r' \\
& + \frac{1}{6} \iiint \frac{\delta^3 E_{\text{xc}}[n_0]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} \delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'') d^3r d^3r' d^3r''.
\end{aligned} \tag{3.22}$$

The linear terms in δn cancel each other [68] and the remaining zeroth order expansion (first two lines) is known as the DFTB1 method [187, 206], inclusion of the second order terms (third line) marks the self-consistent DFTB2 formalism [68] and the most recent DFTB3 [66, 85, 86, 251] approach is recovered when all terms presented here are used.

The total energy functional in Equation 3.22 can be decomposed into three distinct elements, the first of which is the band structure term corresponding to the KS Hamiltonian with fixed charge

$$\begin{aligned}
E_{BS}[n^0] = & \sum_a f_a \left\langle \psi_a \left| -\frac{1}{2} \nabla^2 + U_{\text{ext}} + U_H[n_0] + U_{\text{xc}}[n_0] \right| \psi_a \right\rangle \\
= & \sum_a f_a \langle \psi_a | H[n_0] | \psi_a \rangle = \sum_a f_a \langle \psi_a | H^0 | \psi_a \rangle.
\end{aligned} \tag{3.23}$$

The second line in Equation 3.22 containing the repulsive ion-ion interactions is referred to as the repulsive term

$$E_{\text{rep}}[n^0] = -\frac{1}{2} \int U_H[n_0](\mathbf{r}) n_0(\mathbf{r}) d^3r + E_{\text{xc}}[n_0] - \int U_{\text{xc}}[n_0](\mathbf{r}) n_0(\mathbf{r}) d^3r + E_{\text{II}}. \tag{3.24}$$

The last element of the total energy expansion is the charge fluctuation term responsible for

self-consistency given by

$$E_{sc}[n^0 + \delta n] = +\frac{1}{2} \iint \left(\frac{\delta^2 E_{xc}[n_0]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} + \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \delta n(\mathbf{r}) \delta n(\mathbf{r}') d^3r d^3r' \\ + \frac{1}{6} \iiint \frac{\delta^3 E_{xc}[n_0]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} \delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'') d^3r d^3r' d^3r''. \quad (3.25)$$

3.3.1.1 Band Structure term

The DFTB method relies on expanding the electronic eigenstates in a minimal basis set of atomic orbitals (AO)

$$\psi_a(\mathbf{r}) = \sum_{\mu} c_{\mu}^a \varphi_{\mu}(\mathbf{r}) \quad (3.26)$$

where the AOs, $\varphi_{\mu}(\mathbf{r})$ can be orbitals from a confined pseudo-atom (free atom with additional confinement potential added to the Hamiltonian) obtained from DFT calculations [123] with a scheme discussed by Eschrig [70]. The basis set expansion is limited to the valence electrons as all core electron effects are approximated in the external potential term. Expanding the eigenstates in this basis leads to the bandstructure term of

$$E_{BS}[n^0 + \delta n] = \sum_a f_a \sum_{\mu\nu} c_{\mu}^{a*} c_{\nu}^a \langle \varphi_{\mu} | H^0 | \varphi_{\nu} \rangle = \sum_a f_a \sum_{\mu\nu} c_{\mu}^{a*} c_{\nu}^a H_{\mu\nu}^0 \quad (3.27)$$

where the individual terms $H_{\mu\nu}^0$ are accepted as principal parameters of the method and can be pre-computed using one of the approaches discussed in [68, 69, 74, 123, 205].

3.3.1.2 Repulsive term

The second element of the total energy expansion is the practical equivalent to the DFT exchange and correlation functional and contains all of the effects deemed cumbersome to compute including the original DFT XC part. Almost all of the components of the repulsive contribution are given in terms of the reference density, defined as a superposition of neutral atom densities each dependent only on atomic number and position; the only exception is the ion-ion term which is given as a function of the atomic numbers and pairwise distances directly. As a result,

the whole of E_{rep} is independent of specific chemical setting and describes interactions between reference, neutral atoms which greatly limits the necessary number of parameters and ensures their transferability. The practical formulation uses a sum of pairwise parametrised functions called repulsive potentials in the form of

$$E_{rep} = \sum_{I < J} U_{rep}^{IJ}(R_{IJ}) \quad (3.28)$$

with $U_{rep}^{IJ}(R_{IJ})$ terms depending only on distance between atoms I and J and their atomic numbers. Functional values are found by fitting to intermediate DFT results [186] or empirical properties of experimental systems [84]. A general overview of repulsive potential fitting can be found, for example in Section 4 of Koskinen *et al.* [123].

3.3.1.3 Charge fluctuation term

The charge fluctuation component approximates the higher order terms of Equation 3.22 and is known as the DFTB2 correction when containing second order terms and DFTB3 if the third order term is also included. In most current implementations of density-functional tight binding both contributions are used [7] to achieve higher precision; however, here, only the DFTB2 part will be discussed for simplicity. The derivation of the third order correction follows a similar logic to the reasoning presented here and can be found in more in-depth texts [68, 69, 74, 205].

We start by writing the density fluctuation as a superposition of individual atomic contributions

$$\delta n(\mathbf{r}) = \sum_I \delta n_I(\mathbf{r}). \quad (3.29)$$

which can be done by simply partitioning the space into separate subspaces centred around individual atom. Each contribution is approximated by the zeroth element of the multipole expansion (monopole term) leading to the formula

$$\delta n(\mathbf{r}) = \sum_I \Delta q_I \delta \hat{n}_I(\mathbf{r}) \quad (3.30)$$

where the density profile $\delta\hat{n}_I(\mathbf{r})$ is normalised and spherically symmetric; usually a non-negative Gaussian or Laplace distribution is used. Given this expansion, the charge fluctuation contribution in Equation 3.25 (specifically, its second order term) can be rewritten as

$$E_{\text{coul}} = \frac{1}{2} \sum_{IJ} \Delta q_I \Delta q_J \iint \left(\frac{\delta^2 E_{xc}[n_0]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} + \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \delta\hat{n}_I(\mathbf{r}) \delta\hat{n}_J(\mathbf{r}') d^3r d^3r'. \quad (3.31)$$

For terms where $I \neq J$, the XC contribution vanishes for local XC functionals commonly used in DFTB and the remaining Hartree term can be evaluated analytically since $\delta\hat{n}(\mathbf{r})$ is given by a simple, spherically symmetric profile. The result

$$\frac{1}{2} \sum_{IJ} \Delta q_I \Delta q_J \iint \frac{1}{|\mathbf{r} - \mathbf{r}'|} \delta\hat{n}_I(\mathbf{r}) \delta\hat{n}_J(\mathbf{r}') d^3r d^3r' = \frac{1}{2} \sum_{IJ} \Delta q_I \Delta q_J \xi_{IJ}(R_{IJ}) \quad (3.32)$$

is stored in terms of analytical functions $\xi_{IJ}(R_{IJ})$ which can be calculated given the specific density profile used in the approximation.

For terms where $I = J$, we recall the Taylor series expansion of atomic energy w.r.t. charge fluctuation given by [178]

$$E(\Delta q) \approx E_0 + \left(\frac{\partial E}{\partial \Delta q} \right) \Delta q + \frac{1}{2} \left(\frac{\partial^2 E}{\partial \Delta q^2} \right) \Delta q^2 = E_0 - \chi \Delta q + \frac{1}{2} U^H \Delta q^2. \quad (3.33)$$

We then observe that Equation 3.31 is in fact the second order term from the Taylor expansion of the total energy in Equation 3.22 and the $I = J$ terms of Equation 3.31 can be approximated as

$$\frac{1}{2} \left(\frac{\partial^2 E_I}{\partial \Delta q_I^2} \right) \Delta q_I^2 = \frac{1}{2} U_I^H \Delta q_I^2. \quad (3.34)$$

Combining all of the above, we have the charge fluctuation correction given by

$$E_{\text{sc}} = \frac{1}{2} \sum_{IJ} \xi_{IJ}(R_{IJ}) \Delta q_I \Delta q_J \quad (3.35)$$

where $\xi_{IJ}(R_{IJ}) = U_I^H$ for $I = J$. It is important to note that two different formulas for

$\xi_{IJ}(R_{IJ})$ must not be discontinuous and

$$\xi_{II}(R_{II} = 0) = U_I^H \quad (3.36)$$

which can be used to determine the free parameters in the density profile $\delta\hat{n}_I(\mathbf{r})$.

Atomic populations The density fluctuation in Equation 3.30 was partitioned into individual contributions in terms of extra electron population on each atom Δq_I . While they were never exactly defined, their values can be found using the Mulliken population analysis [163] based on AOs discussed in Section 3.3.1.1. We first write the total number of electrons on atom I as

$$q_I = \int_{\mathcal{V}_I} n(\mathbf{r}) d^3r = \sum_a f_a \int_{\mathcal{V}_I} |\psi_a(\mathbf{r})|^2 d^3r. \quad (3.37)$$

Using the localised basis mentioned in Section 3.3.1.1 we can rewrite that value as

$$q_I = \sum_a f_a \sum_{\mu\nu} c_\mu^{a*} c_\nu^a \int_{\mathcal{V}_I} \varphi_\mu^*(\mathbf{r}) \varphi_\nu(\mathbf{r}) d^3r. \quad (3.38)$$

The integral $\int_{\mathcal{V}_I} \varphi_\mu^*(\mathbf{r}) \varphi_\nu(\mathbf{r}) d^3r$ can be approximated in three ways depending on μ and ν . If both belong to atoms other than I , the integral value is assumed to be zero while if both belong to I , it can be approximated by a Dirac delta since the atomic orbitals (introduced in Section 3.3.1.1) on the same atom are orthonormal. In case μ belongs to a different atoms than ν , we divide the contributions equally between the two leading to the expression:

$$q_I = \sum_a f_a \sum_{\mu \in I} \sum_{\nu} \frac{1}{2} (c_\mu^{a*} c_\nu^a + \text{c.c.}) S_{\mu\nu}, \quad (3.39)$$

where cc is a complex conjugate. Finally, the extra electron population on each atom can be found as

$$\Delta q_I = q_I - q_I^0. \quad (3.40)$$

3.3.1.4 Finding the ground state energy

Now that most of the approximations included in the DFTB method have been presented, it is possible to combine the results of previous sections and rewrite the total energy from Equation 3.22 under the DFTB2 approximation as

$$E = \sum_a f_a \sum_{\mu\nu} c_\mu^{a*} c_\nu^a H_{\mu\nu}^0 + \sum_{I<J} U_{\text{rep}}^{IJ}(R_{IJ}) + \frac{1}{2} \sum_{IJ} \xi_{IJ}(R_{IJ}) \Delta q_I \Delta q_J \quad (3.41)$$

where all of the elements are familiar. As with DFT, we look for the ground state energy by minimising the variational formula $E - \sum_a \varepsilon_a \langle \psi_a | \psi_a \rangle$ assuming ε_a are unknown Lagrange multipliers. Finding the desired minimum implies solving a series of equations

$$\sum_\nu c_\nu^a (H_{\mu\nu} - \varepsilon_a S_{\mu\nu}) = 0 \quad (3.42)$$

for all a and μ which are equivalent to the Kohn-Sham equations in DFT. In the above formula

$$H_{\mu\nu} = H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_K (\xi_{IK}(R_{IK}) + \xi_{JK}(R_{JK})) \Delta q_K, \quad \mu \in I \text{ and } \nu \in J. \quad (3.43)$$

The elements of the final Hamiltonian depend on atomic populations discussed in Section 3.3.1.3 defined in terms of coefficients c_ν^a ; as a result the formula can only be minimised self-consistently although the number of iterations is usually considerably lower than in DFT. Having the ground state energy, all other properties such as atomic forces can be evaluated as the derivative of the total energy using the Hellmann-Feynman theorem [71, 97].

3.3.2 Limitations

The DFTB approach is heavily based on the Density-Functional theory and most of its parameters are computed using DFT. As a result, the method inherits most of the shortcomings of the original Kohn and Sham approach (specifically the exchange-correlation functionals: see Section 3.2) such as issues with self-interaction or overpolarizability. Furthermore, in the formulation presented here, more approximations are introduced on top of DFT, making the method

significantly less flexible. For certain cases, DFT level accuracy can be achieved, however, this should not be expected for all the properties as usually one set of parameters can reproduce one type of results precisely, e.g. lattice constants or vibrational frequencies but not both. The parametrisation itself is a crucial element of the DFTB scheme and while plenty of well-performing sets are established, not all of the periodic table is covered. In essence, DFTB is generally fast and accurate but lacks the transferability of a fully *ab initio* treatment.

3.4 Hybrid Approach

Traditionally we are used to separating problems in different length scale classes; however, it is usually the case that local effects influence the evolution of an intrinsically large system. Investigation of those structures with a coarse-grained method would miss the important phenomena while accurately looking into a small effect might not provide the whole picture. Examples would include crack tip propagation [118] where the crack formation involves bond breaking, a quantum mechanical effect influencing the classical movement of many ions or the study of the local structure of polymer networks without losing track of their large scale rheological properties [231]. The same type of problem can be observed in the simulations of functionalized CNT-polymeric composites where the polymer bulk can only be described using classical, inexpensive, methods but the functional groups interact with the CNTs in an intrinsically quantum manner. A conventional description of those effects could result in missing some key phenomena while a fully quantum-mechanical approach is not computationally feasible.

One of the most common methods of approaching this issue involves hierarchical modelling, where a series of small but accurate simulations are used to develop an empirical model suited to describe a specific phenomenon at a fraction of the cost. Such methods can usually reproduce the particular effect it was designed for with reasonable success [170, 231] but can be impractical when trying to discover new properties due to limited transferability. Alternatively, empirical models designed to be general, such as most forcefields discussed in Section 3.1.4.1, rarely offer sufficient accuracy.

In some problems, the mechanisms that need to be described are strongly coupled together and their separation into separate simulations can prove to be a difficult task. This is often the case when nanoscale effects are initiated by microscale forces, for example the failure of covalent bonds at the CNT-polymer interface as a result of external stress applied to a composite. In this case, it is necessary to apply two levels of theory concurrently and engineer a simulation where a simple and inexpensive model is used to simulate the majority of the system while areas of special interest are focused on with a complex method ensuring an accurate description. In general, it is possible to combine various methods operating at different length scales, for example by extending continuum mechanics with molecular simulations in a quasicontinuum approach [189, 217, 227], including applications to CNPCs [94, 133, 236], or supplementing coarse-grained dynamics with atomistic computations [185]. However, this work is focused on atomistic modelling and the following sections will be devoted to combining two molecular techniques.

Similar simulation techniques have been successfully applied in the past: QM/MM methods discussed in Section 3.4, have been used to study crack propagation in a silicon crystal [18, 28, 55, 118] as well as CNTs with the ONIOM approach [46], successfully predicting elastic properties of defective CNTs [119] and interactions of CNTs with non-covalently bonded molecules [103, 202]. Investigation of CNT-polymer interfaces, however, has been mostly limited to classical molecular dynamics [44, 76, 76, 138, 168] and atomistic-continuum hybrid approaches [94, 133, 236] studying the properties of CNPC structures of 100 nm and larger.

3.4.1 Coupling two classical methods

The most straightforward implementation of the concurrent coupling on the atomistic level involves combining two classical methods; this scheme is understandably not very popular, but the discussion can be helpful as a gentle introduction.

We start by partitioning the system into two areas referred to as inner regions, one designed to be treated with method A (region A) and the other to be simulated with method B (region B). Given a fixed boundary, we construct two subsystems, each including a part of the original

system and a buffer layer of a final width as shown in Figure 3.1. The width of the buffer layer should be chosen to match the characteristic lengths of the method, so the atoms inside the inner region are unaffected by the treatment of the boundary. Energies of each subsystem are calculated by considering individual inner regions with appropriate buffer zones and then the total energy is reconstructed by combining the two contributions. Assuming that the two models are short-sighted and describe only local interactions, the energy of region A could be decomposed into contributions from individual atoms ϵ_i

$$E_{\text{total}}^{(A)} = \sum_i \epsilon_i = \sum_{i \in A} \epsilon_i + \sum_{i \in A_{\text{buff}}} \epsilon_i = E_{\text{inner}}^{(A)} + E_{\text{buff}}^{(A)} \quad (3.44)$$

where A represents region A and A_{buff} the buffer of region A as seen in Figure 3.1. This gives us the energy of the inner region $E_{\text{inner}}^{(A)} = \sum_{i \in A} \epsilon_i$ and the same procedure applied to the second region, yields $E_{\text{inner}}^{(B)} = \sum_{i \in B} \epsilon_i$ which can be used to recover the total energy

$$E = E_{\text{inner}}^{(A)} + E_{\text{inner}}^{(B)} \quad (3.45)$$

which in turn can be used to find other properties of the system such as atomic forces.

3.4.2 Coupling quantum and classical simulation methods

In hybrid quantum/classical modelling the QM description is used to supplement an empirical approach where the latter is deemed inaccurate. This framework has been successfully used to investigate various problems where only a small part of the system corresponds to the active element where the reaction is driven by quantum effects while the remainder of the structure represents the environment and necessitates just a basic description. The applications can be found in multiple fields; some of the most prominent examples include the study of protein [199] and enzymatic [193] reactions, hydrogen dissociation [113], the determination of acidity of zeolite particles [218], determination of selectivity in catalysed reactions [109], simulation of liquid water [20, 30] or previously mentioned crack propagation in silicon crystals [118]. As a general note, we prefer classical models that are robust and inexpensive; they are expected

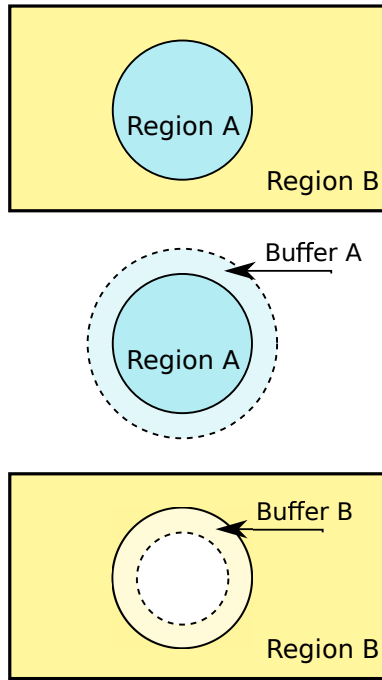


Figure 3.1: Partitioning of the whole system (top panel) into two subsystems (mid and bottom panel) each composed of the inner region and the buffer zone. The division is used to evaluate energies with different methods in the classical coupling scheme; regions coloured blue are treated with method A and those coloured yellow with method B.

only to provide a rudimentary description of atomic interactions and more straightforward base techniques result in faster computations and more transferable final formulation.

A hybrid scheme has areas described by two methods; for this approach to be valid, the properties described by the higher level theory must be local in nature. Interactions within the centre of the quantum region must be computed with accuracy by only considering a finite neighbourhood and if the region is large enough, should be unaffected by the classical treatment of the remainder of the system. Both of those requirements are brought to completion when the *strong locality* condition is fulfilled. It can be defined as

$$\frac{\partial^n}{\partial \mathbf{r}_i^n} \frac{\partial E_{\text{tot}}}{\partial \mathbf{r}_j} \rightarrow 0 \quad \text{as} \quad |\mathbf{r}_i - \mathbf{r}_j| \rightarrow \infty \quad \forall n, i \neq j. \quad (3.46)$$

The majority of quantum systems obey strong locality and the intrinsically long-range effects such as Coulombic or van der Waals interactions can be very accurately treated with classical approximations outside the hybrid framework.

3.4.3 Energy based QM/MM

Assuming strong locality is fulfilled, the total energy of a hybrid quantum/classical system can be found with either a subtractive or an additive scheme [208]. In the former approach, originally developed by Maseras and Morokuma in 1995 [157], the total energy can be found with three isolated calculations. Given a system with the quantum region A and the remainder denoted as B we can write

$$E_{\text{tot}} = E_{QM}(A) + E_{MM}(A + B) - E_{MM}(A) \quad (3.47)$$

where the subscripts correspond to different energy models and the partitioning of the system is shown in Figure 3.2. The main advantage of this scheme is the ease of implementation as there are no explicit coupling terms and the formulation itself ensures no double counting occurs. Since the total energy can be found with a series of three standard simulations, any available quantum and classical model can be used within this framework without any modifications. The most popular implementation of the subtractive approach can be found in the ONIOM package [47, 225] which has been used in multiple successful studies for example concerned with reactions of transition metal complexes [171] or structure, reactivity, and selectivity of enzymes [209], DNA repair [24], prediction of elastic properties of defective CNTs [119] and interactions of CNTs with non-covalently bonded molecules [103, 202]; more can be found in references [141, 142, 221] and in a review by Chung *et al.* [47]. It is noteworthy that ONIOM is not the only implementation of the subtractive scheme and other formulations are not less impressive and also widely used [198].

In the additive approach, the energies of the quantum and classical regions are found directly and added to the explicitly computed term E_{QMMM}^I accounting for interactions across the QM/MM boundary. This scheme, schematically shown in Figure 3.3, can be summarised as

$$E_{\text{tot}} = E_{QM}(A) + E_{MM}(B) + E_{QMMM}^I. \quad (3.48)$$

In this case, the interaction term needs to be specified precisely ensuring no relations are

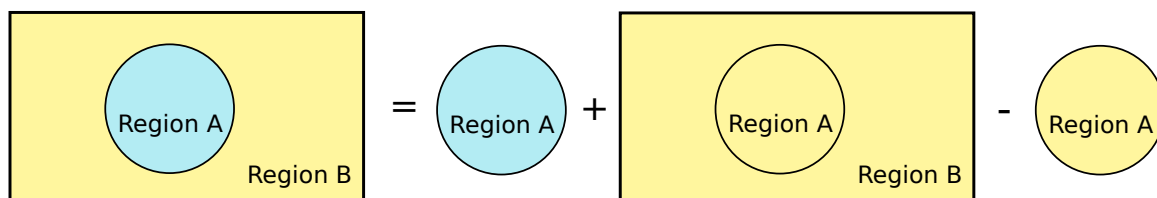


Figure 3.2: Schematic representation of the subtractive scheme for computing QM/MM total energy. Regions coloured blue are treated with the quantum method and those coloured yellow with classical method.

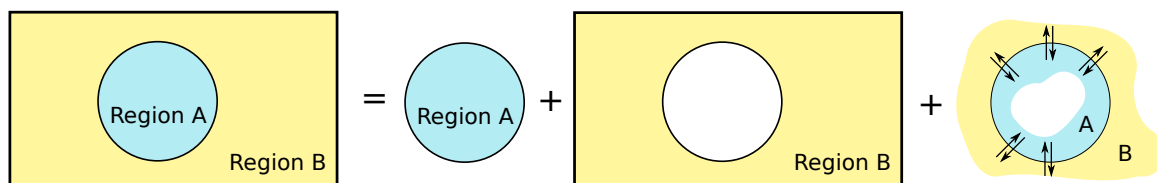


Figure 3.3: Schematic representation of the additive scheme for computing QM/MM total energy. Regions coloured blue are treated with the quantum method and those coloured yellow with classical method while the rightmost picture represents interactions across the QM/MM boundary.

omitted or double counted and a dedicated implementation is required. However, no classical description of the inner QM region is necessary which can make this approach much easier to set-up [196] when the effects in the QM region are strictly quantum. The advantages of this method have been applied to investigate protein reactions [220], enzyme hydroxylation [62] and proton transfer at metal sites in proteins [112].

In the formulations presented here, we do not specify how exactly the interaction between two regions are defined; this can be accomplished in two frameworks of mechanical and electrostatic embedding that are outlined below.

3.4.3.1 Mechanical embedding

In the naive formulation, all interactions between QM and MM regions are treated at the classical level resulting in a mechanical embedding scheme. This is implemented by computing the properties of the quantum subsystem in the absence of the remainder of a system while all other interactions are described with the classical approach. This type of embedding is the default treatment in the subtractive scheme and requires no changes to Equation 3.47 to implement while in the additive approach, the $E_{QM}(A)$ and $E_{MM}(B)$ terms are computed

normally and all atomic interactions across the QM/MM boundary are found according to the classical model and summed to recover the E_{QMMM}^I term.

This treatment has a clear advantage of being relatively simple and robust, but it is considered to be less accurate than the alternative [34, 208] and as a result is less prevalent in most cases [34, 63, 208].

3.4.3.2 Electrostatic embedding

The accuracy of the hybrid simulations can be improved by treating the interactions between QM and MM atoms at the quantum level. Instead of formulating a dedicated coupling term, it is possible to include an approximate description of the charge distribution of the classical atoms in the QM calculations. As a result, the electronic structure of the quantum region is relaxed in the presence of the remainder of the system and the interaction energy is naturally contained within the QM term. In practice, the charges are usually approximated by partial charges from the MM model as monopoles located on the atomic coordinates [56, 72, 198, 214]; higher-order multiple approximations can also be used, but are less common. This approach is natural to the additive scheme by simply considering the interaction term to be contained inside the QM energy term. In the subtractive scheme, the atomic charges of atoms in region A (see Figure 3.2 for notation) need to be set to zero in both classical simulations while the charge distribution describing system B is included in the calculation of $E_{QM}(A)$ [198].

In the standard formulation, only the QM system is polarised by the MM region. However, in case a more precise description is desired, it is possible to iteratively relax the charges of each system in the presence of the other to achieve a self-consistent equilibrium [174, 190, 215]. This necessitates a polarizable classical model [148] alongside a QM method capable of treating polarizabilities making this formulation considerably more complex; as such, it is more suitable for single point calculations than dynamical studies. Both standard electrostatic and polarizable embedding techniques can lead to much more accurate simulations compared to the mechanical approach, but the formulation can be much more complex making it less suitable for large scale investigations.

3.4.3.3 Covalent bond termination

The partitioning of the system into QM and MM regions is reasonably simple when the two are composed of separate molecules. However, when the quantum/classical boundary cuts through covalent bonds, the resulting interface needs to be properly truncated. This can be achieved by including dedicated frozen orbitals to contain the unpaired electrons [82, 132, 166, 208, 232] or by terminating the dangling bonds with hydrogen atoms or artificial pseudo-atoms [72, 195, 199, 208, 214]; the latter approach is generally more popular due to simplicity. Unfortunately, a quantum mechanical description, while local, is not a nearest neighbour model and the imperfect termination strategies presented here can have a significant impact on the electronic structure of terminated atoms.

3.4.4 Force-mixing based methods

In the case of dynamical simulations discussed in Section 3.1, the primary property of interest is the force on each atom necessary to integrate the equations of motion. This leads to an alternative formulation of the QM/MM coupling where the focus is not on the total energy of the system but on a purely local quantity - the atomic force.

Here, three distinct zones are defined as shown in Figure 3.4, the inner QM region where the forces are calculated with a quantum method, the outer MM region where the classical approach is used and the transition zone, where the forces are found by directly interpolating between two levels of theory. The transition force $\mathbf{F}^i$ can be computed by linear interpolation

$$\mathbf{F}^i = \lambda \mathbf{F}_{\text{QM}}^i + (1 - \lambda) \mathbf{F}_{\text{MM}}^i. \quad (3.49)$$

The λ parameter in Equation 3.49 is usually varied from one at the boundary with the QM region to zero at the end of the transition zone. However, it can also be set to zero at the midpoint or even throughout the whole zone as QM forces evaluated at the outer edge of the transition zone (QM/MM boundary) can be incorrect [181] and including them can lead to unphysical dynamics. This formulation can also be interpreted as the buffered force approach

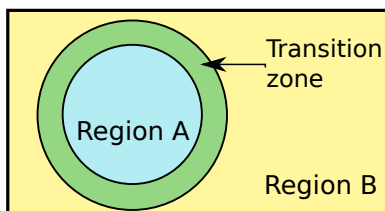


Figure 3.4: Schematic representation of the transition zone force mixing scheme for computing QM/MM forces. Regions coloured blue are treated with the quantum method and those coloured yellow with classical method while the forces on transition zone (in green) atoms are found by directly interpolating between two levels of theory.

summarized in Figure 3.5, where the quantum simulations are carried out on the QM region expanded by the buffer zone but forces on the buffer atoms are discarded.

The straightforward inclusion of the buffer layer is one of the main advantages of the force-mixing QM/MM approach as if it is sufficiently wide, the inner QM forces should be identical to those obtained from a full QM simulation and most edge effects can be ignored; this is explored further in Chapter 4 for CNT-polymer composite systems. In practice, using an infinitely large buffer is impractical, but as its size can be tweaked, this formulation offers a possibility to continuously exchange computational efficiency for accuracy until an appropriate balance is found. It is important to note that the buffer region can also be used in the energy-based concurrent hybrid method but the formulation is significantly more complex and it is therefore less common [63].

An additional benefit of the force-mixing method is the relatively straightforward solution to the problem of changing the QM region on-the-fly referred to as adaptability. It should be possible to reassign the quantum zone at will with little to none downside as energy and forces are generally not conserved in this framework (see Section 3.4.4.3). While adaptive simulations can be performed with Energy based QM/MM [63], the approach focusing on forces requires many fewer modifications and is therefore more popular with applications in simulations of liquid water [20, 30] or crack propagation in silicon crystals [118].

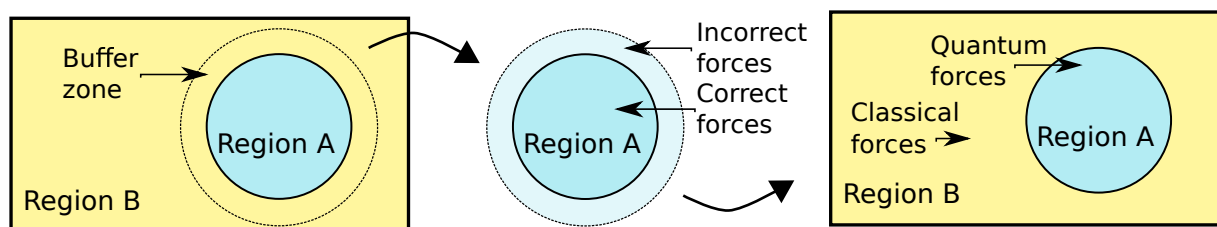


Figure 3.5: Schematic representation of the buffered force mixing scheme for computing QM/MM forces. Classical region A, coloured yellow, is treated with classical method while the forces on the atoms in the QM zone (region B coloured in blue) are found by investigating the QM region expanded by the buffer zone but forces on the buffer atoms are discarded.

3.4.4.1 Covalent bond termination

The termination of covalent bonds in the force mixing approach follows the strategies discussed in Section 3.4.3.3. However, the introduction of the buffer region makes the edge effects corresponding to an artificial truncation of dangling bonds much less disruptive as the forces on atoms affected the most are discarded.

3.4.4.2 Mechanical and electrostatic embedding

The two embedding approaches presented for energy based QM/MM (see Sections 3.4.3.1 and 3.4.3.2) are still applicable in the force mixing formulation. Treating the QM/MM interactions classically results in mechanical embedding and including the information about the inner system's charge distribution in the quantum computation leads to electrostatic embedding, considered to be more accurate. However, the significance of a precise description of the electrostatics is reduced with the introduction of a buffer region. The interactions diminish with distance and the benefit from electrostatic embedding is reduced as the width of the buffer layer is increased.

Peguiron *et al* [182] have performed a more detailed analysis. In their study, a selection of silicon-based systems with reasonably strong electrostatic interactions (absolute point charges of up to $1.28 e$) was studied by comparing the force evaluation errors resulting from buffered force QM/MM with mechanical and electrostatic embedding. The result show that beyond a buffer width of $6 \text{ \AA}$, the two methods are comparable, and the report concludes with the statement

“...the contribution of electrostatic embedding (as opposed to simple cluster embedding) to the accuracy of the bf-QM/MM forces is less relevant than the contribution of the buffer region.”. The investigation analyses the electrostatic embedding with the monopole approximation to the atomic charge distribution and it is possible that a more detailed description would have a greater impact.

3.4.4.3 Limitations

The main disadvantages of the force-mixing approach stem from the fact that observables are derived from two separate Hamiltonians rather than a combined one. As a result, the energy and momentum in a dynamical simulation might not be conserved, and the action-reaction principle at the QM/MM boundary can be violated. The first issue can be easily addressed by subtracting an equal fraction of the net force (which is usually very small) from each atom restoring momentum conservation. The energy issue is generally tackled by performing dynamical simulations in a canonical ensemble which, while not rigorous, works well in practice [20, 30, 63]. Finally, the effect of violating the action-reaction principle can be mitigated by matching the forces at the QM/MM boundary. This is usually achieved through carefully tuning the λ parameter from Equation 3.49 adjusting the classical model to match the quantum mechanical results at equilibrium conditions [87, 118] as discussed in Section 4. However, this approach often requires large buffer sizes to smoothly vary λ which adds to the computational cost. Alternatively, the action-reaction principle can be restored completely with an approach such as Learn on the Fly from Csányi *et al.* [55] where QM forces are not used directly but the classical potential is locally re-fitted throughout the simulation to accurately reproduce QM forces on atoms in the quantum region. As a result of this procedure, a single, continuous Hamiltonian describing the whole system is composed ensuring smooth transitions between the regions, without any discontinuities which may affect the action-reaction principle.

3.4.5 Conclusions

As with any accurate computational method, the concurrent coupling of quantum and classical simulation methods is much slower than classical MD due to the necessity of having to perform QM calculations. When it comes to well-defined computations with no quantum effects, it is much better to use the well parametrised, pre-optimized forcefield that could offer equally accurate results with a lower computational cost. However, with the growing interest in multi-lengthscale problems, concurrent modelling is bound to be applied to increasingly diverse situations as including semi-empirical or fully *ab initio* models offers excellent transferability. Ideally, this approach could be used as a black box to model any system that requires a representation of quantum mechanical phenomena in a molecular mechanics framework. Currently, the only alternative is offered by the reactive forcefields such as ReaxFF [237] or REBO [27]; however, those methods can be hindered by low transferability due to a large number of parameters that need to be pre-fitted to describe complex quantum effects[3, 38, 95, 207].

Both the total energy and force-mixing varieties of QM/MM have been successfully used in the past and have a unique set of advantages and disadvantages making them suitable for different sets of studies. In the case of the dynamical evolution of CNT-polymer systems presented here, the scheme based on force-mixing seems to be a more natural fit as the straightforward introduction of the buffer region makes the termination of covalent bonds less disruptive and a simple application to adaptive simulations means the QM region can be changed frequently ensuring the expensive quantum simulations are performed only when necessary.

3.5 Summary

In this chapter, the concepts behind the methodology used in this study were briefly summarised. The following work is mostly concerned with dynamical simulations using a QM/MM method coupling classical forcefields with density-functional tight binding, and those three main ingredients were introduced here.

Chapter 4

Multiscale simulations of CNPCs: methods

Partially reproduced from

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4.1 Introduction

Experimental investigation of CNPC interfacial properties discussed in Section 2.4.1 can be instrumental when evaluating the interfacial strength. However, measuring the properties of a single CNT-polymer interface, let alone a single attachment can be challenging due to the nanometre diameter of the nanotubes. As the mechanism of interfacial load transfer is believed to depend on the local atomic structure [138, 153, 244, 249], the molecular resolution offered by computational studies can provide complementary insight into the underlying processes.

However, studying this problem using computational simulations is challenging because it is

inherently multiscale (see Section 2.4.2): failure is a macroscopic phenomenon, yet it originates from local changes in chemical bonding that occur at the nanoscale. In CNPCs, effects that would benefit from a QM description, are present only in regions where bond-breaking or bond-forming processes are occurring while the behaviour of the surrounding environment can be described adequately by a less accurate, classical model. As such, the multiscale nature of the problem lends itself to the application of a hybrid approach the will be introduced in Section 3.4, which combines an accurate QM Hamiltonian with a computationally inexpensive classical forcefield.

While similar simulation techniques have been successfully applied in the past, investigation of CNT-polymer interfaces has been mostly limited to classical molecular dynamics and atomistic-continuum hybrid approaches. The complexity of polymer-based composites makes the application of QM/MM simulation techniques a challenging task as it is often unclear which elements of the system should be treated with which level of theory [19]. Here, we demonstrate a concurrent hybrid simulation technique with an automated, dynamic selection of QM regions based on atom-resolved potential energies. We use the presented approach to study a simplified model of the CNT-polymer interface consisting of the fundamental building-block of the interface, namely the attachment of a single CNT and polymer chain. We show that the presented approach can be successfully applied to study the critical failure of such systems and reproduces fully-QM results at a modest computational cost. The method is thoroughly validated and used to evaluate a variety of strategies for grafting polymer chains to the CNT surface highlighting well-performing candidates.

The remainder of the chapter is structured as follows: in Sec. 4.2 we describe our novel hybrid simulation method; in Sec. 4.3 we show the results of a dynamical study of the mechanism of load transfer at the CNT-polymer interface. Sec. 4.4 is concerned with validation; Sec. 4.5 describes the QM/MM study of fracture in defective CNT and finally Sec. 4.6 contains the conclusions of this chapter.

4.2 Hybrid simulation method

The method demonstrated here is based on the “Learn on the fly” approach [55, 58] and aims to compute a purely local quantity - the force on each atom [54]. Forces are calculated using the quantum method in the chosen region and a classical forcefield in the rest of the system instead of deriving all of them from a combined Hamiltonian. The detailed procedure used in this study is described in detail below and shown schematically in Fig. 4.1 while more general information about the force mixing approach can be found in Section 3.4.4.

Classical forcefields are designed to describe atomic interactions in the vicinity of an equilibrium configuration. However, when the structure is significantly disturbed (as would be the case during a fracture event), the description can be much less accurate. Within a classical picture, the total potential energy of an atom exceeding a certain threshold indicates the structure locally moving out of its stable configuration, at which point the classical treatment is no longer accurate and a quantum mechanical description is desired. In our scheme, atoms fulfilling this criterion are flagged and individual inner QM clusters are constructed by including all particles within a selected number of bond hops from each particle. After flagging is completed, overlapping clusters are joined to avoid unnecessary calculations, although they could be treated separately to facilitate better parallelisation as discussed by Csányi *et al.* [54] and more recently by Caccin *et al.* [32]. Selecting only out-of-equilibrium atoms has an additional benefit of ensuring that the computationally expensive quantum mechanical calculations are only performed when needed. In most simulations, the majority of timesteps do not involve any QM computations which allows for very efficient calculations.

In practice, the flagging mechanism determines the composition of inner quantum regions by comparing the per-atom potential energy with the per-atom energy threshold. The former is evaluated based on the classical forcefield: for each force-field term (bond stretch, angle, dihedral etc.) in which an atom is involved, that atom is assigned a proportional fraction of that term’s energy ($\frac{1}{2}$ for two-body terms, $\frac{1}{3}$ for three-body terms etc.). The per-atom energy is recorded by keeping track of the exponential moving average of the value. The latter, per-atom energy thresholds, are computed based on mean atomic energies. Prior to the main simulation,

the system is evolved for a few thousand timesteps in the NVT ensemble throughout which the mean energies per atom are computed. The energy threshold for a given atom is then set to be

$$E_{\text{thresh}}^i = (1 + \alpha)E_{\text{mean}}^i \quad (4.1)$$

It is important to note that the flagging mechanism is hysteretic: there is a lower energy threshold for an atom to remain within a QM region than to enter it. This is achieved by setting the multiplicative factor α to be 0.1 for atoms within a QM region and 0.2 for those outside at a given timestep.

Once the inner QM clusters are found, the next step involves including the buffer region which is constructed by expanding the inner cluster through adding atoms within a fixed number of bond-hops. The full cluster constructed from inner and buffer regions is carved out of the structure and any dangling bonds are hydrogenated to form a structure used to compute quantum mechanical properties. It is important to consider the size and the geometry of the buffer region used to ensure accurate force evaluation and it is important to find the right balance between computational speed and accuracy. This discussion is picked up in Section 4.4.1.

Clusters that are prepared in the manner described above are used to compute quantum forces on the flagged atoms. In our simulations, the QM region is not embedded in the electric field of the MM system but rather placed in a vacuum. The issue is further discussed in Section 3.4.4.2 where the study by Peguiron *et al.* [181] is used to show that even for systems with strong electrostatic interactions, the electrostatic embedding (EE) strategy is not necessary once a sufficiently large buffer is used. In our simulations, the atomic charges are much lower: up to 0.4e as opposed to 0.5 - 1.2e in the oxide system from Peguiron *et al.* [181], which indicates that EE should be even less impactful for structures investigated here.

After QM calculation, the quantum mechanical forces are used to replace the classical forces on the atoms in the inner region while QM forces on atoms in the buffer region are discarded. In this formulation, the boundary between inner and buffer regions is abrupt. However, a gradual

transition between the two regions requires using the low accuracy forces evaluated on the buffer atoms which is considered disadvantageous; this has been discussed in more detail in Refs.[19] and [181] and Section 3.4.4. Discontinuities which may affect the action-reaction principle are treated by carefully re-fitting the parameters of the classical forcefield to reproduce the QM relaxed geometries and the elastic response around equilibrium. The re-fitting is performed for two and three body interactions in the polymer chain and the CNT by matching the QM and classical length and elastic response at 0-3% strain of the 10-monomer polypropylene chain and a 40 Å, end-capped (10, 0) CNT respectively. Assuming the flagging mechanism works correctly, the classical atoms just outside the QM/MM boundary are in their stable configuration and matching the quantum and classical descriptions around the equilibrium ensures that the forces at the QM/MM boundary derived using both models are comparable. This approach to treating the boundary between two levels of theory is validated in Section 4.5.

A typical simulation using the QM/MM routine consists of a multitude of iterations following the above description. It is summarized below and shown schematically in Figure 4.1.

1. **Classical evaluation.** Forces and energies on all atoms are calculated using a classical forcefield.
2. **QM flagging.** Atoms that move out of an equilibrium configuration, which indicates less accurate classical description, are flagged once their potential enrgy moves above the threshold defined in Equation 4.1.
3. **Cluster carving.** A cluster of flagged atoms, including an encapsulating region of buffer atoms, is carved out of the system, dangling bonds are passivated with hydrogen atoms, and the resulting cluster is treated in vacuum.
4. **Cluster QM calculation.** The Prepared cluster is simulated using a quantum-mechanical method.
5. **Force mixing.** Classical forces on flagged atoms in the simulation are replaced by the quantum mechanical forces.

6. **Time evolution.** The system is evolved in time using the Verlet algorithm with the mixed quantum/classical forces; the end state of the system becomes the new initial state.

Within the following work, the CVFF [57] as implemented in LAMMPS [184] was used as a base classical potential. Two and three body forcefield terms for the polypropylene backbone and CNT carbon atoms were rescaled using the procedure described above and in Section 4.5. In this study, density-functional tight binding (DFTB) [188] implemented in the PLATO [116] simulation package was used as the quantum mechanical method, but could readily be extended to a large number of quantum mechanical codes interfaced to the Atomic Simulation Environment (ASE) framework [98]. The implementation of the QM/MM coupling described here can be found in the Multi Cluster Force Mixing (MCFM) module in the MatSciPy library [129]. DFTB calculations were performed self consistently with the parameters by Krishnapriyan *et al.* [125], using an electronic temperature of 0.2 eV and Pulay mixing. It is important to note that in principle any combination of two atomistic simulation techniques can be coupled using this scheme as long as access to per-atom potential energy is provided by the method being used as the computationally inexpensive force evaluator (the MM element). The reactive forcefield simulations used for comparison were performed using the ReaxFF forcefield [237] with parametrization from Ref. [110] extending the CHO forcefield [43] with nitrogen atom interactions. Throughout the simulation, an NVT ensemble was enforced using the Langevin thermostat as implemented in ASE.

4.3 Effects of Attachment Point Composition on CNT-polymer Interfacial Shear Strength

The QM/MM technique was used to simulate a (10,0) CNT with a polypropylene (PP) strand attached to the surface of the CNT as a representation of a CNT-polymeric interface. The attached polymer was composed of 25 PP monomers which corresponds to more than two times the persistence length of the polymer thus ensuring an appropriate representation of an

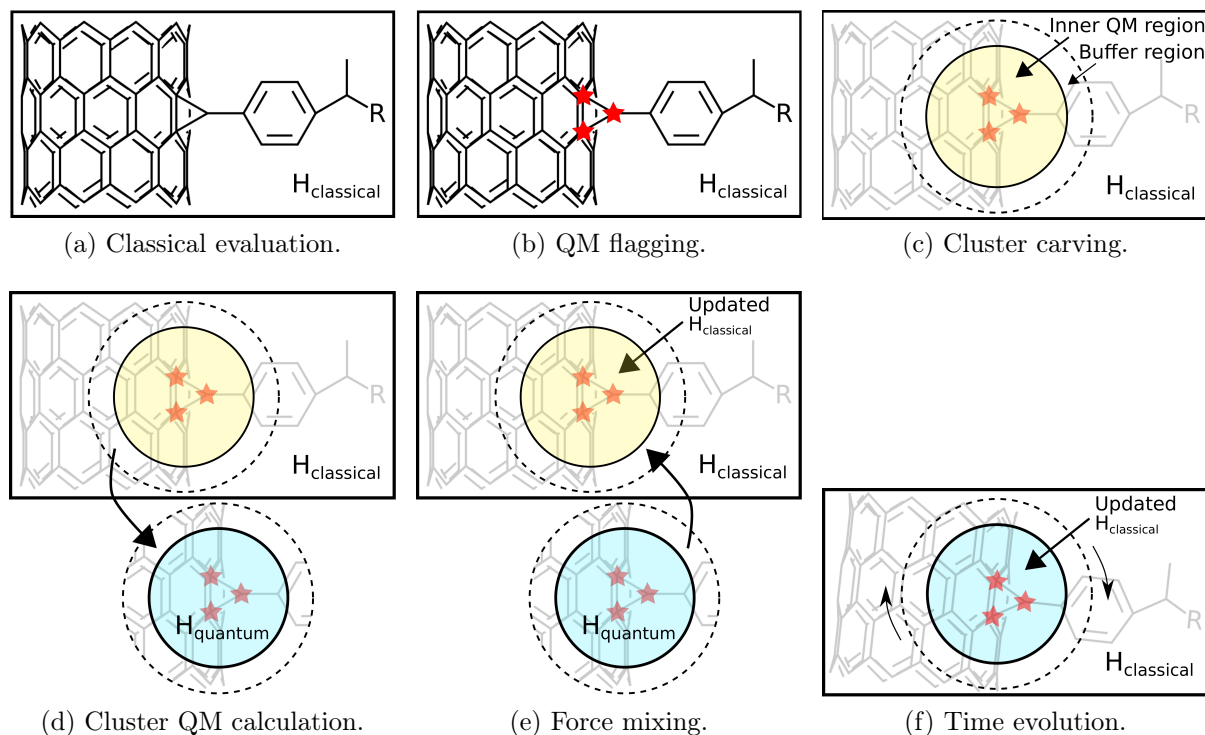


Figure 4.1: Schematic representation of QM/MM hybrid timestep

actual chain. A velocity of 10^{-3} Å/fs in the outward radial direction with respect to the CNT was applied to one of the chain atoms to simulate an external load leading to critical failure; the simulation setup is described in Figure 4.2. Throughout the simulation, the force on the pulled out atom was recorded to measure the system's response.

The study was designed to compare CNT-polymer grafting mechanisms by investigating CNT-PPs systems as the one described above, with various molecules used to join the CNT surface and polymer chain. The attachments, shown in Figure 4.3 are composed of the bromide salt residue with a benzene ring (panels a and d), single carbon atom with a benzene ring (panels b and e) as well as single nitrogen atom with a benzene ring (panels c and f). Each of the attachment types is used to compose two systems: one where a single bond connects the molecule with the CNT surface (panels a, b, c) and one when two single bonds are used (panels d, e, f).

For each configuration, the force necessary to break the interfacial connection was found by analysing the atomic force on the pull-out atom as a function of simulation time which has a linear relation with its displacement. The curves were smoothed by averaging over a 30 fs

window to account for carbon-carbon bond vibrations. The critical force was measured by finding the maximum recorded value and taking an average over a 100 fs window to account for chain oscillations. For each grafting mechanism, the process was repeated for a set of six simulations at different temperatures $T=50, 100, 250, 200$ and 300 K to get the mean and standard deviation.

The results of the study using the QM/MM approach were compared with the outcomes of similar simulations with the ReaxFF forcefield [237]. The resulting smoothed force vs time curves are shown in Figures 4.4 and 4.5. The first series of plots show the results for the simulation with QM/MM approach as the force evaluation method while the second portray the results for ReaxFF [237] with three simulations at temperatures $T = 10$ K, 100 K and 300 K presented for each method. Results obtained from both methods were evaluated against a fully QM simulation of a similar, slightly smaller system composed of a 20 Å CNT, 10 PP monomers and the same connecting molecules, performed at $T=100$ K; the system size was reduced for this study for computational feasibility. The critical force for systems with different attachments computed using the described methods is shown in Figure 4.6. The results from the QM/MM simulations are in agreement with the fully QM results which indicates that the hybrid approach can effectively reproduce the results of the quantum mechanical model it is based on.

We can use the QM/MM results to investigate the properties of interfaces composed of different attachments. In general, systems in which the doubly bonded attachments were used perform much better than their counterparts in all cases. The systems are otherwise identical which indicates that altering the chemistry at the attachment point to increase the binding energy can lead to an increase in the CNT - polymer interface strength by to a factor of two. In fact, in the doubly-bonded systems, the critical failure is caused by the polymer chain breaking instead of detaching from the CNT which shows that carefully selecting the grafting strategy can lead to maximising the interfacial shear strength (ISS) to the limit dictated by the strength of the polymer used in the composite.

The key insights from those simulations are not captured when ReaxFF is used to drive the dynamics. The breaking force needed to detach the polymer chain from the CNT surface is

systematically overestimated and the distinction between high and low strength systems is not accurate. While attachment (b) is reported to break at relatively low load, all of the other systems are considered to be of similar, high strength. In general, ReaxFF with parameters from [110] offers a correct qualitative description of systems where the key elements are carbon-based; in cases, (d), (e) and (f) the rupture occurs inside a carbon-based polymer chain while in system (b) only carbon atoms are present and the ReaxFF simulations correctly predict relative strengths of those systems. On the other hand, in cases (a) and (c), where the attachment includes various atoms different than carbon, the electronic structure of the functional group is more intricate and the parameterised description of bonding is not accurate. As a result, ReaxFF predicts that for systems (a) and (c), the critical failure occurs at a much higher pull-out strength. Similar conclusions can be drawn from the analysis the displacement of the pull-out atom at the rupture time which, for cases (a) and (c) is significantly higher when the simulation is driven using ReaxFF than QM/MM or QM methods. Finally, in case of ReaxFF simulations, the failure of attachments (a) and (c) is caused by the rupture the inside the polypropylene chain, while the DFTB based hybrid approach shows that it is due to the polymer detaching from the CNT. This is shown in detail in Figure 4.2.

While it should be possible to reproduce the QM results exactly with ReaxFF forcefield by carefully re-fitting the parameters, the results would need to be validated against fully QM simulations for each system in the study. This approach is time consuming and highly limiting in terms of exploring properties of unknown structures. The method demonstrated here is designed to be more transferable; the approach relies on the results of *ab initio* or semi-empirical computations and as such could be used to make predictions about previously unseen compositions and screen for high-performance candidates as presented here. Additionally, the approach could be applied to complement the current state of the art studies of CNT-based structures [31, 179].

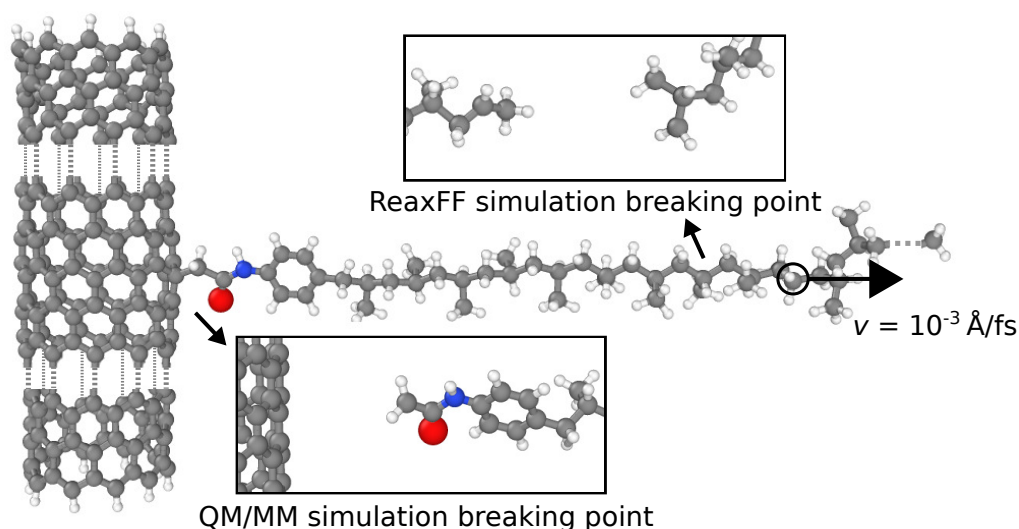


Figure 4.2: A system representing CNT-polypropylene composite composed of a (10,0) CNT joined with a short PP strand using a bromide salt residue and a benzene ring. The gray atoms represent carbon, white hydrogen, red oxygen and blue nitrogen. The arrow indicates a fixed velocity used to simulate external load. Additionally, the critical failure points for simulations with QM/MM approach and ReaxFF forcefield are shown.

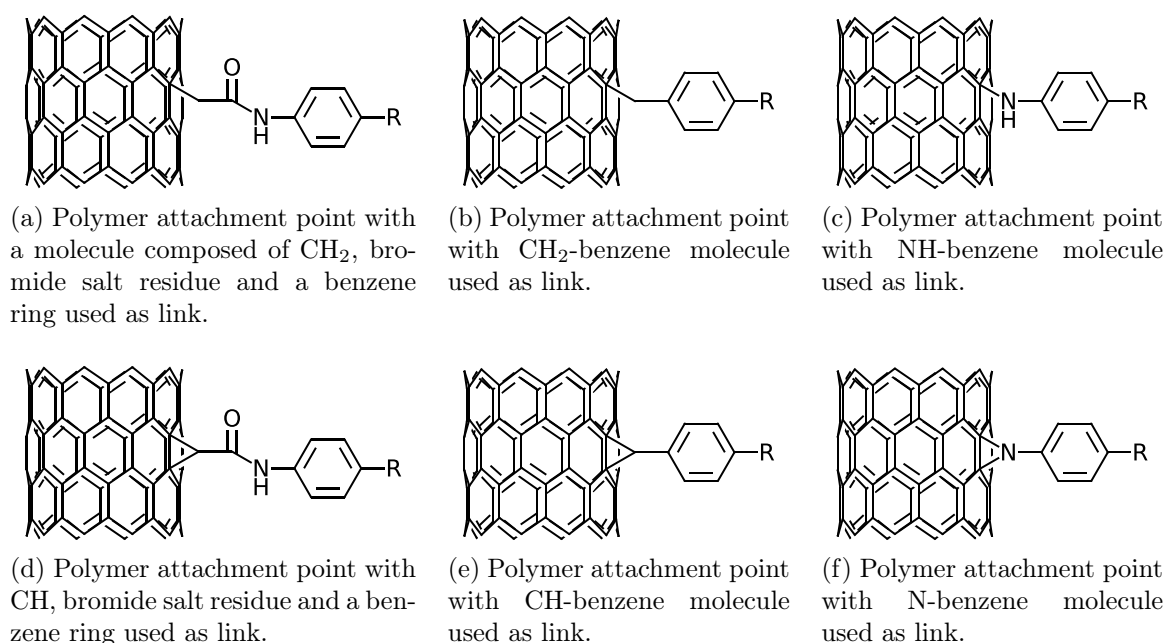
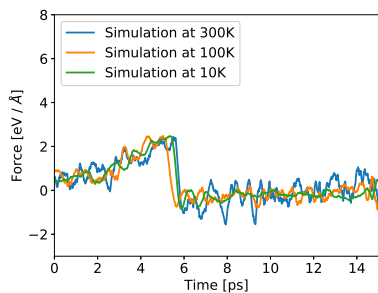
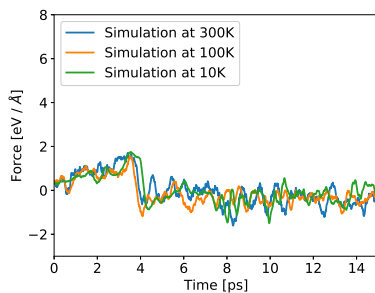


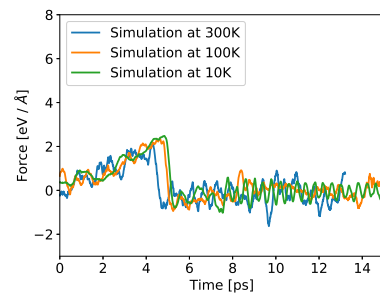
Figure 4.3: CNT attachment point with different molecules used as link between the benzene ring and CNT surface.



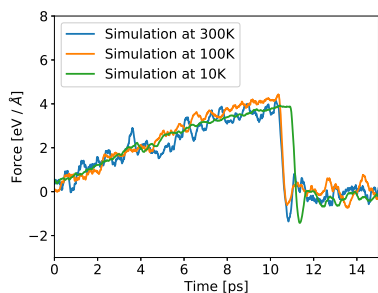
(a) Results for a system linked by CH_2 , bromide salt residue and a benzene ring.



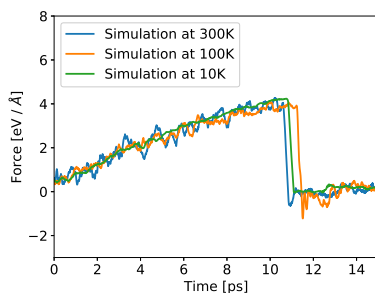
(b) Results for a system linked by CH_2 -benzene molecule.



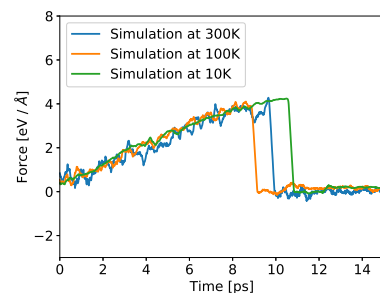
(c) Results for a system linked by NH-benzene molecule.



(d) Results for a system linked by CH, bromide salt residue and a benzene ring.

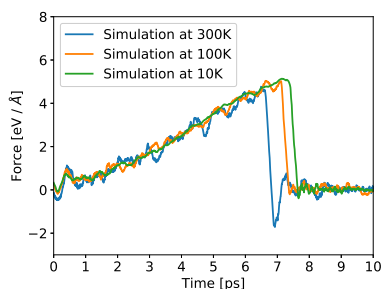


(e) Results for a system linked by CH-benzene molecule.

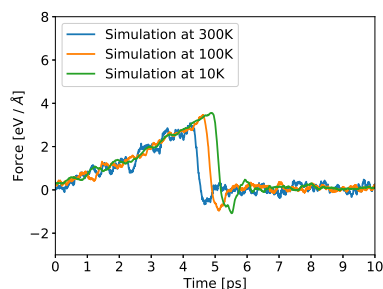


(f) Results for a system linked by N-benzene molecule.

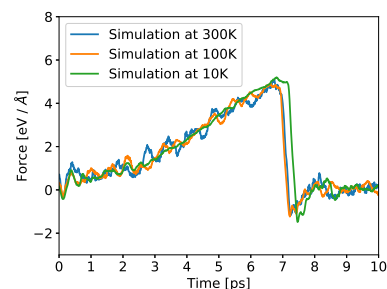
Figure 4.4: Force on the pulled-out particle for simulations with a system composed of a (10,0) CNT, an attachment molecule, benzene ring and a polypropylene strand in form of CNT-X-benzene-PP. Attachment points shown on Figure 4.3. QM/MM was used as the force evaluation method in all runs.



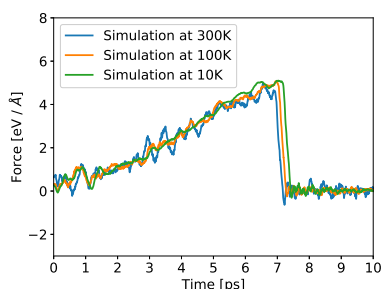
(a) Results for a system linked by CH_2 , bromide salt residue and a benzene ring.



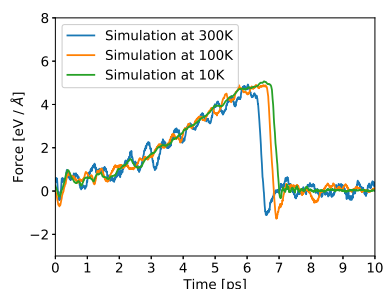
(b) Results for a system linked by CH_2 -benzene molecule.



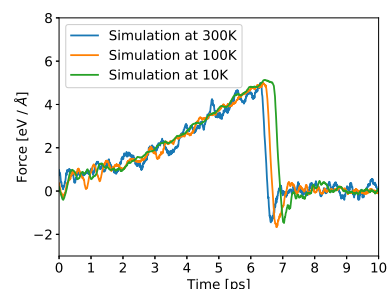
(c) Results for a system linked by NH-benzene molecule.



(d) Results for a system linked by CH, bromide salt residue and a benzene ring.



(e) Results for a system linked by CH-benzene molecule.



(f) Results for a system linked by N-benzene molecule.

Figure 4.5: Force on the pulled-out particle for simulations with a system composed of a (10,0) CNT, an attachment molecule, benzene ring and a polypropylene strand in form of CNT-X-benzene-PP. Attachment points shown on Figure 4.3. ReaxFF was used as the force evaluation method in all runs.

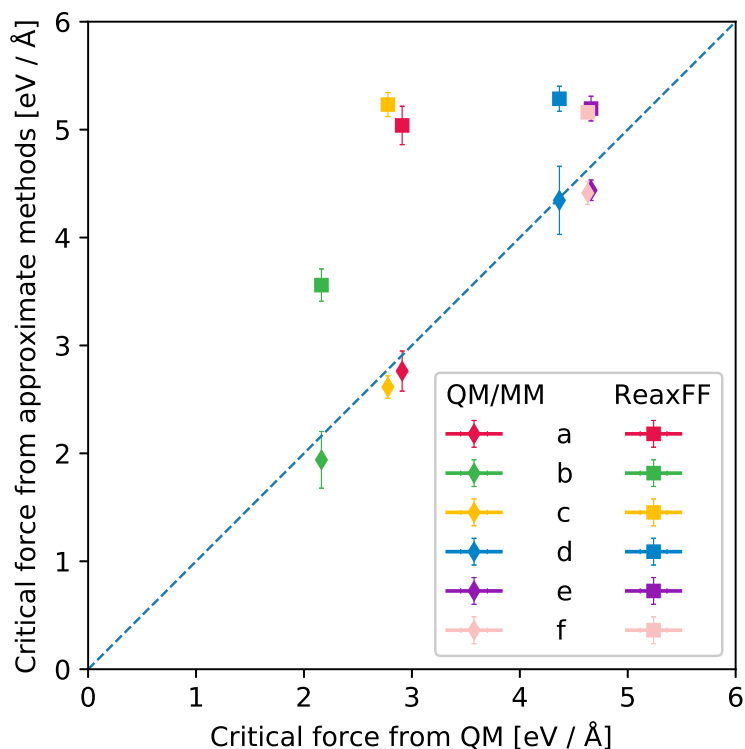


Figure 4.6: Critical force on the pulled-out particle for simulations of six similar systems using both QM/MM approach and ReaxFF for force evaluation. Each structure was composed of a (10,0) CNT, an attachment molecule, benzene ring and a polypropylene strand in the form of CNT-attachment molecule-benzene-PP; different attachment point chemistries are shown in Figure 4.3. Each point is located at coordinates dictated by the breaking force from a full QM simulation on the x -axis and breaking force from an approximated method on the y -axis. Each colour represents a single attachment chemistry and shapes represent the simulation method, squares for ReaxFF and diamonds for QM/MM.

4.4 Validation

The methodology demonstrated here has not been used to study this class of materials before therefore a significant effort must be directed at validating and fine-tuning the approach. In this section, the locality of quantum mechanical calculations, the details of QM clusters selection and the errors in QM/MM force evaluation will be investigated.

4.4.1 Force Locality

As mentioned in Section 4.2, a hybrid scheme has areas described by two levels of theory and for this approach to be valid, the interactions described by the higher level theory must be localised to a small neighbourhood. Properties of atoms within the quantum region must be computed with high accuracy by considering only the finite neighbourhood and if the region is large enough, should be unaffected by the classical treatment of the remainder of the system. Both of those requirements are brought to completion when the *strong locality* condition is fulfilled. It can be defined as [54]

$$\frac{\partial^n}{\partial \mathbf{r}_i^n} \frac{\partial E_{\text{tot}}}{\partial \mathbf{r}_j} \rightarrow 0 \quad \text{as} \quad |\mathbf{r}_i - \mathbf{r}_j| \rightarrow \infty \quad \forall n, i \neq j, \quad (4.2)$$

where E_{total} is the total energy and $\mathbf{r}_i$ and $\mathbf{r}_j$ are the positions of atoms i and j . The non-metallic systems obey strong locality and the intrinsically long-range effects such as Coulombic or van der Waals interactions can be accurately treated with classical approximations outside the hybrid framework [54].

Here, the force locality has been tested for ten different configurations of a functionalized CNT structure shown in Figure 4.7 as a representation of a CNT-polymer composite. For each structure, the forces acting on individual atoms were calculated for the equilibrated configuration, the central C_1 carbon atom (see Figure 4.7 for notation) was displaced by 0.01 Å and the atomic forces were recalculated for the new structure. The relative change in forces acting on individual atoms as a function of their distance from the central C_1 atom is given in Figure 4.8. The

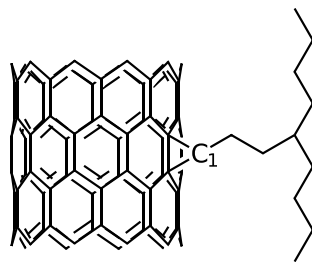


Figure 4.7: A system representing a CNT-polyethylene composite composed of a (6,6) CNT functionalized with a short PE strand.

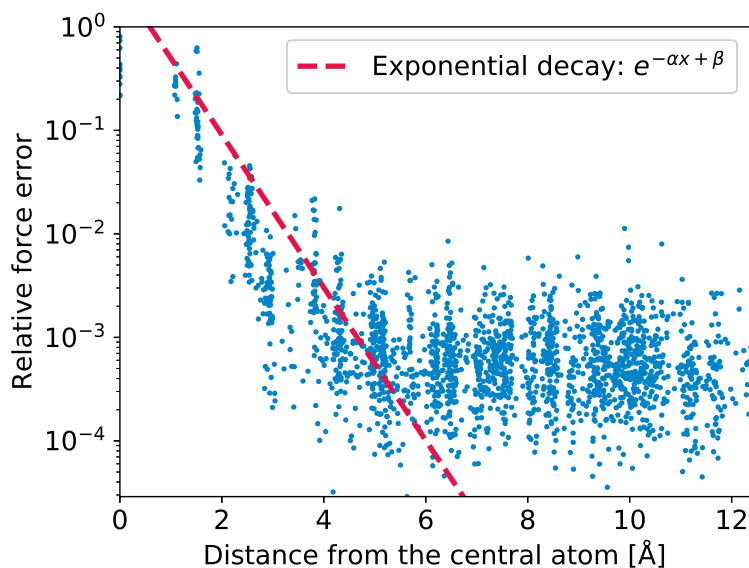


Figure 4.8: A plot of the relative changes in atomic forces as a result of displacing the C_1 carbon atom, given as a function of atom's distance from the central C_1 carbon. System and the notation are shown in Figure 4.7.

change in forces decays exponentially with increasing distance until an accuracy comparable with simulation noise is achieved. This result indicates that the strong locality assumption is indeed correct for the functionalized CNT systems and CNPC structures. Strong force locality demonstrated here justifies the choice of buffered force QM/MM approach without the use of electrostatic embedding as using a buffer region with sufficient width allows forces to converge to reference values obtained from fully quantum mechanical calculations; this discussion is picked up in Section 4.4.2.

4.4.2 Cluster Size Convergence

Following the study in Section 4.4.1, the locality of atomic forces was tested further by investigating the effect of changes in the buffer size on the accuracy of force evaluation. In this study, ten randomly perturbed structures composed of a (10,0) CNT with a polypropylene strand attached to the surface of the CNT using a benzene molecule (shown in Figure 4.9) were investigated by evaluating forces on atoms around the attachment point (shown in blue in the Figure 4.9) while varying the buffer size from 2 to 25 neighbour hops; a sample buffer region is denoted by green atoms in the Figure 4.9.

Two strategies for selecting the buffer region were compared: first, where the buffer was obtained by expanding the inner QM region by isotropic neighbour hopping in all directions as shown on Figure 4.9a and the second one where the buffer region was expanded by neighbour hopping along the CNT axis, retaining the CNT structure. The former approach, effectively using a shorter CNT to approximate the whole CNT is schematically shown in Figure 4.9b.

Figure 4.10 shows the maximum value of relative force error (F_{err}) for a given configuration. It was calculated as the difference in atomic force obtained from simulations of the given cluster and the full system, divided by the force average. The linear dependence of $\log(F_{\text{err}})$ on cluster size indicates an exponential decay of interaction strength and points to the strong locality assumption. The increase in force errors around 500 buffer atoms is most likely connected to the CNT end-states. The CNT end-states are located closely around the Fermi level and their occupancy is highly dependent on the geometry of the end-caps which changes when different elements of the CNT become the cluster terminating parts. If the occupancy is the same as in the full CNT the errors are low but the opposite is true otherwise.

Both strategies require a similar buffer size in order to yield a relative error below 5%. As a result the isotropic bond hopping was selected due to the ease of implementation. In this formulation, the required accuracy was achieved with the buffer region with the width of six neighbour hops which was chosen for practical calculation.

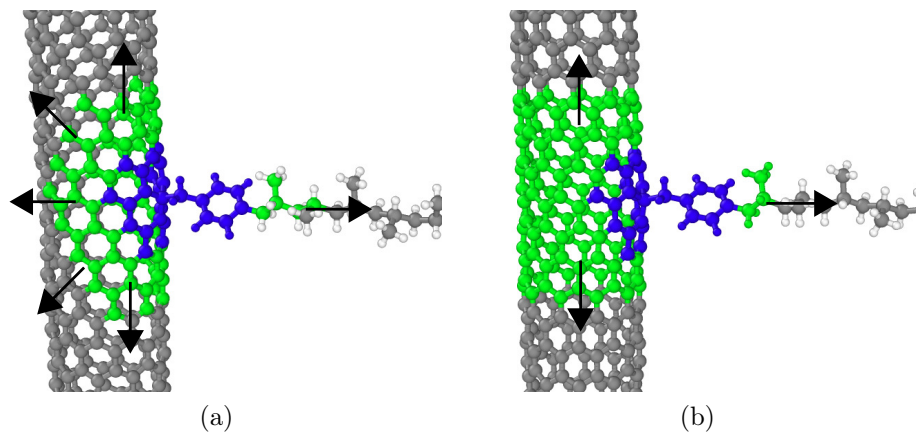


Figure 4.9: Two strategies for finding the buffer region in a QM/MM simulation: (a) cluster expansion by isotropic bond-hopping; (b) cluster expansion by bond-hopping along the CNT axis. Inner QM atoms are shown in blue while a sample buffer region is shown in green.

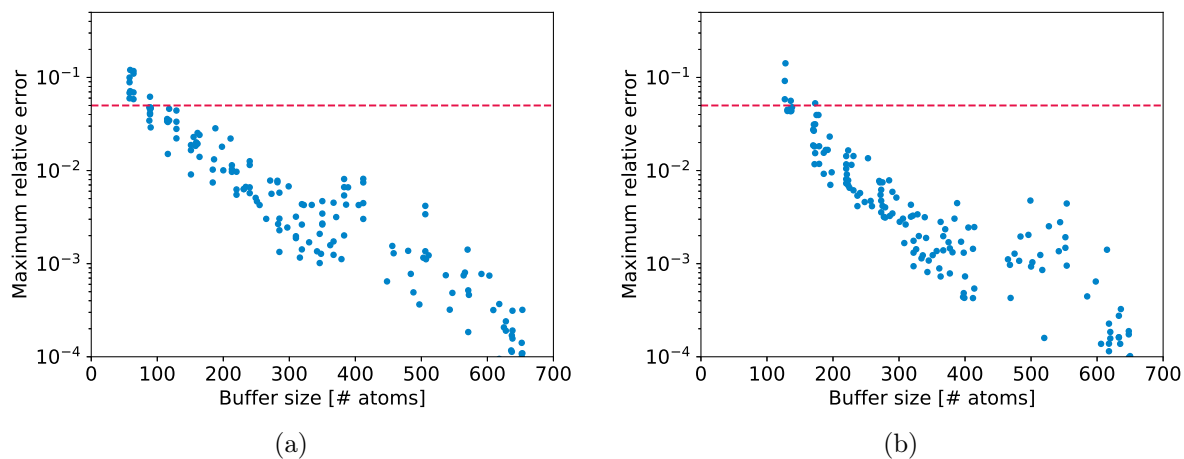


Figure 4.10: Maximum relative force error as a function of buffer size in terms of the number of atoms for two strategies for finding the buffer region: (a) cluster grown by isotropic bond-hopping; (b) cluster grown by bond-hopping along the CNT axis in panel (b)

4.4.3 QM/MM errors

During the run, the accuracy of the force evaluation was monitored by comparing the values obtained from the hybrid method with the ones from a tight binding simulation of the whole system; the root mean squared of the force differences is shown in Figure 4.11. The errors in force evaluations remain consistently below $0.05 \text{ eV/\AA}$ which is considered low, given that the average atomic force in the simulation is approximately $1 \text{ eV/\AA}$. The increase in errors in the later parts of simulations in Figure 4.11a and 4.11d appear after the interfacial failure, therefore should not affect the presented results greatly. The errors originate from the fact that the full system DFTB is not well suited to describe unpaired electrons in dangling bonds. This leads to differences in force on the polymer chain atom that was involved in the broken bond, depending on which structure is simulated: a full system or a cluster containing just one of the parts of the broken polymer chain.

4.5 CNT fracture

It is important that the discontinuities at the QM/MM boundary are minimised to ensure the stress is transferred correctly and there are no unphysical forces originating at the artificial surface. In this work we aim to avoid those issues by refitting the classical potential to match the stable bond lengths and elastic response around equilibrium as discussed in Section 4.2. This approach has been validated by investigating the elastic response of a defective CNT with buffered QM/MM approach, showing that forcefield refitting ensures stresses are transferred correctly leading to an accurate description of CNT failure.

A $40 \text{ \AA}$, end-capped (10,0) CNT with a single atom vacancy was strained quasi-statically by iteratively straining the structure in 1% increments and optimising the geometry while constraining the positions of end-atoms. The structure is shown in Figure 4.12. Throughout the simulation, the energy-based criterion was used to flag the quantum mechanical regions. In the beginning, all atoms were treated classically and throughout the run, the QM inner region and the buffer were selected automatically at 7% strain, accurately flagging the defective part

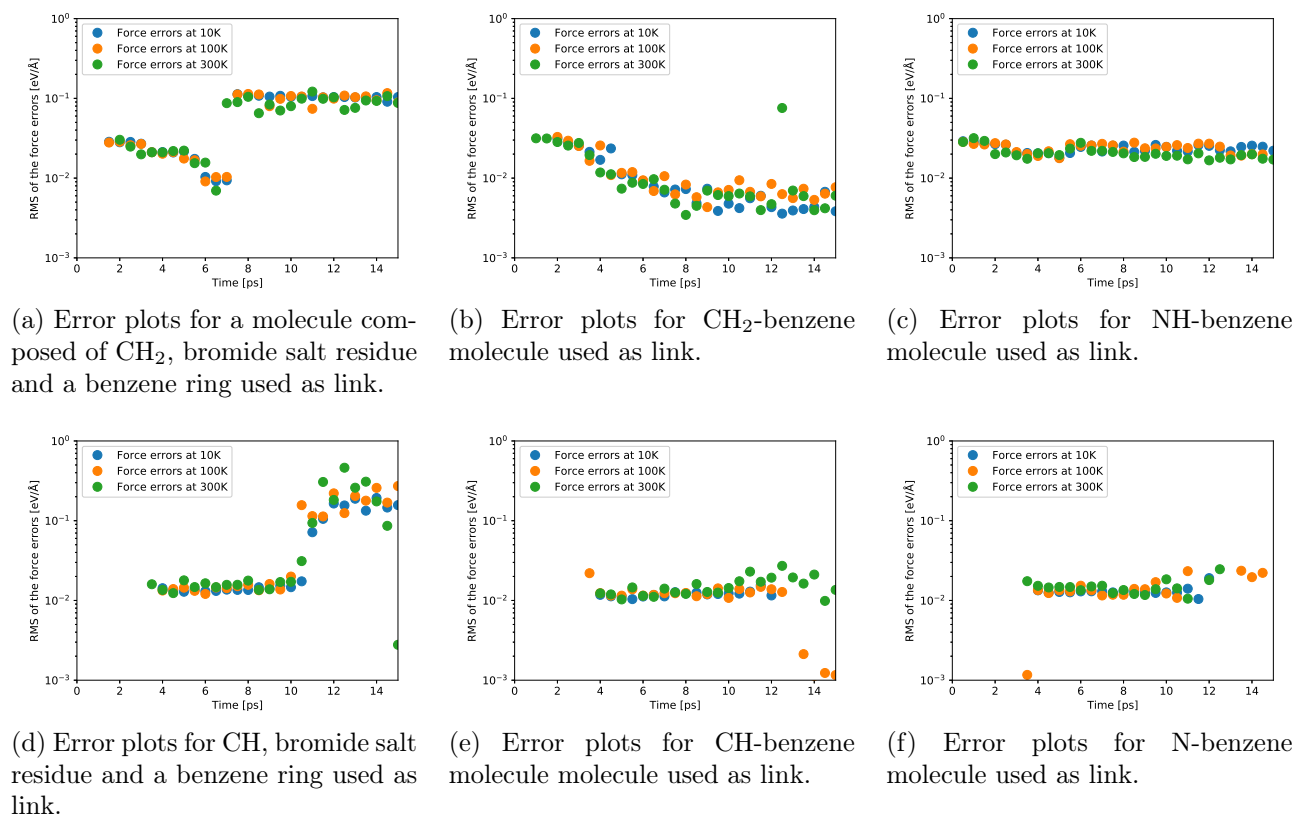


Figure 4.11: Accuracy of QM/MM force evaluation measured by comparing the hybrid force values with the values obtained with a complete tight-binding simulation. Force errors obtained by taking a root mean squared (RMS) of the difference in force values for two different simulation techniques for each timestep; for reference, forces within the simulations oscillate around $1 \text{ eV}/\text{\AA}$. Results are presented for six similar systems with different attachments following notation from Figures 4.3 and 4.4.

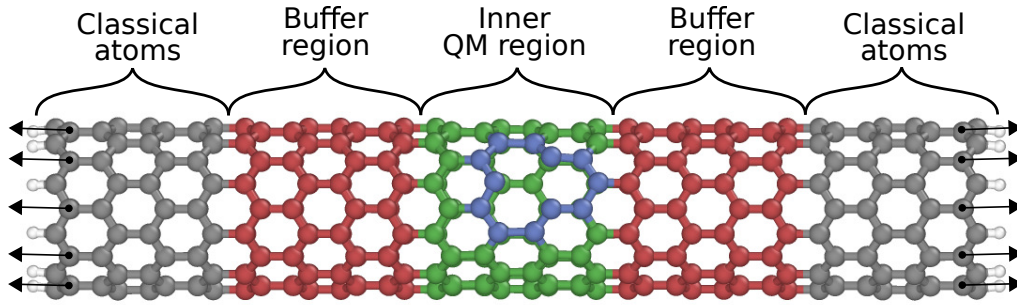


Figure 4.12: Figure representing the CNT system in equilibrium. Green region represents inner QM atoms, red the buffer region while grey and white represent the fully classical carbons and hydrogens respectively. Blue markings are to indicate the neighbours of the vacancy in the CNT.

of the CNT once the system moved away from its equilibrium structure; this is shown in Figure 4.13.

The study was performed three times using a CVFF, DFTB and the QM/MM approach presented here. The two and three body terms in the forcefield CVFF were re-fitted to match the DFTB equilibrium length of the CNT as well as its elastic response in the range of 0 - 3% strain. Even though the force-mixing approach is naive, a simple forcefield re-fitting ensures that stresses are accurately transferred through the classical-quantum barrier, demonstrated by the QM/MM scheme accurately reproducing the DFTB critical stress; shown in Figure 4.13.

4.6 Conclusions

The results presented in this chapter demonstrate that an accurate description of QM effects such as bond breaking is essential when simulating interfacial critical failure in CNT-polymer composites. Such effects govern the initial evolution of the failure process and an accurate description of the surrounding electronic structure is required to simulate them correctly.

The need to include QM description in the large-scale MD simulation necessary to describe the load transfer through the polymer chains creates a difficult multiscale challenge. Here, it has been successfully addressed by employing a quantum/classical hybrid simulation technique with automated, with dynamic flagging offering QM accuracy only in the crucial parts of the system

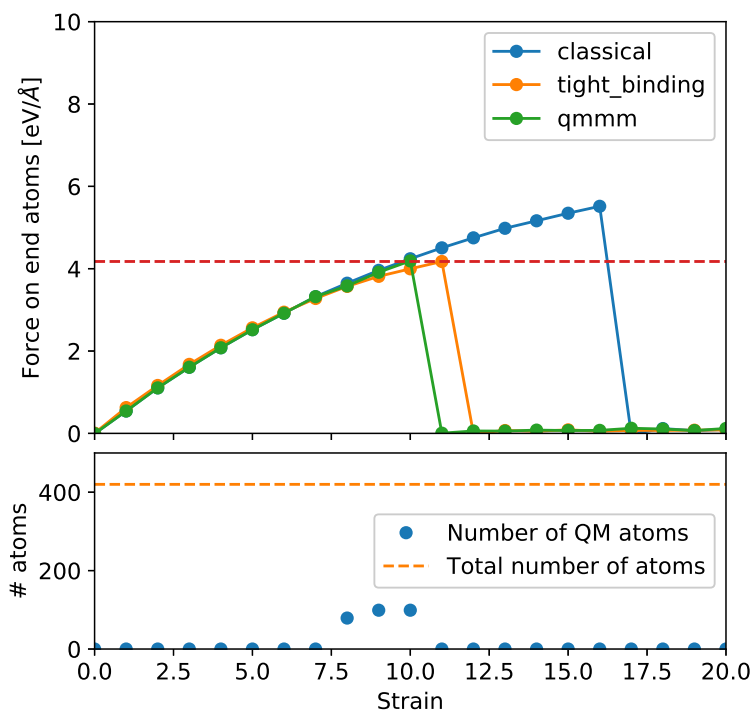


Figure 4.13: A plot of average force on constrained, end atoms as a response to applied strain in the top panel and the number of QM atoms as a function of strain in the bottom panel.

thus maintaining modest computational cost. The method was shown to produce similar results to a fully QM technique it is based on for problems of critical failure in CNT and polymer-based systems.

The hybrid method demonstrated here is best suited to investigate problems where the crucial effects dictating the behaviour of the system are local in nature; most critical failure effects, especially in non-homogenous systems fall into that category. In this class of problems, the QM/MM approach could be used to take advantage of accuracy and predictive power of methods such as DFT at modest computational cost, allowing for studies at a large length and time-scales. As a result, the method could be used as an improvement over classical forcefields in problems where transferability is important such as an investigation of various attachment strategies in the search for high-performing CNT-polymer interfaces.

Herein, the QM/MM approach was used to study different CNT-polymer interfaces in order to identify the frailest element of the CNT-polymer interface and test potential high-performing replacements. The findings indicate that the chemistry at the attachment point significantly contributes to the effective ISS of the interface and using a carefully chosen attachment can

lead to increasing the ISS to the limit dictated by the strength of the polymer used in the composite. Those results highlight a promising strategy for improving the quality of CNPC interfaces that will be further explored in the following chapter.

Chapter 5

Multiscale simulations of CNPCs: applications

Results under review in

Golebiowski, J. R., Kermode, J. R., and Haynes, P. D. and Mostofi, A. A. Atomistic QM/MM simulations of the strength of covalent interfaces in carbon nanotube-polymer composites. Under review in Physical Chemistry Chemical Physics

5.1 Introduction

Despite some success, the current generation of CNPCs has fallen short of the theoretical limit [49, 146], indicating that the superior mechanical properties of the fillers might not be fully utilised and improving the efficiency of matrix-fibre load transfer is necessary to realise the potential of CNT reinforcement fully. Experimental and computational studies of CNPCs reviewed in Chapter 2, have highlighted the quality of the interface as a critical factor in composite reinforcement and have shown that it can be significantly improved by the introduction of chemical crosslinks between nanotubes and the polymer matrix.

Work presented in Chapter 4 demonstrates that the choice of CNT functionalisation can have a

significant impact on the effective strength of the covalent interface which in turn can lead to an improvement in CNPC properties. As mentioned in Section 2.4.2, the effect of varying the functional groups has been extensively researched from the perspective of nanotube dispersion in the polymer matrix. However, not much effort has been devoted to discriminating various functionalisation strategies based on the quality of the resulting interface. In this work we aim to complement the current knowledge by extending the investigation of critical factors affecting the ISS presented in Chapter 4 to more realistic composite samples. We study how the chemical structure at the interface determines its failure characteristics directly by simulating carbon nanotube pull-out from a crosslinked polyethylene matrix. The high level of control offered by computational studies is used to investigate four seemingly identical systems that differ only in the choice of the functional group linking the polymer matrix to the nanotube allowing for a direct comparison. The investigation is focused on CNT-polymer seams composed of commonly used amine, carbene and carboxyl functional groups as well as $[2 + 1]$ cycloadditions, highlighting the differences in interfacial strength and failure characteristics as a result of changing chemical compositions. Our findings aim to make practical recommendations and guide further experimental work. Additionally, the molecular resolution offered by computational studies is employed to analyse interfacial failure modes and atomic structure at the polymer attachment point leading to a better understanding of critical factors affecting the ISS.

Precise computer simulations play a crucial role in this investigation; however, achieving the desired accuracy can be challenging as it relies on the correct description of the multiscale mechanism of critical failure. This issue was initially raised in Section 2.4.2 and has been the main focus of Chapter 4 where a novel concurrent QM/MM modelling approach has been demonstrated and validated, showing that the method can be effectively used to investigate multiscale mechanisms involved in CNPC interfacial failure. This approach with small modifications has been used to drive the simulations presented in this chapter, demonstrating that it can be effectively used on a larger scale where the QM/MM coupling is necessary to carry out fast and accurate calculations.

Modifications to the QM/MM approach presented in Chapter 4 are briefly summarised in Section 5.2 alongside the detailed description of the simulation setup. Section 5.3 is devoted to

the analysis of the results of the single fibre pull-out simulations, and the chapter is concluded in Section 5.4.

5.2 Computational methods

Single fibre pull-out simulations conducted in this study were carried out using the molecular dynamics algorithm with atomistic interactions computed by the QM/MM hybrid method introduced in Chapter 4. Compared to the previous study, the recipe for finding the energy threshold used in the flagging mechanism (see Section 4.2) was modified and a dispersion correction was introduced.

5.2.1 Technical details

We used the generalized Amber force-field (GAFF) [242], as implemented in LAMMPS [184], as our MM model. The standard GAFF model was refitted for bond and angle terms in the CNT and the polyethylene chain, in order to match the lattice constant and elastic response around the equilibrium obtained with the forcefield and the QM method for a (10,0) CNT and a 25 monomer PE chain as described in Section 4.5. The QM method used is density-functional tight binding (DFTB) [188], as implemented in the PLATO [116] simulation package. DFTB calculations were performed with self-consistent charge equilibration using the parameters by Krishnapriyan *et al.* [125], with an electronic temperature of 0.2 eV and Pulay mixing. In this work we do not use the electrostatic embedding approach for our quantum calculations but rather use a mechanical embedding technique and rely on a wide buffer to ensure an accurate description of forces in the core of the QM regions, following the discussion in Peguiron *et al.* [181]; see Section 4.2 and 3.4.4 for details. Throughout the pull-out simulations, an NVT ensemble was enforced using the Langevin thermostat with the friction coefficient of 0.01 as implemented in Atomic Simulation Environment [98]. The simulations were carried out at a temperature of 100 K. The effect of changing the temperature from 100 K to 300 K was found

to be negligible (see Section 5.3). The MD simulations used to generate the initial composite sample were performed in LAMMPS [184] using the General Amber force field [242].

5.2.2 Flagging mechanism

Not unlike before, the flagging protocol aims to select atoms residing in areas of the energy landscape where the classical description might be inaccurate by comparing atomic energies derived from the forcefield with predefined thresholds. These energy thresholds are obtained prior to the main pull-out simulation by simulating the initial system in equilibrium for ten picoseconds while recording per-atom energies. The mean and standard deviation of these per-atom energies determine the flagging threshold according to

$$E_{\text{thresh}}^i = E_{\text{mean}}^i + aE_{\text{std}}^i + b, \quad (5.1)$$

where the parameter a is selected to balance accuracy and computational efficiency and the parameter b represents a small offset to ensure numerical stability for atoms with small energy variance. The thresholds are calculated separately for each atom and as a result, the protocol selects particles based on how much its energy is elevated compared to its normal thermal oscillations. The flagging mechanism that we have used has an in-built hysteresis in the sense that there is a lower energy threshold for atoms that were flagged for quantum mechanical treatment at the previous time-step than for atoms that were treated classically in the previous time-step. This approach prevents oscillations in the QM region size and shape which could introduce instabilities. This is achieved by setting $a = 4$ for atoms within a QM region and $a = 6$ for those not in a QM region at a given time-step. The parameter b was fixed at 0.05 eV.

In most simulations, the majority of time-steps did not involve any QM computations and, when QM was necessary, the total number of atoms treated with the higher level theory was usually below 1% of the total number of atoms (7000) at any given time. An example can be seen in Figure 5.8 which shows the number of QM atoms at each time-step for some representative examples of the pull-out simulations.

5.2.3 Force dispersion correction

Dispersion contributions were not included in the DFTB Hamiltonian and the QM forces were adjusted post-hoc by including an empirical correction, following the approach discussed by Zhechkov *et al.* [258]. The corrected force on atom i is given by $F^i = F_{\text{QM}}^i + \eta F_{\text{LJ}}^i$, where F^i is the corrected force and F_{LJ} is the Lennard-Jones (LJ) term of the generalised Amber force-field (GAFF) [242] that is used to describe the classical interactions in the non-QM regions of the system. The correction term is computed based on the pairwise LJ interactions in the whole system.

The parameter η was chosen by examining an ensemble of ten different structures each composed of ten 48-monomer long polyethylene chains packed into a bulk using Monte Carlo based sampling as implemented in the MedeA software package [158]. For each structure, two calculations were performed, one where the whole system was simulated with a QM method and the other where only one selected chain was simulated with the QM method and the forces were corrected by the approach presented above. The optimal value of η is 0.2 and was chosen so that the sum of squared difference between the forces on the selected chain from the former and the latter are minimised. Momentum conservation was ensured by adjusting the sum of total forces to zero.

5.2.4 Simulation setup

The strength of the CNT-polymer interface was quantified by performing single fibre pull-out tests *in silico*. In this study, a carbon nanotube embedded in a crosslinked polyethylene matrix was gradually pulled out of the sample while the response of the system was analysed.

The initial polymeric slab was composed of fifty 48-monomer polyethylene-like chains, each made out of six alternating units of propylene, acetylene and propylene organised in the following fashion: $\text{H} - (-\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 -)_6 - \text{H}$. The target structure was a polyethylene slab, periodic along the x - and y -axes with a free surface along side z ; the thickness was 50 Å and the target density was 0.3 g/cm³. The configuration of the

polymeric slab was obtained using a Monte Carlo based sampling of translational, rotational and conformational degrees of freedom based on the energies derived from the PCFF force-field [222] as implemented in the MedeA software package [158]. The density of the slab was fixed at approximately one-third of the experimental value to ensure the stability of the Monte Carlo simulation; the density was adjusted to match experimental later in the process.

The next step involved creating the CNT-polymer composite by introducing a CNT to the polymer bulk. Firstly, a void inside the polymer cell was created by introducing seven repulsive beads spaced equally between the centre of slab's free surface and a point inside the polymeric structure located at the midpoints of the periodic axis and 35 Å away from the surface into the slab in the non-periodic axis. The positions of the beads were fixed and they interacted with the polymer matrix via a Lennard-Jones repulsive potential creating a void that could accommodate a CNT. The strength of LJ repulsion was increased quasi-statically by changing the depth of the potential well from 0.1 to 4 kcal/mole and the equilibrium distance from 1 to 8 Å over the course of ten iterations each involving a change of parameters followed by a geometry relaxation with the FIRE [23] algorithm with stopping criteria for the force below 10^{-10} eV/Å or relative energy change below 10^{-10} . After ten iterations, the values were kept constant for 0.1 ns in an NVT simulation at 300 K to allow for local equilibration.

After the process was completed, a 30 Å long, (10,0) CNT fragment was placed inside the void; its position was chosen so that its longitudinal axis was aligned with the axis of the repulsive beads. The CNT C-C bond lengths were 1.42 Å and the terminated ends of the CNT were passivated with hydrogen atoms, the positions of which were optimised using the PCFF forcefield [222] in LAMMPS [184]. CNT functionalisation was later achieved by introducing three additional PE chains, identical to those used to construct the polymer bulk, which were attached to the CNT surface using amine, carbene or carboxyl functional groups or a $[2 + 1]$ cycloaddition resulting in functionalisation density of one group per 100 CNT carbon atoms. The resulting interfaces are schematically shown in Figure 5.1. Polymer chains grafted to the CNT surface were identical to those used to construct the polymer matrix and their position and orientation were selected to avoid particle overlap.

Afterwards, the system was equilibrated using an approach based on that of Ref. [126], which involves a series of temperature changes and compressions in the NPT ensemble. Firstly, the structure was compressed under the pressure of 0.5 GPa for 0.3 ns and then relaxed over the course of another 0.3 ns. The next step consisted of heating the sample to 800 K over 0.5 ns and subsequent cooling down to 300 K over the same period; this was followed by a compression-relaxation procedure like the one in the very beginning. After a more extended, 1 ns equilibration the process was completed.

Finally, the crosslinking of the polymer network was carried out with a procedure based on the comparison of distances between active carbon atoms in the acetylene molecules. When the separation between two atoms became smaller than a cutoff of 3.5 Å, a new bond between them was formed and the atom-types of participating atoms were changed to reflect their new cross-linked state; for generating realistic structures, it is important to note that only one atom in each acetylene unit may participate in cross-linking. This protocol was applied during a 0.5 ns simulation in an NVT ensemble at 800 K to generate a fully-connected polymer network.

The procedure described above yields a slab composed of 53 cross-linked polyethylene chains reinforced with a 30 Å CNT functionalised with three groups, each forming a link between the nanotube and the matrix providing an atomistic model representation of a CNT-polymer composite material; an example structure is portrayed in Figure 5.2. The CNT accounts for 12% of the total weight and the average density of the resulting cross-linked PE was found to be approximately 0.945 g/cm³, which is consistent with experimental findings [238]. The cross-link density of the polymer network, defined as a ratio of cross-linked carbon atoms to total carbon atoms was found to be approximately 10%. This protocol was repeated 40 times in order to produce an ensemble of ten different structures for each of the interface types.

CNT pull-out was simulated with the QM/MM method by extracting the CNT from the polymer slab at a constant velocity while analysing the response of the system. After equilibration for 10 ps, the terminating ring of carbon atoms aligned with the composite slab free surface was constrained to move outwards from the slab with a velocity which was gradually increased over the course of 1 ps from 0 Å/fs to 10⁻³ Å/fs (equivalent to the strain rates that could

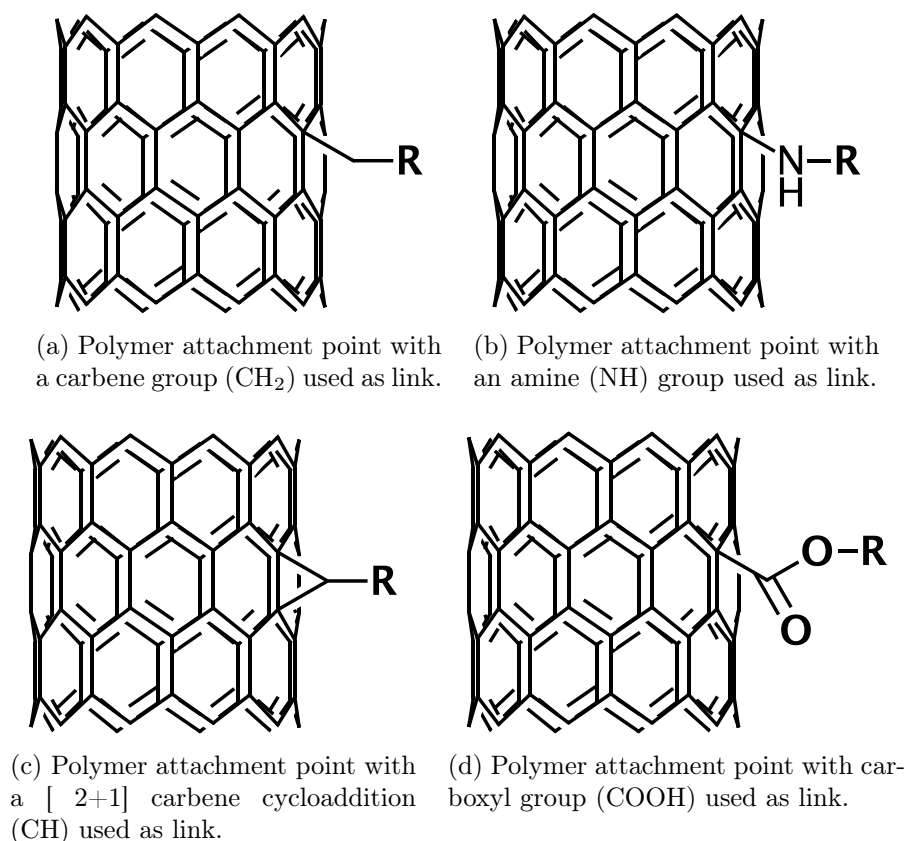


Figure 5.1: Schematic representation of interfacial structure between the CNT and polymer matrix. The four panels show different functional groups used to connect polyethylene chains (represented as R) to the CNT.

be observed in ballistic tests [107, 130]); the constrained CNT atoms are marked in green in Figure 5.2. Following the velocity ramp-up, the pull-out simulation was carried out by keeping the pull-out velocity constant and recording the forces acting on the constrained ring of atoms.

5.3 Results and Discussion

Carbon nanotube pull-out simulations discussed in the previous section have been used to investigate the critical strength of the interface between CNTs and crosslinked polyethylene composed of carbene, amine and carboxyl functional groups as well as $[2+1]$ cycloadditions. For each class of attachments, the initial structure was prepared as discussed in section 5.2 while the functional group used to graft polymer chains to the CNT surface was varied; four different attachment strategies lead to four different types of interfaces which are shown schematically in Figure 5.1. The simulation procedure including generating the initial atomic structure and sim-

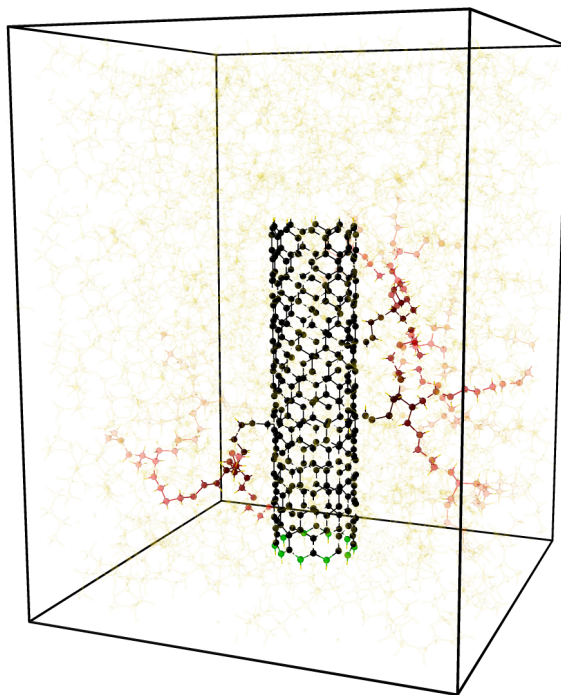


Figure 5.2: A representative atomic configuration for the CNT-PE system, composed of 53 48-monomer PE chains cross-linked by C-C bonds, reinforced with a 30 Å, (10, 0) functionalised CNT; three polymer chains are covalently bonded to the CNT surface resulting in a functionalisation density of one group per 100 CNT carbon atoms. Amine, carbene or carboxyl functional groups or a $[2 + 1]$ cycloaddition were used to link the CNT and polymer matrix throughout the study; this figure shows the carbene attachment. CNT atoms and functional groups are marked in black while the polymer atoms are coloured with a gradient changing from black to yellow depending on the distance from the attachment point measured in bond hops. The ring of carbon atoms at the bottom of the CNT marked in green was constrained to move at a constant velocity inducing nanotube pull-out.

ulating the CNT pull-out has been performed for an ensemble of ten independent configurations for each functionalisation chemistry.

For each simulation, the component parallel to the pull-out direction of the force acting on the constrained ring of atoms was recorded at each time-step and used to plot the pull-out force as a function of CNT displacement. The resulting curve was smoothed using a 100 fs time window with a top-hat smoothing filter to average out high-frequency vibrations associated with internal modes of the CNT. The smoothed curve displays local peaks that are associated with bond-breaking events; we use the value of the force at each of these peaks (which we refer to as the “critical force”) as an indicator of the strength of the interface. The method for determining the exact location of each bond-breaking event is discussed in more detail below. The main focus of this work is the comparison of strengths of various functionalised interfaces, although presented analysis relies on the peaks in pull-out force as a proxy; this is possible since all test are performed on identical CNTs and comparing the critical force is semantically the same as comparing the ISS.

The top panel of sub-figures in Figure 5.8 show a typical example of the smoothed force-displacement curve, with peaks corresponding to failure marked with stars; there are three such events per simulation as each system is prepared with three functionalised attachments between the CNT and the polymer matrix. The bottom panel of sub-figures in the same figure show the number of atoms flagged for QM calculation at each point of the simulation. It can be seen that the more computationally-demanding QM calculations are only performed when necessary, i.e., just before, during and just after each bond-breaking event and that atoms are promptly de-flagged following a failure event. It can also be seen that at any point during the simulation, the number of atoms for which QM forces are calculated is a small fraction of the total number of atoms in the system (typically less than 1% of the total number of atoms at any given time).

Finding the critical strength of individual attachments The times at which individual fracture events took place was found in an automated fashion by analysing the distance between

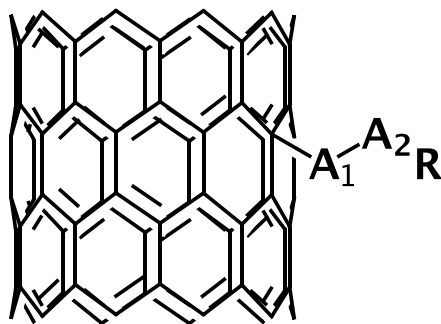


Figure 5.3: Polymer attachment point with two atoms used for attachment monitoring annotated as A_1 and A_2 .

two atoms in the functional group grafted to the CNT denoted as A_1 and A_2 in Figure 5.3. The bond between the two selected atoms is generally elongated when the attachment is transferring load between the polymer matrix and CNT and returns to equilibrium distance after a critical failure. A sudden change in the A_1 - A_2 distance is used as an indicator of the time of the individual failure event.

The critical strength necessary to break an individual attachment is found by analysing the relation of the CNT pull-out force and the nanotube displacement. The peaks of the smoothed curve are located, and the values of maxima closest to the rupture location are chosen as the critical strengths. The plot of pull-out force alongside the appropriate interatomic distances for three CNT attachments for one of the simulations of a system with CH_2 functional attachments is shown in Figure 5.4.

Temperature dependence The pull-out simulations were carried out at a temperature of 100 K instead of room temperature of 300 K in order to reduce thermal variations of atoms and make QM flagging more consistent, limiting unphysical fluctuations in the set of flagged atoms. The effect of changing the temperature from 100 K to 300 K was quantified by conducting two series each of ten simulations exploring pull-out of a CNT functionalised with carbene groups at temperatures of 100 K and 300 K; all simulations were performed as discussed in Section 5.2.4. The results of the critical force on the constrained CNT atoms, critical strength of individual attachments and the fracture energy of the interface are shown in Figure 5.5, Figure 5.6 and Figure 5.7, respectively. The discrepancy of results between tests performed at

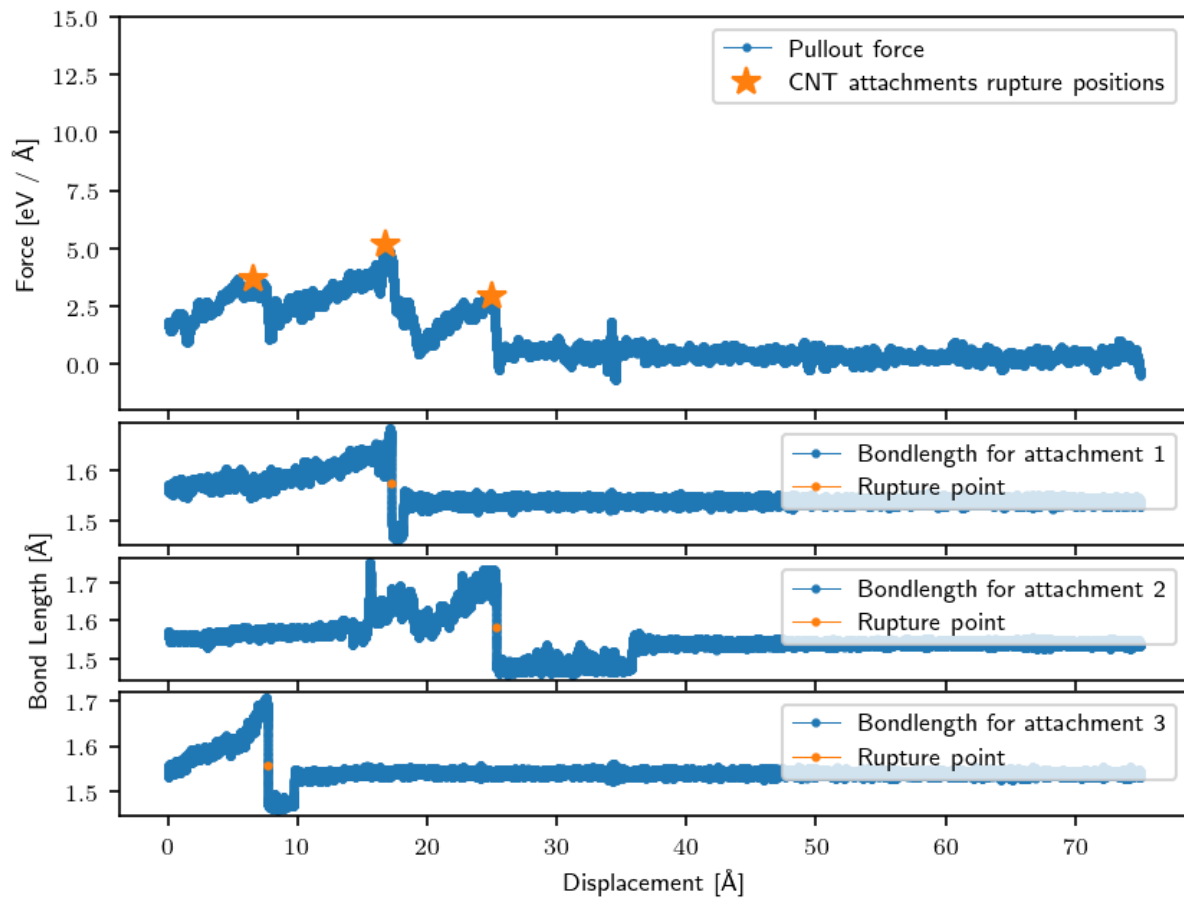


Figure 5.4: Top panel: Force vs displacement plots for a selected simulation for the CH_2 system. Lower panels: plots of selected bond-length used to monitor all three individual attachment status.

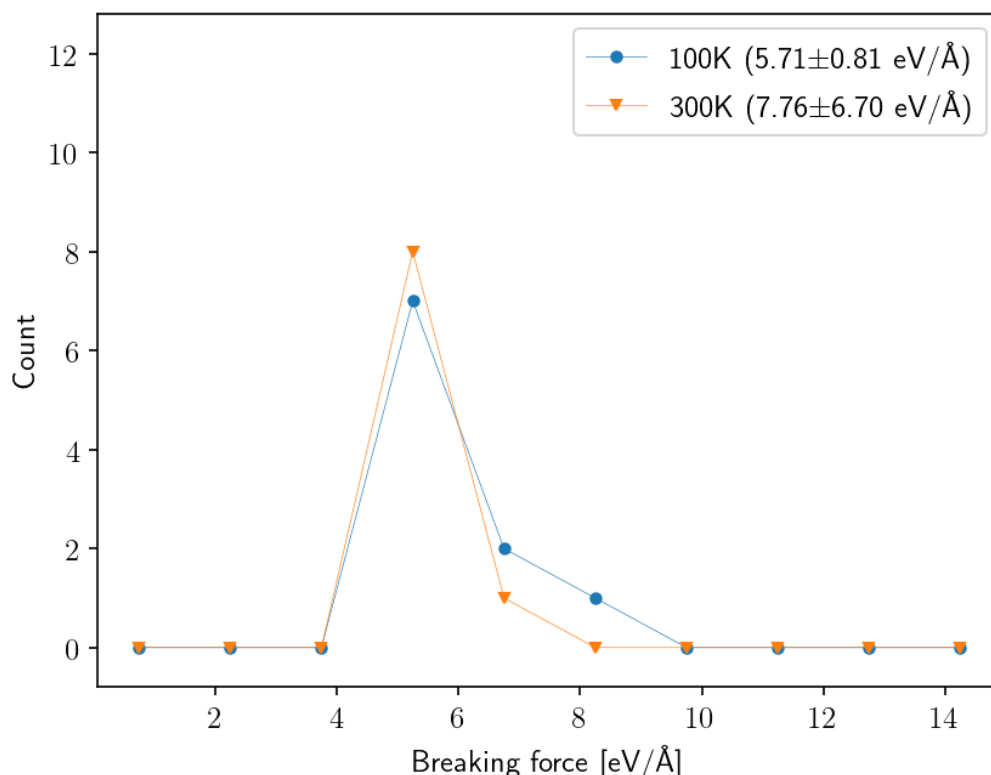


Figure 5.5: Distribution of the critical force on the constrained CNT atoms for the CH interface at two temperatures. The bins used in the histogram have the width of $1.5 \text{ eV/\AA}$ with the leftmost edge of the first bin located at 0; the markers are placed at the midpoint of each bin.

different temperatures is small, and as a result, simulations performed at 100 K were considered to be a good approximation of the behaviour at room temperature.

5.3.1 Discussion

The critical forces recorded from each pull-out simulation have been aggregated and the distributions describing the strength of the interface in each case forms the key result of this work: the histograms and aggregate statistics are shown in Figure 5.9. We find that interfaces based on amine (NH), carbene (CH_2) and carboxyl (COOH) functional groups are characterised by similar strength; there is, however, an improvement in ISS of approximately 50% when the $[2 + 1]$ cycloaddition (CH) is used to attach the polymer to the CNT. The first three functionalisations rely on a single covalent bond to graft PE chains to the CNT, whereas the cycloaddition is grafted with a pair of single bonds. The systems that we have investigated are identical except for the chemistry of the attachments, indicating that the functionalisation can indeed

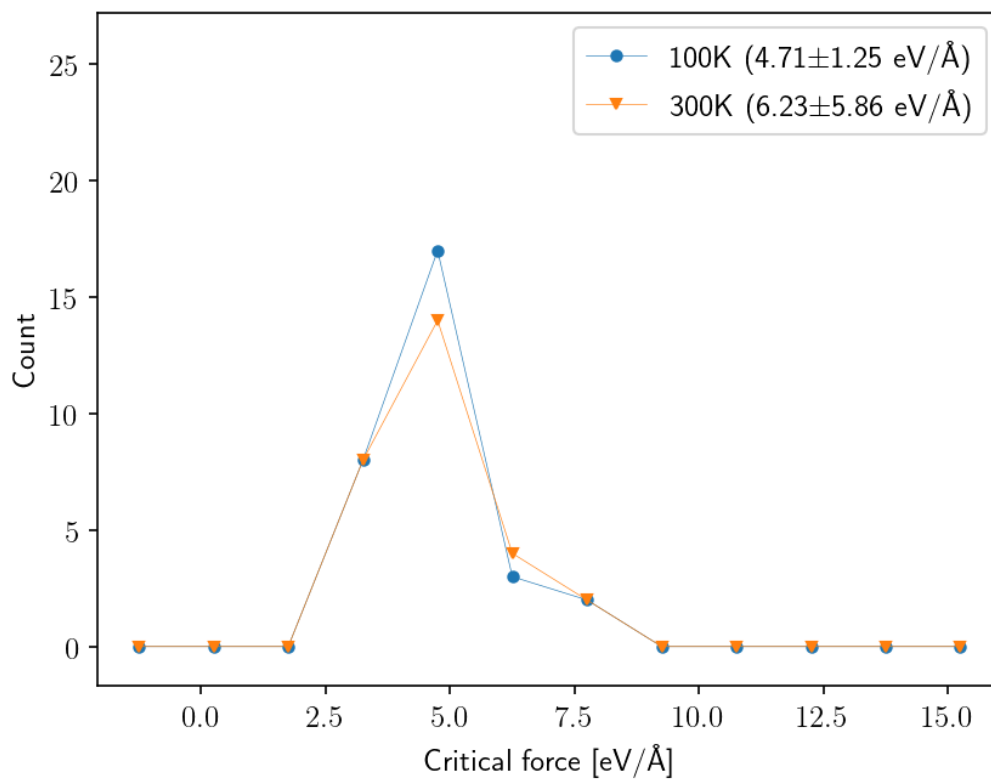


Figure 5.6: Distribution of critical strengths of individual attachments for the CH interface at two temperatures. The bins used in the histogram have the width of $1.5 \text{ eV}/\text{\AA}$ with the leftmost edge of the first bin located at 0; the markers are placed at the midpoint of each bin.

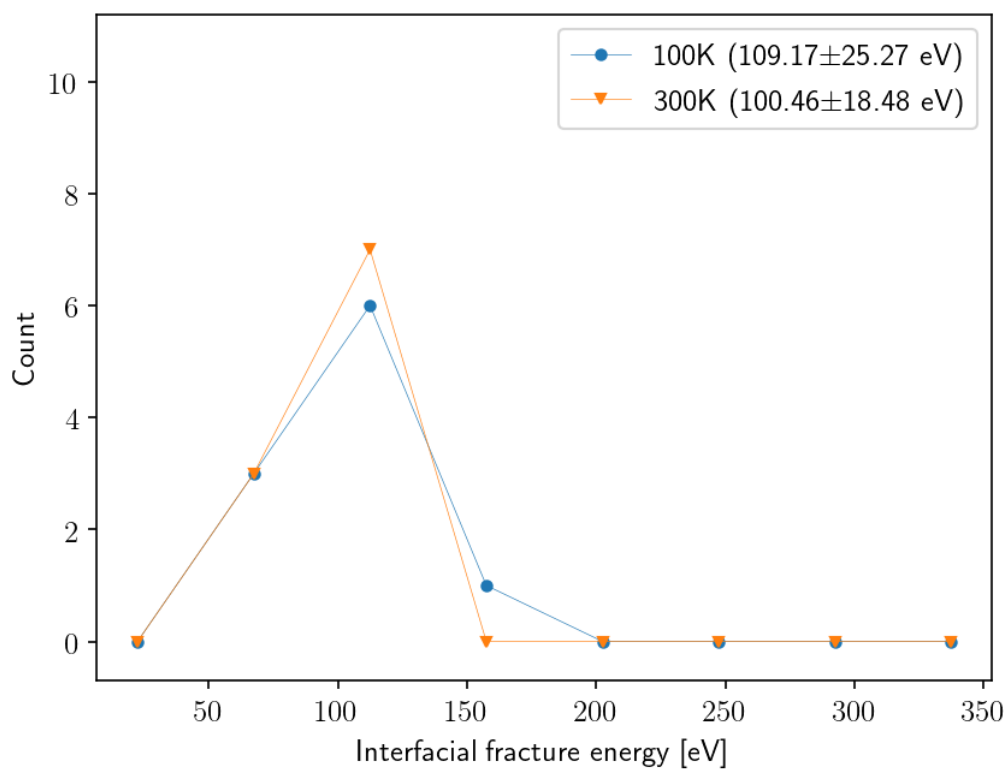


Figure 5.7: Distribution of fracture energy for the CH interface at two temperatures. The bins used in the histogram have the width of 45 eV with the leftmost edge of the first bin located at 0; the markers are placed at the midpoint of each bin.

be chosen to enhance the ISS of the composite. In their study, Milowska *et al.* [160] have shown that the first group of attachments (NH, CH₂ and CH) have a similar binding energy of approximately 1.3 eV while the [2 + 1] cycloaddition is characterised by a higher value of approximately 2.3 eV. This indicates that the binding energy of a functional group can be seen as a proxy for the critical force of the attachment and therefore used to gauge the strength of the resulting interface.

Furthermore, the area under the pullout force-CNT displacement curve provides a measure of the interfacial fracture energy; the distribution of fracture energies across the ensemble of ten simulations for each functional group are portrayed in Figure 5.10. The results show that interfaces based on amine, carbene and carboxyl functional groups have similar fracture energy; however, an improvement of approximately 70% is found when a [2 + 1] cycloaddition is used to anchor the polymer chains to the CNT. The difference between fracture energy values of the carboxyl-based interface and amine- or carbene-based ones was analysed with a two-sided t-test for the null hypothesis that two independent samples (with the COOH-based interface as the first sample and combined results for NH and CH₂ interfaces as the second sample) have identical expected values. The test concluded with a p -value of 0.037. In comparison, a similar test performed with amine, carbene and carboxyl interfaces in one sample and the [2 + 1] cycloaddition-based connection as the second resulted in a p -value of 5×10^{-7} , reinforcing the conclusion that our findings can be used to clearly divide the interfaces into two major classes with significantly different fracture energy performance. The difference in mean fracture energy between the two groups is approximately 70%, showing that the application of functional groups with higher binding energy can have a beneficial effect on interfacial fracture energy.

The mechanism of interfacial failure has been further studied by inspecting the yield strength and atomistic structure of individual attachments in each of the composite systems. The analysis reveals that in systems where CH₂, NH and COOH functional groups were used to form the interface, critical failure occurred by the failure of the functional group and detachment of polymer chains from the CNT surface demonstrating that the grafting point itself is the weakest element of the interface. On the other hand, in the case of [2 + 1] cycloadditions (CH), two equally common failure modes were observed: detachment of the functional group from

the CNT and bond-breaking within the polymer matrix. The distribution of the strength of individual attachments, discriminated by their failure mode is shown in Figure 5.11. The [2+1] cycloaddition-based interface and the polymer backbone fail at a similar load, demonstrating that their strengths are comparable and a further increase of the strength of the interface would not yield any effective improvement without fortifying the polymer matrix itself. Our results show that the functionalisation chemistry can be tuned to improve the ISS up to a limit defined by the strength of the polymer backbone.

Additional effort has been devoted to the analysis of the [2 + 1] cycloadditions (CH) based interface by exploring the effect of the attachment point geometry on the yield strength. Due to the structure of carbon nanotubes, [2 + 1] cycloaddition can be found in two configurations, attached to two CNT atoms located parallel to the CNT axis or at an angle of 45 degrees. Figure 5.12 shows the normalised distribution of the strength of individual attachments divided into these two configurations. It can be seen that the orientation of the attachments is not a major factor for the designing of high-strength CNT-polymer interfaces based on functional groups attached with two bonds.

Comparing our calculated ISS with experimental measurements is very challenging for systems as complex as real CNT-polymer composites. However, focusing on the maximum recorded pull-out force normalised by the CNT diameter (carbon-to-carbon distance across the nanotube), we have compared our results to the experimental work of Barber *et al.* [10]. They performed pull-out experiments of carboxyl-functionalised CNTs measuring 80 ± 30 nm in diameter and $5 \mu - 10 \mu$ m in length recording the maximum pull-out force of $F_{\max} = 5.3 \pm 3 \mu$ N. When normalised by the CNT diameter, it is equal $F_{\max}/d_{\text{CNT}} = 4.13 \pm 3.61$ eV/Å² which can be compared with our results for the carboxyl-based interface of $F_{\max}/d_{\text{CNT}} = 0.65 \pm 0.06$ eV/Å² for CNTs with diameter 7.93 Å and length 30 Å. The two results, while not the same, are one standard deviation apart which we deem satisfactory. It is important to note that demonstrating quantitative agreement between experiment and theory for these kinds of processes is extremely challenging due to the differences between the experimental system and the simulated one. Discrepancies include the pull-out rate as well as the type (multi wall vs single wall), size and aspect ratio of the CNTs; the functionalisation density is unfortunately not provided by Barber

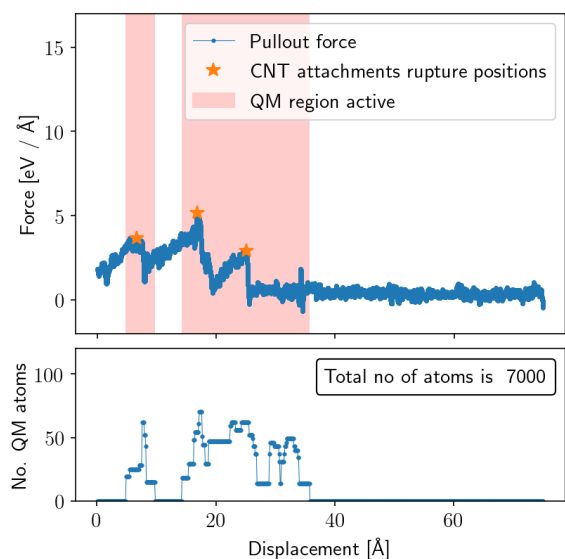
et al. but it is highly likely that the values differ between ours and the experimental study making the comparison even more difficult.

5.4 Conclusions

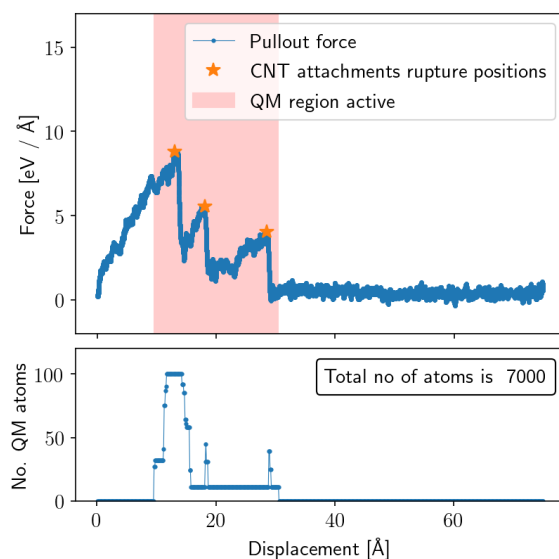
In this work, the critical failure of covalently bonded CNT-polymer interfaces have been investigated by simulating the pull-out of a CNT fibre from a crosslinked polyethylene matrix using a hybrid QM/MM method. The study focused on the strength and failure modes of composite interfaces composed of polymer chains grafted to the CNT surface by amine, carbene and carboxyl functional groups and via $[2 + 1]$ carbon cycloaddition.

The results presented show that interfaces based on CH_2 , NH and COOH functional groups exhibit similar strength and other factors such as CNT dispersion should be the main deciding factor when discriminating between them. However, a significant improvement in ISS can be observed when $[2 + 1]$ cycloadditions are used to facilitate polymer grafting with the resulting interface found to be 50% stronger than the counterparts. The latter functional group is characterised by higher binding energy than the former three [160] indicating a correlation between the functional group adsorption energy and the resulting ISS. Additionally, in the case of the attachment linked with two single carbon bonds, two observed failure modes, the detachment of the functional group from the CNT surface and the rupture of the polymer inside the matrix, were observed to occur at similar critical strengths. This demonstrates that in the case of $[2 + 1]$ cycloaddition-based interfaces, the grafting strength is on par with the strength of the polymer backbone effectively maximising ISS for the composite studied here.

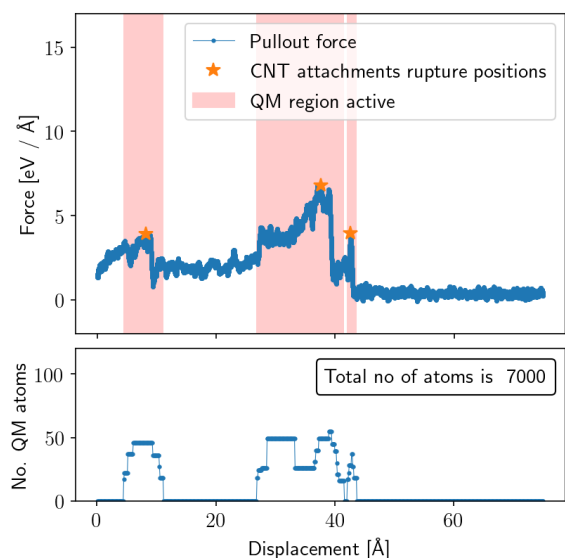
Finally, successfully carrying out a pull-out simulation on a representative volume element of a CNT-polymer composite has shown that the QM/MM method presented and validated in Chapter 4, can be effectively applied to large scale studies where the multiscale nature of the approach is fully utilised. This result confirms that this class of methods can be effectively used to study failure mechanism in CNT-polymer composites, expanding the currently available simulation toolkit.



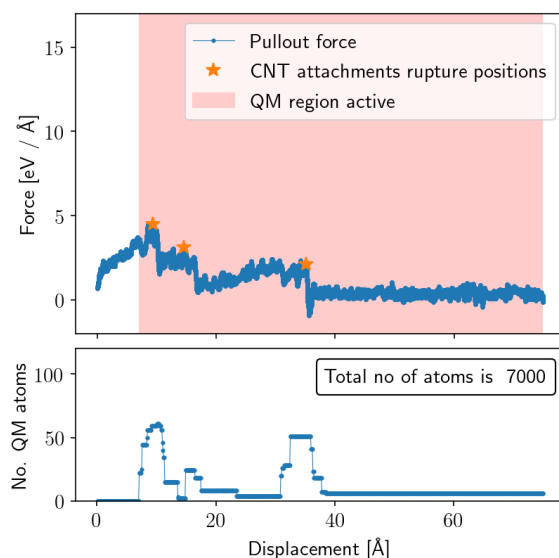
(a) Force-displacement curve for the system with a carbene group (CH_2) used as link.



(b) Force-displacement curve for the system with a $[2+1]$ carbene cycloaddition (CH) used as link.



(c) Force-displacement curve for the system with an amine (NH) group used as link.



(d) Force-displacement curve for the system with a carboxyl group (COOH) used as link.

Figure 5.8: For each sub-figure, the top panel shows force vs displacement plot for a single representative simulation of the CH_2 -functionalised system. The force peaks associated with bond-breaking events are highlighted (stars). Shaded areas show times when at least one atom was treated quantum mechanically. Bottom panel shows the total number of atoms marked as quantum mechanical at a given time. In the simulation presented in panel (d), the functional groups are not de-flagged following the detachment from the CNT as changes in bonding make it challenging for the classical force-field to provide an accurate description. Still, the number of QM atoms is greatly limited post-rupture as fewer than ten require a quantum description.

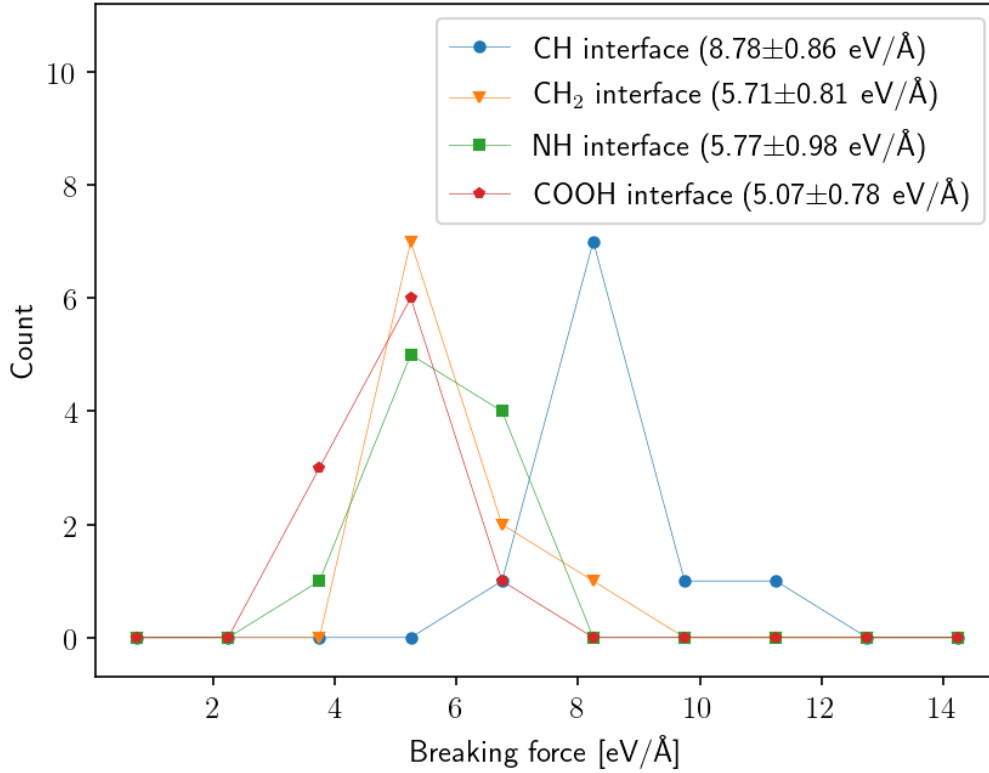


Figure 5.9: Histograms of maximum forces necessary to pull out a CNT embedded in a polymeric matrix. Different colours represent results for composite systems with different interfaces as discussed in Section 5.2. The means and standard deviations of each functionalisation is shown in parenthesis in the legend. The bins used in the histogram have a width of $1.5 \text{ eV/\AA}$ with the left-most edge of the first bin located at 0; the data points are shown at the midpoint of each bin.

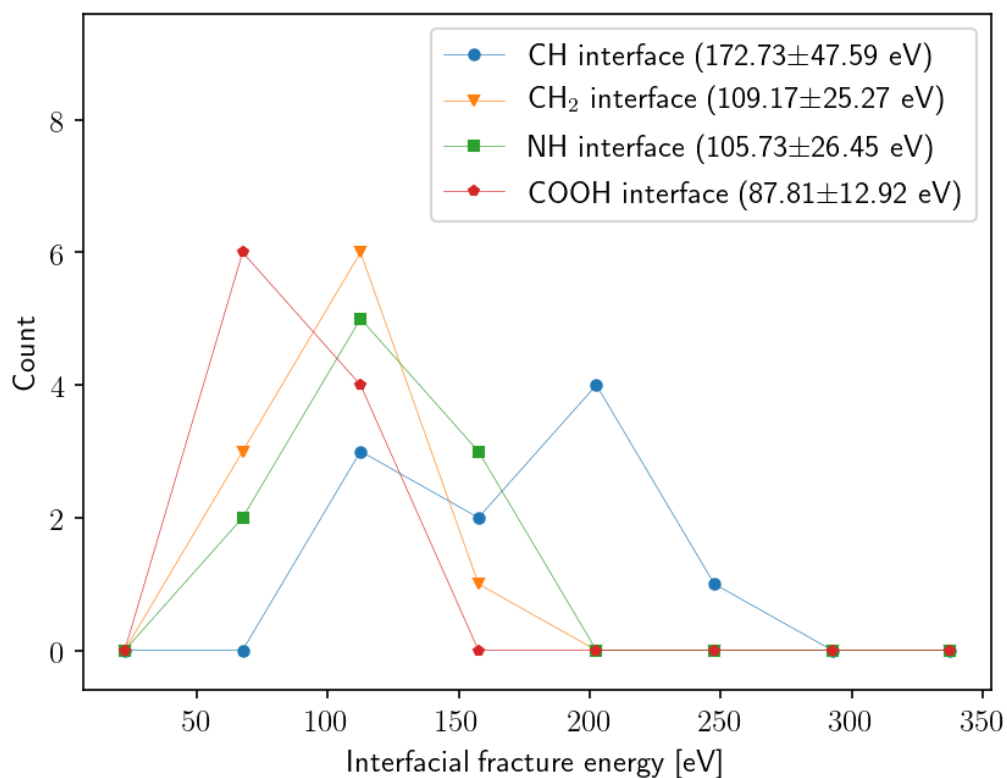


Figure 5.10: Histogram of interfacial fracture energy for composite systems with various interfaces. Numbers in parenthesis represent means and standard deviations of the results in eV, respectively. The bins used in the histogram have the width of 45 eV with the leftmost edge of the first bin located at 0; the markers are placed at the midpoint of each bin.

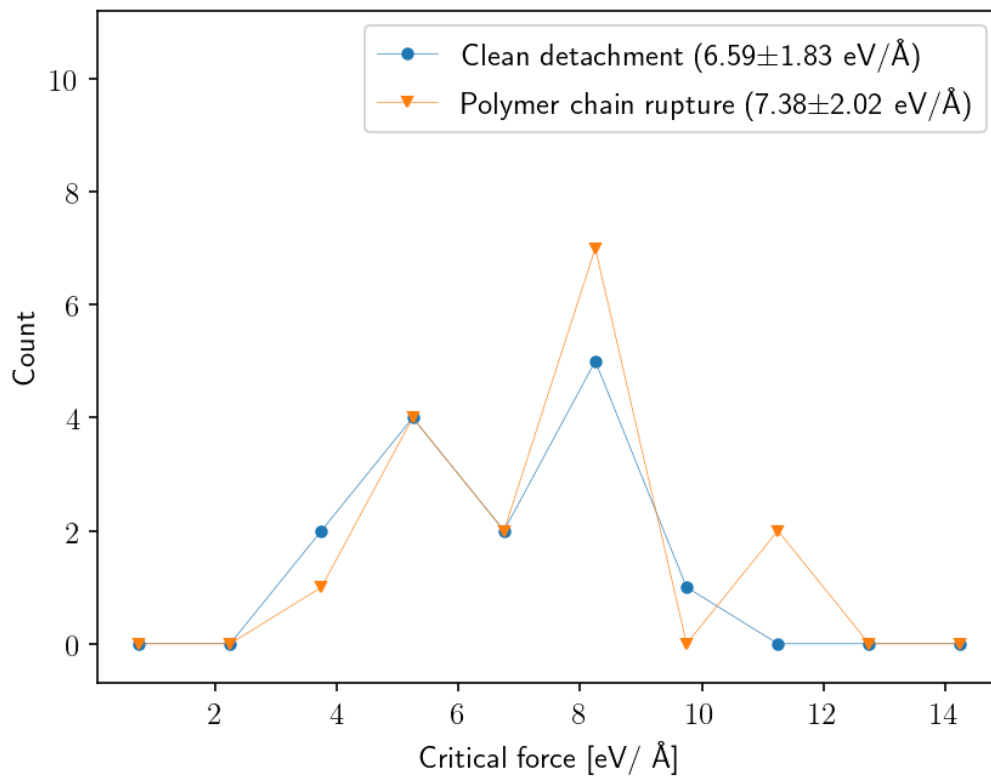


Figure 5.11: Distribution of critical strengths of individual attachments for simulations with interfaces exhibiting various modes of rupture. Mean and standard deviation of the results are shown in the legend. The bins used in the histogram have a width of 1.5 eV/Å with the left-most edge of the first bin located at 0; the data points are placed at the midpoint of each bin.

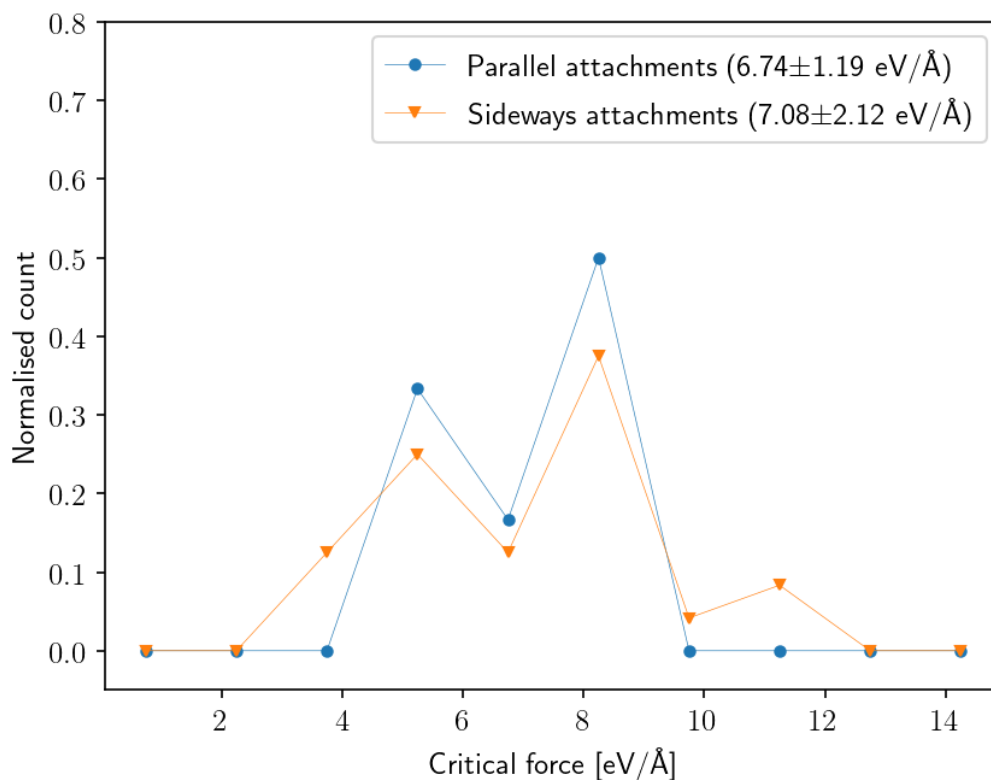


Figure 5.12: Distribution of critical strengths of individual attachments for simulations with interface composed of CH groups in various orientations. The total number of sideways attachments is 24 while the number of parallel ones is 6, therefore the counts are normalised for ease of comparison. The means and standard deviations of the results are shown in the legend. The bins used in the histogram have a width of $1.5 \text{ eV/\AA}$ with the left-most edge of the first bin located at 0; the data points are placed at the midpoint of each bin.

Chapter 6

Summary and future outlook

In this work, I focus on investigating the properties of the CNPCs to understand the mechanism of critical failure at the interfacial between the CNT and the polymer matrix; identify key factors determining the ISS and propose high-performance interfacial compositions to guide further development of CNPCs. Composites central to this study (discussed in Chapter 2) exhibit excellent mechanical properties such as high elastic modulus, strength and low specific weight making them a promising structural material with the potential to replace more conventional choices in demanding fields, for instance, aerospace or ballistic protection. However, the properties of CNPCs are far from ideal as their mechanical characteristics lag behind the theoretical upper bounds discussed in Section 2.3. This shows that the potential improvement offered by CNT reinforcement is not yet fully realised. The quality of composite reinforcement is dictated by the capacity for load transfer between the soft polymer matrix and carbon nanotubes characterised by significantly higher Young's modulus. The efficiency of this mechanism is governed by the alignment and the dispersion of the fibres along with the quality of the interface and all three need to be improved to optimise CNPC properties. Due to the large surface to weight ratio in carbon nanotubes, the quality of the interface is considered of high importance and is the main focus of this work where I aim to propose ways for CNT-polymer composite enhancement by increasing the strength of the interfacial connection.

The main focus of the presented work is to study the best performing class of composite

interfaces (discussed in Sections 2.4.1.2 and 2.4.2.2) consisting of covalent crosslinks between the matrix and reinforcing fibres. CNT functionalisation, used to promote such nanotube-polymer bonding, can have a profound effect on the properties of the composite by affecting the alignment and dispersion of the nanotubes; see Section 2.4. The impact of various functionalisation strategies on those properties has been studied extensively. On the other hand, the effect of changing interfacial chemistry on the ISS is not fully explored thus the focus of this work is to complement the current knowledge by analysing in what respect the composition of the CNT-polymer attachment contributes to the effective strength of the interface.

Computational analysis of the failure process in CNT-polymer composites is challenging as it is a multiscale phenomenon that originates from local changes in chemical bonding that occur at the nanoscale but propagates via stress transfer through the polymer matrix at micrometre lengths. To precisely model the former, a rigorous quantum mechanical treatment is required. However, simulating the evolution of an extended polymer system with the same level of precision is unnecessary and often infeasible. In this work, I tackle this challenge using a concurrent multiscale approach, relying on the force-mixing scheme discussed in Section 3.4.4, where the majority of the system is described with a computationally inexpensive classical interatomic potential (described in Section 3.1.4.1) and regions in which bond-breaking is about to occur are identified on the fly during the dynamical simulation and are treated quantum mechanically. The method, with DFTB as summarised in Section 3.3 used as the QM model, has been used to study the fracture of CNT-polymer attachment representing a simplified model for the composite interface. Results of that investigation show that the hybrid method results are in excellent agreement with fully-QM benchmark simulations and offers qualitative insights missing from classical simulations.

The above-mentioned method is further discussed in Chapter 4, where the application of this approach to investigations of critical failure at the CNT-polymer interface is described and tested. I show that while an entirely classical simulation gives qualitatively different results for the strength of the polymer-CNT attachment site, as compared to a fully quantum-mechanical simulation, my hybrid approach is in excellent agreement but with a fraction of the computational cost. Presented results also demonstrate that an accurate description of quantum

mechanical effects is essential when simulating interfacial critical failure in CNPCs. My hybrid approach promises significant improvement over classical forcefields for problems in which the latter suffer from poor transferability, as in the case study presented in this work.

Finally, chapter 5 is concerned with applying the new hybrid approach to investigate the properties of the covalently bonded CNT-polymer interface. This is achieved by simulating carbon nanotube pull-out from a crosslinked polyethylene matrix showing how chemical structure at the interface determines its failure characteristics. My findings indicate that the choice of the functional group linking the polymer matrix to the CNT surface significantly contributes to the effective strength of the interface, which can be increased by around 50% (up to the limit dictated by the endurance of the polymer backbone) by choosing groups with higher binding energy. This study should be of interest to both computational and experimental researchers in this area and will help guide the development of CNPCs with tailored covalently-bonded interfaces.

6.1 Future outlook

The majority of future work should revolve around the sustained development of the concurrent multiscale modelling approach leading to further applications of the method in order to study the load transfer at the CNPC interfaces. More specifically, once the efficiency of the QM/MM algorithm is improved, the method could be used to perform larger and longer dynamical simulation and consequently answer more complex questions regarding the mechanism of critical failure between CNTs and the polymer matrix.

As a general rule, it is best to direct the optimisation efforts at the most resource intensive element of the algorithm. In the case of the hybrid method demonstrated here, it is the quantum mechanical force evaluation. The most straightforward approach for decreasing the QM calculation wall-time involves employing more computational resources by spreading the computation over multiple parallel nodes. This can be achieved by splitting a larger quantum region into an array of one-atom clusters, where each is accompanied by its buffer, and treating

them concurrently as proposed by Csányi *et al.* [54] and Caccin *et al.* [32]. It is also possible to use an HPC-enabled quantum method which natively supports large-scale parallel calculations thus decreasing the necessary development time.

An alternative approach would involve algorithmic improvements to the method aimed at decreasing the frequency of quantum mechanical calculations by storing and re-using past results rather than discarding the products of QM computations once the atomic forces are known. This goal could be achieved by extending the method demonstrated here to support the Learn on the Fly approach [54] where instead of using the quantum and classical forces directly, a universal parametrised Hamiltonian is fitted to reproduce them. This is achieved by minimising $|F_u - F_{(\text{clas}, \text{QM})}|$ where $F_{(\text{clas}, \text{QM})}$ represents the force on atom derived from a classical Hamiltonian if the particle is in the classical region and a force derived from a quantum Hamiltonian if the particle is in a quantum region while F_u denotes forces found from the universal Hamiltonian describing the whole system. Initially, the universal Hamiltonian is equal to the classical one, although once the results of QM calculations are obtained, its parameters within the quantum region are tuned to describe the QM effects better. The parameters of the fitted Hamiltonian do not have to be evaluated at every time step as the predictor-corrector scheme is introduced. First, the system is evolved in time by a number of timesteps using initial parameters in the predictor phase and the new parametrisation is found. The system is then returned to the starting configuration, and the evolution is repeated with new coefficients marking the corrector phase. This approach could lead to a significant reduction in the number of necessary quantum computations as only one per several timesteps is required to keep the parameters updated. It has been shown that for silicon-based systems one QM calculation per 5-10 classical timesteps is sufficient to retain high accuracy, although there is no guarantee that the same will hold for polymer structures and therefore the improvement could be less impressive.

Alternatively, the frequency of quantum mechanical simulations can be decreased by introducing a statistical model that leverages past QM results to predict the outcome of the perspective calculations. In the approach discussed by Kermode *et al.* [139] results of the quantum mechanical computation are added to a continuously growing database that is subsequently used to train a Gaussian Process regression model predicting atomic forces. Each time a new QM

calculation is required, the model trained on the current dataset is queried, returning its predictions alongside the uncertainty. If the uncertainty is sufficiently low, the results returned by the statistical model are used to perform an MD step. Otherwise, the quantum method is called, and the outcomes are applied to both, evolve the system in time and augment the perpetually growing database. In this scheme, the quantum model is used frequently at first, but once enough data has been gathered the majority of the work is delegated to the relatively inexpensive Gaussian Process regressor as “...ML-predicted atomic forces will suffice as long as the dynamics visits configuration is ‘well represented’ within the existing database”[139]. It is important to note that the original scheme is proposed as a method of evaluating forces on all atoms in the system, but it could also be adapted to operate concurrently on disjoint clusters as long as the QM database is shared. Furthermore, other machine learning models used to predict *ab initio* results could be adapted to work within the framework of active learning; potential candidates involve schemes where the predictions are available alongside their uncertainty such as the Gaussian approximation potentials method [14]. Such approaches should be effective in the case of CNT-polymer composites studied here. This is because the systems investigated in this work are repetitive. Polymeric chains, just as carbon nanotubes, are naturally composed of duplicate elements while the functional groups used to form the interfacial crosslinks share chemical composition and structure. As a result, the information gathered from one part of the system can be efficiently used to predict the properties of a QM cluster located elsewhere.

Efficiency improvements can be used to either increase the fidelity of the calculations by choosing a more precise quantum mechanical approach such as DFT or to carry out simulations at larger length and time scale which would be required to answer more intricate questions about the load transfer at the CNT-polymer interface. The former could improve the credibility of presented results since the rigorous *ab initio* treatment such as DFT (while not without its limits) is better suited as the “gold standard” than the DFTB model. Additionally, the application of highly accurate quantum model could allow for an investigation of more complex CNT-functional group interactions such as the conjugation between delocalised states discussed in Ref. [134, 247]. The latter avenue, concerned with extending simulation time and length scales, is generally more exciting in terms of applications and leads to the further investigation of

CNT-polymer interfacial critical failure, aimed at answering research questions that are now too difficult to study.

The CNT pull-out simulations with a QM/MM method presented in this work are limited to relatively high pull-out velocities; the 10^{-3} /fs used here can be reproduced by straining a composite element with the rate of 2 s^{-1} which can be observed in shock loading conditions rather than in the slow failure of common structural elements. Accessing longer timescales could lift this limitation, therefore, making lower pull-out velocities available for investigation. This, in turn, could be used to study how the strain rate affects the interfacial failure mechanism and what is the best approach to tailor the composition of the CNT-polymer connection to desired conditions.

The availability of longer lengthscales can enable the investigation of much larger and therefore more realistic composite elements. As discussed in Chapter 5, the nanotubes used in this work are approximately an order of magnitude shorter than the ones studied in laboratory experiments and they are exclusively single walled with small diameters in comparison to much wider MWCNTs more commonly used in experiments. Qualitative conclusions drawn from the small scale studies are still applicable in larger systems, but the quantitative findings show some disparity between two settings that could be reduced by using appropriately sized nanotubes. The larger size of studied CNTs should also result in a higher overall number of chemical crosslinks between the nanotubes and the polymer matrix allowing for more fine-grained control over the density of functionalisation. This could be used to study its effect on the ISS.

The issues highlighted here are just some of the many potential problems left to be explored. The topic of interfacial load transfer in CNT-polymer interfaces is a broad and interesting one with plenty of important applications.

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