

UNIVERSIDAD POLITÉCNICA DE MADRID
Escuela Técnica Superior de Ingenieros Industriales



**Local and global structure of
semi-flexible polymer packings in
two and three dimensions**

DOCTORAL THESIS

Submitted for the degree of Doctor by:

Daniel Martínez Fernández

Master's Degree in Chemical Engineering

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Under the supervision of:

Dr. Manuel Laso Carbajo (ISOM & ETSII, UPM)

Dr. Nikolaos Ch. Karayiannis (ISOM & ETSII, UPM)

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ABSTRACT

Polymers have received growing interest over the last two centuries, and important advances have been made in the field of polymer science. Currently, polymer-based materials are present in a wide range of daily life and industrial applications due to their diverse and unique properties. The macroscopic behaviour of the material is strongly related to its microscopic structure. Thus, the understanding of the structure-property relationship is essential to predict and control the specific characteristics of new polymer-based materials with enhanced characteristics. Atomistic simulations can shed light on this, serving as a bridge to connect theoretical predictions with experimental findings.

In the past, the Laboratory of Simulation of Materials (LSM) has conducted, employing off-lattice Monte Carlo (MC) simulations, diverse studies on the structure and phase behaviour of linear, fully flexible polymer chains under a wide range of conditions. Motivated by these previous works, the present doctoral thesis aims to extend the analysis of structure, phase behaviour, and crystallisation to linear, semi-flexible athermal polymers. Hence, by employing extensive MC Simulations, the effect of chain stiffness on self-assembly is analysed at the level of monomers and chains for packings of hard-sphere polymers in two (2D) and three (3D) dimensions from dilute conditions up to the random close-packed (RCP) limit.

Semi-flexible polymers are modelled here as linear chains of tangent hard spheres. Chain stiffness is modulated by a harmonic bending potential that depends on a constant and an equilibrium bending angle. The studied bending angles range between obtuse (fully collapsed configurations) and acute angles, reaching the limit for fully extended configurations (rod-like polymers). Polymer systems in 3D are represented under bulk conditions following periodic boundary conditions (PBCs), while 2D systems are modelled as extremely-confined thin films corresponding to monolayers with a layer thickness equal to monomer diameter.

In the present work, a hierarchical modelling methodology is followed, which is practically implemented by the *Simu-D* simulator-descriptor software. This suite was developed by the LSM for the generation, equilibration, and characterisation of polymer-based systems under diverse conditions, including extreme ones. Extensive MC simulations are executed under constant volume and temperature. Simulations are carried out with different equilibrium bending angles and average chain lengths in a wide range of concentrations, reaching the jammed state in both 2D and 3D. Finally, simulation trajectories are processed to analyse the

structure and phase behaviour of the corresponding polymer systems. Refined descriptors are applied to study the local and global structure. The Characteristic Crystallographic Element (CCE) norm descriptor gauges the local order, at the level of monomers, and the Long-Range Order (LRO) identifies the orientational global order, at the level of chains.

As a first prominent result, the RCP limit of semi-flexible polymers is identified in 2D and 3D as a function of equilibrium bending angle. In addition, a collection of results on phase behaviour is provided in 2D and 3D. We gauge the emergence of unstable nematic phases in 2D as concentration increases, while the isotropic to nematic transition is clearly observed for rod-like polymers in 3D. Regarding local order, all semi-flexible polymers in 3D crystallise in close-packed morphologies once a critical volume fraction is reached as a function of the equilibrium bending angle. In 2D the degree of crystallization depends strongly on the equilibrium bending angle, especially near the RCP limit. In parallel, results have been extracted on the influence of chain stiffness on the chain conformations, structure, and chain size of random (as opposed to ordered) packings in 3D of semi-flexible polymers.

RESUMEN

Polímeros han recibido un creciente interés durante los últimos dos siglos e importantes avances se han realizado en el campo de ciencia de polímeros. En la actualidad, materiales basados en polímeros están ampliamente presentes en la vida diaria y en aplicaciones industriales debido a sus diversas y únicas propiedades. El comportamiento macroscópico del material está fuertemente relacionado con su estructura microscópica. Así, la comprensión de la relación estructura-propiedad es esencial para predecir y controlar las características de nuevos materiales poliméricos con propiedades mejoradas. Simulaciones atomísticas pueden dilucidar esto, sirviendo como puente para conectar predicciones teóricas con descubrimientos experimentales.

En el pasado, el Laboratorio de Simulación de Materiales (LSM) ha realizado, empleando simulaciones de Monte Carlo (MC), diversos estudios en la estructura y comportamiento de fase de cadenas poliméricas flexibles bajo un amplio rango de condiciones. Motivado por estos estudios, esta tesis doctoral busca extender el análisis de la estructura, comportamiento de fase y cristalización a polímeros semi-flexibles atermales. Por tanto, empleando simulaciones MC, el efecto de la rigidez de cadena en la autoorganización es analizado al nivel de monómeros y cadenas para sistemas de polímeros de esferas duras en dos (2D) y tres (3D) dimensiones desde condiciones diluidas al límite de *Random Close-Packed* (RCP).

Los polímeros semi-flexibles son modelados como cadenas lineales de esferas duras tangentes. La flexibilidad está modulada por un potencial armónico de flexión que depende de una constante y un ángulo de enlace de equilibrio. Los ángulos de enlace estudiados varían entre ángulos obtusos (configuraciones colapsadas) y agudos, alcanzando el límite para configuraciones totalmente extendidas. Sistemas poliméricos en 3D son representados siguiendo condiciones periódicas de contorno, mientras sistemas 2D son prácticamente modelados como películas finas de una monocapa de espesor igual al diámetro de monómero.

En el trabajo presentado, se sigue una metodología jerarquizada de modelización, que es implementada por el software simulador-descriptor *Simu-D*. Este fue desarrollado por el LSM para la generación, equilibrio y caracterización de sistemas poliméricos bajo diversas condiciones, incluyendo extremas. Largas simulaciones MC son ejecutadas a volumen y temperatura constante con diferentes ángulos de enlace de equilibrio y longitudes medias de

cadena en un amplio rango de concentraciones. Finalmente, las trayectorias de simulación son procesadas para analizar la estructura y comportamiento de fase de los correspondientes sistemas poliméricos. Descriptores precisos son empleados para estudiar la estructura local y global. El *Characteristic Crystallographic Element norm* es un descriptor que mide el orden local, al nivel de monómeros, y el *Long-Range Order* identifica el orden orientacional global, al nivel de cadenas.

Como un primer prominente resultado, el límite RCP de polímeros semi-flexibles es identificado en 2D y 3D en función del ángulo de enlace de equilibrio. Además, un conjunto de resultados sobre el comportamiento de fase es presentado para 2D y 3D. La aparición de fases nemáticas inestables en 2D fue medido con el incremento de la concentración, mientras la transición de isotrópico a nemático es claramente observada para polímeros extendidos en 3D. Respecto al orden local, todos los polímeros semi-flexibles en 3D cristalizan en morfologías compactas cuando una densidad crítica es alcanzada en función del ángulo de enlace de equilibrio. El grado de cristalización en 2D depende fuertemente en el ángulo de enlace de equilibrio, especialmente cerca del límite RCP. En paralelo, resultados han sido extraídos sobre la influencia de la flexibilidad en las conformaciones, estructura y tamaño de cadenas de empaquetamientos aleatorios (en oposición a ordenados) de polímeros semi-flexibles en 3D.

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ACRONYMS AND SYMBOLS

1D	1 dimension
2D	2 dimensions
3D	3 dimensions
AMO	Amorphous
BCC	Body-Centred Cubic
BFM	Bond Fluctuation Model
CA	Cosine Angle (potential)
CB	Configurational Bias (pattern)
CCB	Continuum Configurational Bias
CCAM	Chain-Connectivity-Altering Move
CCE	Characteristic Crystallographic Element (norm)
CeSViMa	Centro de Supercomputación y Visualización de Madrid
CNT	Classical Nucleation Theory
CPU	Central Processing Unit
CRY	Crystal, crystalline
DB	Double-Bridging
FCC	Face-Centred Cubic
FIV	Fivefold symmetry
FJ	Freely-jointed (chain/model)
FR	Freely-rotating (chain/model)
GET	Generalised Entropy Theory
GN	Geometric Neighbours (model)
HCP	Hexagonal Close-Packed
HEX	Hexagonal
HPC	High-Performance Computing
HON	Honeycomb
HS	Hard Sphere(s)
IDR	Intramolecular Double-Rebridging

<i>ich</i>	Chain <i>i</i>
IdExM	Identity Exchange Move
ISO	Isotropic phase
IUPAC	International Union of Pure and Applied Chemistry
<i>jch</i>	Chain <i>j</i>
L-BFM	Larson-type Bond Fluctuation Model
LM	Localised move
LJ	Lennard-Jones
LRO	Long-Range Order
LSM	Laboratory of Simulation of Materials
MC	Monte Carlo
MD	Molecular Dynamics
MRJ	Maximally Random Jammed
NCP	Nematic Close Packed
NEM	Uniaxial nematic mesophase
NVE	Microcanonical ensemble
NVT	Isochoric or Canonical ensemble
NPT	Isobaric-isothermal ensemble
μVT	Grand Canonical ensemble
OBL	Oblate mesogen, nematic mesophase
PBC	Periodic Boundary Condition
PEN	Pentagonal
PNC	Polymer Nanocomposites
PRO	Prolate mesogen, nematic mesophase
RCP	Random Close-Packed
rHCP	random Hexagonal Close Packing
sEB	simplified End-Bridging
sIEB	simplified Intramolecular End-Bridging
SCLM	Simple Cubic Lattice Model
SQU	Square
SW/SS	Square-Well/Shoulder
TRI	Triangular
UPM	Universidad Politécnica de Madrid
VMD	Visual Molecular Dynamics
WLC	Worm-Like Chain

T_g	Glass transition temperature
N	Number of entities (atoms, molecules, chains...) for Statistical Physics
V	Volume
T	Temperature
P	Pressure
E	Energy
μ	Chemical potential
$\mathbf{r}$	Coordinates vector
$\mathbf{p}$	Momenta vector
$\mathcal{H}(\mathbf{r}, \mathbf{p})$	Hamiltonian
$\mathcal{K}(\mathbf{p})$	Potential of motion, kinetic energy
$\mathcal{V}(\mathbf{r})$	Potential of position, dynamic energy
Γ	Phase space, particular point in the phase space
$\mathcal{A}$	Instantaneous value of some property
$\mathcal{A}_{\text{obs}}$	Observable macroscopic property
t_{obs}	Observation time
τ_{obs}	Number of discretization steps
dt	Length of discretization time
$\rho_{\text{ens}}(\Gamma)$	Probability density of the phase space
w_{ens}	Weight function of the phase space
Z_{ens}	Partition function of the ensemble
k_B	Boltzmann constant
ζ	Random number
P_{mn}	Transition probability (from state m to state n)
N_{at}	Total number of spherical monomers
N_{ch}	Number of chains
N	Number of monomers in a chain or chain length
N_{av}	Average chain length
Δ	Dispersity index
N_s	Number of monomers as individual entities
N_{part}	Number of spherical nanoparticles
N_{cyl}	Number of nanocylinders
N_{ent}	Total number of entities

σ, σ_1	Monomer diameter, collision distance, characteristic length of the system
l	Bond length
dl	Bond tolerance/gap
θ	Bending angle
k_θ	Bending constant
θ_0	Equilibrium bending angle
U_{bend}	Bending potential
N_θ	Number of bending angles
ϕ	Torsion angle
U_{tor}	Torsion potential
r_{ij}	Distance between the centres of spheres i and j
U_{HS}	Non-bonded potential for Hard-Sphere model
$U_{SW/SS}$	Non-bonded potential for Square-Well/Shoulder model
ε	Interaction intensity
σ_2	Interaction range
U_{LJ}	Non-bonded potential for Lennard-Jones model
L	Length dimensions of the simulation cell
d_{conf}	Number of confined dimensions
d_{wall}	Distance between confining surfaces
V_{at}	Total volume occupied by monomers
V_{cell}	Volume of the simulation cell
φ	Packing density
φ^{FCC}	Densest packing density of the face-centred cubic crystal
φ^{HCP}	Densest packing density of the hexagonal close-packed crystal
φ^{MRJ}	Packing density at the MRJ state
φ^{RCP}	Maximum achieved packing density, Packing density at the RCP state
φ^F	Packing density of the freezing point
φ^M	Packing density of the melting point
S_{at}	Total surface occupied by monomer on the large faces
S_{cell}	Surface area of the large faces in the dimension confined
φ_{sup}	Surface coverage or superficial density
φ_{sup}^{TRI}	Densest surface coverage of the hexagonal crystal of the $p6m$ wallpaper group (or Triangular, TRI, crystal)
$\varphi_{sup}^{MRJ,2D}$	Surface coverage at the MRJ for 2D systems

φ_{sup}^{RCP}	Maximum achieved surface coverage
l_{disp}	Maximum amplitude for the displacement of an individual monomer
n_{ccb}	Maximum number of end-segment monomers to be affected by the CCB move
r_{clust}	Inclusion distance of the cluster
ΔL_{max}	Maximum length modification of simulation cell dimensions for the volume fluctuation move
$\mathbf{s}$	Scaled coordinates for the volume fluctuation move
n_{dis}	Number of trial configurations for the CB pattern
P_{acc}	Final acceptance probability for an MC move
w_{rev}	Weight of the reverse transitions
w_{for}	Weight of the forward transitions
n_{CCAM}	Total number of neighbour monomers that can initiate a CCAM
$N_{coord}(X)$	Coordination number of the X reference crystal
$N_{el}(X)$	Number of geometric symmetry elements of the X reference crystal
$N_{act}(k, X)$	Number of actions for each geometric symmetry element
$\mathbf{R}_j^X$	“Ideal” coordinates of the X reference crystal
$\mathbf{S}_{k,m}^X$	Transformation matrix for each symmetry action
ε_i^X	CCE norm for the site i for the X reference crystal
$\varepsilon_i^{X,0}$	Penalty function to the CCE norm
ε^{thres}	Critical threshold
$P(\varepsilon^X)$	Probability distribution function of CCE norms
S^X	Order parameter for the X reference crystal
τ_c	Degree of order, degree of crystallinity or total crystallinity
$\mathbf{I}$	Inertia tensor
$\mathbf{x}_{cm}$	Coordinate vector of the centre of mass
$\mathbf{u}$	Unit vector along the long axis of the molecule
δ	Identity tensor
$\mathbf{Q}$	Second-order tensor of the orientational LRO
$\mathbf{n}$	Nematic director
$\mathbf{Q}'$	Diagonalised second-order tensor $\mathbf{Q}$
λ	Eigenvalues
q	Orientational long-range order (LRO) parameter
$w_{intra}(r)$	Intramolecular pair radial density function
$g_{inter}(r)$	Intermolecular pair radial distribution function

$g_{total}(r)$	Total pair radial distribution function
$\mathbf{R}$	End-to-end vector
R^2	Square end-to-end distance
R_g^2	Square radius of gyration
l_p	Persistence length
R_{max}	Chain contour length
ν	Flory exponent
d	Dimensionality of the system
C_N	Characteristic ratio
C_∞	Flory's characteristic ratio
n	Scaling exponent of the chain size
$\varphi^{*,\text{semi}}$	Crossover packing density between dilute and semi-dilute regimes
$\varphi^{*,\text{marg}}$	Crossover packing density between semi-dilute and marginal regimes
$\varphi^{*,\text{conc}}$	Crossover packing density between marginal and concentrated regimes
$\mathbf{T}$	Tetratic order tensor
q_4	Tetratic order parameter

Chapter 1: INTRODUCTION

The present manuscript presents the development and results of the research study for the obtention of the degree of Doctor in Environmental, Chemical and Materials Engineering (R.D.99/2011), conducted in the Laboratory of Simulation of Materials (LSM) of the Universidad Politécnica de Madrid (UPM). This doctoral thesis aims to study the short- and long-range structure of linear, semi-flexible chains of tangent hard-sphere monomers, both in two (2D) and three dimensions (3D) under a variety of conditions. This study is achieved through extensive molecular simulations employing the Monte Carlo (MC) method [1]. Specifically, particular emphasis has been placed on the analysis of the local (at the level of monomers) and global (at the level of chains) structure, phase behaviour, self-organisation, and crystallisation of random packings of athermal linear semiflexible polymers as a function of the equilibrium bending angle and the packing density or volume fraction, mainly in the vicinity of the Random Close-Packed (RCP) or Maximally Random Jammed (MRJ) limits.

For the development of the research study, a hierarchical methodology is adopted: first, the creation of the semi-flexible systems to be studied; second, the execution of extensive MC simulations to produce a succession of uncorrelated and fully equilibrated system configurations; and finally, the analysis of the simulation trajectories in a post-simulation step (“post-processing”) employing diverse descriptors. Systems are modelled employing the simplest model, that of hard spheres. The chain stiffness of semi-flexible systems is modulated through a tuneable harmonic potential for the bending angle, whose intensity dictates the rigidity of the polymer backbone as a function of the bending constant (k_θ) and the equilibrium bending angle (θ_0). MC simulations are performed using the *Simu-D* simulator-descriptor [2], built around polymer-orientated algorithms and particularly chain-connectivity-altering moves (CCAMs) and created by the Laboratory of Simulation of Materials (LSM). The *Simu-D* software suite has been developed to simulate and successively identify computer-generated configurations of complex systems based on polymers, under a wide variety of conditions, including extreme conditions such as extreme confinement (leading eventually to monolayer thin films), jamming, and nanocomposites with nanofillers at very high concentrations or having very large sizes. The simulation trajectories are analysed in the post-processing step to

extract the diverse results exposed in this doctoral thesis. In particular, for the study of phase behaviour and order of semi-flexible systems, two distinct descriptors are used: the global structure, at the level of the chains, is gauged by the orientational, long-range (nematic) order parameter (q), and the local structure, at the level of monomers, is identified by the Characteristic Crystallographic Element (CCE) norm descriptor [3, 4].

Some of the results presented here have already been published in the following articles:

- **Martínez-Fernández, D.**; Herranz, M.; Foteinopoulou, K.; Karayiannis, N.C.; Laso, M. *Local and Global Order in Dense Packings of Semi-Flexible Polymers of Hard Spheres*. *Polymers*, 2023, **15** (3), 551.
<https://doi.org/10.3390/polym15030551> [5].
- Pedrosa, C.; **Martínez-Fernández, D.**; Herranz, M.; Foteinopoulou, K.; Karayiannis, N.C.; Laso, M. *Densest packing of flexible polymers in 2D films*. *The Journal of Chemical Physics*, 2023, **158** (16), 164502.
<https://doi.org/10.1063/5.0137115> [6].

The thesis is structured in the following chapters: first, the motivation behind and the objectives are covered in Chapter 1; in Chapter 2, a scientific background is presented on the basic concepts along with a literature survey on the earlier works of various authors in the field and the subjects tackled in the present project; Chapter 3 describes the methodology adopted in this research, including theoretical concepts about molecular simulation and Monte Carlo, the description of the molecular model and the simulated systems, an explanation of the MC algorithm behind the *Simu-D* suite, and the descriptors used to analyse the generated system configurations; Chapter 4 presents and discusses the main results focusing on semi-flexible polymers in 3D (bulk) and both fully flexible and semi-flexible polymers in 2D (thin films); finally, the main conclusions are summarised in Chapter 5, together with the current efforts of the LSM for future research lines in Chapter 6.

1.1 Motivation

Over the last few decades, polymers have played a crucial role in different applications and processes in the industry as well as in our daily lives. Polymers and plastics are at the heart of a wide range of applications and processes in modern life due to their diverse and unique properties: from clothes, paper, bags, food packaging, bottles, fibres, and toys to electronic devices, 3D printing materials, construction materials, insulators, solar cells, fuel cells, and biomedical applications such as drug delivery or biosensors [7-12]. In the industry, polymers are essential because of their unique characteristics, such as low density, barrier properties, viscoelasticity, corrosion resistance, insulation, low production cost, ability to be produced in massive quantities, etc. Therefore, these materials have a remarkable social and economic

impact on our daily lives. However, the excessive use of polymers requires a reduction or better management of them because of their environmental impact. Due to these reasons, since the emergence of synthetic polymers, polymer science research has focused on the design and synthesis of novel, polymer-based materials with enhanced properties.

In order to develop new polymer materials, there is an ever-growing interest in studying the properties and characteristics of polymers through a deep understanding of their physical, chemical, mechanical, optical, and rheological behaviour in the bulk, on surfaces, and at interfaces. The microscopic structure at the level of atoms is strongly related to the macroscopic properties of the end material. As a consequence, understanding the structure-property relationship is a key factor in predicting and controlling the specific characteristics of polymers to create new polymer-based materials with improved behaviour.

However, the complex structure of polymers at the atomistic level cannot be easily determined through analytic methods based on theoretical models or through experiments, even using the most advanced devices and equipment. For this reason, molecular simulation can be an excellent alternative research route to theoretical and experimental methods by the introduction of highly sophisticated algorithms which allow the generation of representative system configurations. These, in turn, can be analysed following the foundations of statistical physics. Thus, molecular simulation allows for the verification of molecular theories and helps to establish a relationship between microscopic structures and macroscopic properties through algorithms. Moreover, advances in hardware, making computers more powerful and affordable, as well as the creation and employment of new efficient algorithms have benefited the field of molecular simulation over the last decades. Although simulations are not expected to replace experiments, it is now widely accepted that they constitute an invaluable companion in research studies that can be used for the preliminary design of novel materials and address complex and often costly “what if” questions. Furthermore, they are considered an environmentally friendly research approach, as no materials need to be synthesised and then treated as waste. In parallel, extreme conditions like very high values for pressure or temperature make no difference in simulations compared to regular conditions, and frequently they could even accelerate the execution time. However, we should highlight that simulations come also with important disadvantages as, especially for Monte Carlo algorithms, they could require significant investment in manpower to be applicable from one physical system to the other. Other more conventional methods, like Molecular Dynamics, can often be too slow to track the evolution of sluggish systems, for example, polymers in the glassy state or at very high concentrations.

In the past, the Laboratory of Simulation of Materials (LSM) has conducted different studies, employing off-lattice Monte Carlo simulations, on the structure and phase behaviour of linear, fully flexible chains of hard spheres under diverse conditions [13-32], where the Hard-Sphere (HS) model was frequently used due to its simplicity and ability to be connected with

theoretical models. From these studies, some important conclusions have been drawn, for example, that the volume fraction at the maximally random jammed (MRJ) state for hard-sphere chains is the same as for monomers. In other words, starting from dilute conditions and compressing the system, the HS chains can be packed as densely and efficiently as the monomers with the corresponding density being approximately 10% lower than the maximum possible one for non-overlapping hard spheres as encountered in the face-centred cubic (FCC) or hexagonal close-packed (HCP) crystals [13-16, 18]. Additionally, the local and global chain structure, as well as the topological constraints (entanglements), have been analysed as a function of the volume fraction, determining four distinct scaling regimes [15-17, 33-35] revealing a connection between entanglements (intermolecular topology) and knots (intramolecular topology). Furthermore, it was established that an athermal, random packing of chains will be driven by entropy to a crystalline structure given enough observation time once a critical packing density is met, a trend which is in perfect qualitative agreement with the one exhibited by individual monomers, free of any constraints related to chain connectivity [18-24].

Although our understanding of the structure at the atomic level and phase behaviour of polymer chains has improved significantly over the last few years, the complete connection between the unique characteristics of polymers and their structure at the microscopic level is not fully elucidated. Hence, motivated by the previous studies of LSM, this doctoral thesis aims to extend the research on the structure, phase behaviour, and crystallisation of linear chains of hard spheres through the inclusion of chain stiffness via a bending potential.

1.2 Objectives

As stated previously, the main objective of this doctoral thesis is to study the structure and behaviour of linear semi-flexible chains of tangent hard spheres of uniform size, both in two and three dimensions, performing extensive Monte Carlo (MC) simulations. For that, chain stiffness is practically realised via a harmonic-spring-like bending potential that depends on a bending constant (k_θ) and an equilibrium bending angle (θ_0). Particularly, the study is focused on the effect of packing density (φ) and equilibrium bending angle (θ_0) on the structure, ordering, and crystallisation of athermal semi-flexible chains, comparing with the results obtained in the past for freely-jointed (fully flexible) chains and monomers [14-19, 21, 35]. The research has been extended to include the effect of confinement, realised through the presence of flat impenetrable surfaces in one [29] or three dimensions [30]. Thus, the present research contributes to improving our understanding of the structure of dilute, dense, and jammed random/ordered packings of athermal polymer chains.

MC simulations are performed using the *Simu-D* simulator-descriptor [2]. The software suite is accordingly modified and extended to create, equilibrate, and analyse a wide collection

of semi-flexible systems in both 2D and 3D. Consequently, a series of objectives is defined to achieve the main goal of this doctoral thesis.

- Develop and include in the MC algorithms an energetic bending potential to control the chain stiffness of the semi-flexible chains.
- Include a new volume fluctuation move into the *Simu-D* suite [2] to modify the volume of the simulation cell. This move allows first to create densely-packed systems by shrinking and second to cast MC simulations in the NPT ensemble in both two and three dimensions.
- Create thin-films of a single monolayer of polymer chains (effectively a macromolecular system in two dimensions) through adsorption and shrinking simulations.
- Generate and equilibrate a large collection of semi-flexible systems spanning a wide range of parameters such as packing fraction (ϕ), average chain length (N_{av}), and equilibrium bending angle (θ_0).
- Develop an analysis tool to gauge the (long-range) global order (isotropic/nematic) of semi-flexible systems.
- Analyse the local order of extremely-confined 2D films and 3D bulk polymer systems through the Characteristic Crystallographic Element (CCE) norm descriptor [3, 4].
- Determine the effect of chain stiffness and packing density on the short- and long-range structures of semi-flexible polymers in both two and three dimensions.
- Study the crystallisation of semi-flexible polymers of short chain length and determine the combined effect of the packing density and chain stiffness (equilibrium bending angle) on the local and global order.
- Study the packing ability of athermal, fully flexible polymers and their monomeric analogues confined in thin films (2D packings) to compare against semi-flexible polymers under the same conditions.
- Identify the random close-packed (RCP) limit and the corresponding structure of semi-flexible polymers in 2D and 3D and compare with the corresponding established findings for fully flexible HS chains and monomers.

Chapter 2: BACKGROUND

Polymer or macromolecule is a large molecule formed by repetition, through covalent bonds, of simpler “structural units” called monomers. IUPAC defines polymer more specifically as “*a molecule of high relative molecular weight, the structure of which essentially comprises the multiple repetitions of units derived from molecules of low relative molecular weight*” [36]. However, this definition is neither sufficient nor practical to distinguish between intermediate molecular weight molecules and polymers. Therefore, in practice, a molecule is considered a polymer, especially a synthetic one, if the addition or removal of one or a few repeat units does not have a notable effect on molecular properties [36].

Since ancient times, human beings have used materials based on polymers, such as wood, vegetable fibres, wool, cellulose, etc. For example, some South American cultures had used natural rubber as material for different purposes, such as toys or containers, before the arrival of Europeans [37]. However, until the beginning of the nineteenth century, the study on polymers was neither thorough nor systematic. The term “*polymer*” was first coined by J.J. Berzelius in 1883. During that century, the development of the first synthetic polymers was initiated by the modification of natural polymers. In 1843, Hancock in England and Goodyear in the USA developed the vulcanisation of rubber by combining it with sulphur. The first completely synthetic polymer was Bakelite in 1907, produced by Leo Baekeland from phenol and formaldehyde [38].

The dawn of polymer science is widely accepted to have begun in 1920 when Hermann Staudinger defined the term macromolecule and laid the foundation of the polymerisation process [39]. Although his work was initially considered very controversial, the idea of a macromolecule as a huge molecule formed by the repetition of “structural units” was widely accepted in 1928. Finally, this work granted him the Nobel Prize in Chemistry in 1953.

Throughout the twentieth century, new synthetic polymers were invented, and important advances were made in the field of polymer science, having a huge impact on modern science, technology, and eventually on our daily lives. Consequently, some researchers were awarded Nobel prizes for their work in polymer science, such as Ziegler and Natta, Flory, and de Gennes.

Among many of these pioneers, it is worth mentioning Wallace Carothers who, through his research, made progress in synthetic polymerisation [40], which resulted in the invention of nylon (1935) and other synthetic fibres. In the 1950s, Karl Ziegler and Giulio Natta progressed in catalytic polymerisation with the development of Ziegler-Natta catalysts [41]. Theoretical advances have been made in polymer chemistry with the contributions of Flory [42, 43] and in the rheological properties of polymers with theories such as the tube model of Doi-Edwards [44] and the reptation theory of de Gennes [45], including further extensions and modifications [46-49]. In recent decades, advances in polymer science and the development of new polymer materials such as plastics, fibres, and elastomers have been a constant.

Polymeric materials present high versatility because of their atomic structure, i.e. their nature, spatial arrangement, and sequence of monomers, which can lead to different physicochemical properties even if the same chemical monomer is used. Many different factors can affect the microscopic behaviour and, eventually, the macroscopic properties. Consequently, the classification of polymers depends on various criteria, such as chemical composition, chain architecture, copolymer sequence (if there are multiple repeated units with different chemical constitutions), and isomerism (structural isomers and stereoisomers).

Chain connectivity and architecture of polymers can range in complexity from the simplest linear chains to ones that bear short or long branches distributed along the chain backbone in regular or random patterns, or star and cyclic structures. Figure 2.1 shows some schematic representations of different polymer chain structures. In this study, only linear chains are considered. However, the MC algorithm can be extended to tackle more complicated architectures such as, for example, the H-shaped [50, 51] or short-chain branched and star [52] polymers.

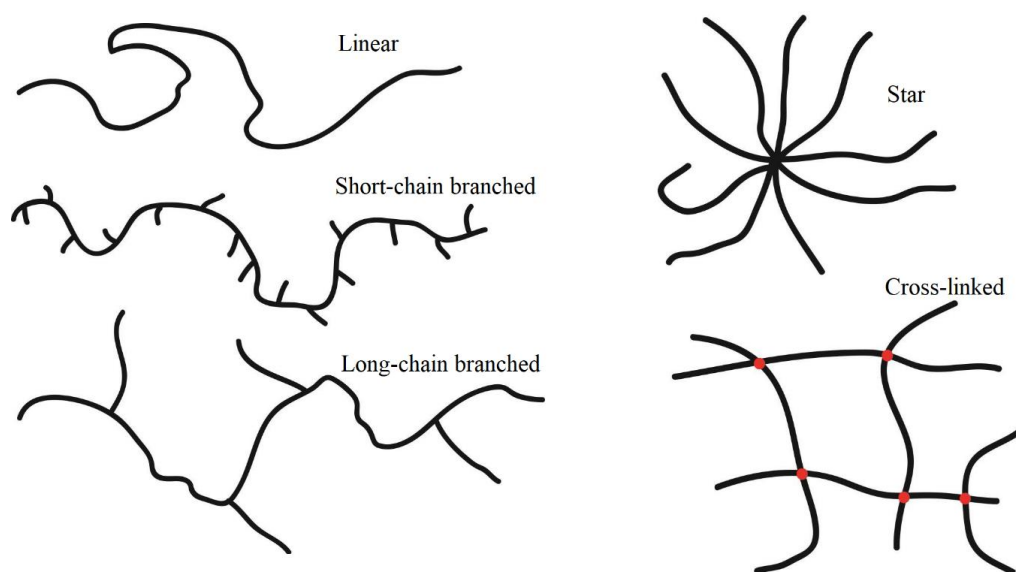


Figure 2.1: Examples of different polymer chain structures. From top to bottom, and left to right: linear, short-chain branched, long-chain branched, star, and cross-linked.

The structure and behaviour of the polymer at the atomistic level are intimately related to the macroscopic properties of the end material. For this reason, according to Flory, “*the comprehension of configurational statistics of polymers is indispensable for a rational interpretation and understanding of properties*” [43]. Therefore, the structural, dynamic, and rheological properties of the polymers can be determined through the statistical description of the spatial configuration of the monomers in a chain, i.e. the polymer conformation and configuration, and could eventually lead to (macroscopic) property prediction.

Because of the wide range of morphologies that polymers can present, the prediction of the properties for all types of polymers, employing a single general model, is impossible and many aspects of the behaviour and structure of general atomic and particulate systems are still unknown or poorly understood. In parallel, the behaviour of a specific macromolecular system cannot be generalized to other systems or different processing conditions, although universal scaling laws do exist [45, 53]. However, our fundamental knowledge of these aspects is continually enriched by advances in experimental, theoretical, and simulation methods. Theoretical models have been developed to predict the effect of the processing conditions on the phase transition in order to analyse the final morphologies [54, 55], and traditional experiments have provided insights into the phase behaviour of monomeric and polymeric systems through the synthesis and characterization of colloidal and granular systems, thanks to their simplicity and large size compared to traditional polymers [56-64]. In parallel, thanks to continuous advances in computer hardware as well as modelling algorithms and methods, molecular simulation remains an effective methodology that can efficiently sample the continuous set of configurations of a polymer system. The two most commonly encountered classes of algorithms for molecular simulation correspond to Molecular Dynamics (MD) and Monte Carlo (MC), including more novel realisations and methods [65-69]. Given the complexity of polymers and the wide range of characteristic length and time scales associated with them, hierarchical multiscale methods are adopted to tackle the challenge of connecting the atomic structure with the macroscopic properties [70-77].

2.1 Molecular Simulation

Molecular simulation is an essential tool to relate the behaviour of atoms, molecules, and macromolecules to the macroscopic properties of the end material without requiring a physical experiment process. In this way, through resolving a series of mathematical equations that define, more or less accurately, the laws of nature, molecular simulation provides a better understanding of complex systems that lack analytical solutions or are experimentally very hard to meet, expensive, time-consuming, or even hazardous for both the researchers and the environment. Therefore, molecular simulations act nowadays as a bridge between theory and experiments, by using experimental results to improve the underlying simulation models and

then compare them with theoretical predictions and concepts. However, molecular simulations can be too slow and inefficient to analyse specific physical systems compared to experimental methods. A faster output may be obtained by taking assumptions and approximations in the model, but this will affect the accuracy of the model. Thus, a trade-off is required between the desired accuracy and the computational complexity of the model.

Furthermore, in the case of systems of macromolecules, the complexity of molecular simulation increases because of the wide spectrum of characteristic time and length scales that polymers present. Besides, molecular simulations have to take into account the chemical nature of the multiple repeat units and their corresponding bonded and non-bonded interactions. Thus, simulations of systems of macromolecules can become highly complex and time-consuming because of the combination of high chemical intricacy, the wide range of characteristic time and length scales, and the slow dynamics of very long and well-entangled chains. For that reason, different molecular simulation methods and approaches have been developed and continually improved to address specific systems and phenomena with different physical-chemical details and properties. Often, these methods are combined together through hierarchical multiscale schemes, where information is exchanged between various levels of description starting at the level of atoms [74-80].

The history of molecular simulation is closely related to the development of computers. The first models that would correspond to molecular simulations consisted of a large number of gelatine balls as molecules to analyse the random packing of liquids [81]. The model required the physical manipulation of large numbers of elements. Thus, the analysis was very time-consuming, inconvenient to handle, and required large volumes and spaces; it also experienced limitations because external influences such as gravity could not be ignored or implemented. For that reason, the mathematical/statistical approach obtained from computers, through approximations of controlled precision, was a paramount aspect of the development of molecular simulation.

The first molecular simulations were performed by von Neumann, Ulam, Metropolis *et al.* for the Manhattan Project employing the Los Alamos' computer MANIAC, which was considered the most powerful computer in its time, to simulate neutron diffusion in a fission weapon core [82]. Their work established the foundations of the current Monte Carlo (MC) simulation, which is built on the extensive use of random numbers [1]. A couple of years later, the first Molecular Dynamics (MD) simulation was carried out by Alder and Wainwright in 1956 to study the phase behaviour of hard-sphere packings [54]. Unlike the Monte Carlo method, MD simulation solves the classical equations of motions for a set of particles. These pioneering works have established the fundamentals for the rapid development of molecular simulation over the last decades. Effectively and also due to the constant increase in the

performance of computers, molecular simulation has established itself as a research tool of paramount importance along with experiments and theory.

In general, we can distinguish between two prominent branches in atomistic simulations: Monte Carlo (MC) and Molecular Dynamics (MD). The former is a stochastic method that samples the different (micro)states of a system under a statistical ensemble employing physical and non-physical algorithms with a probability proportional to the Boltzmann factor of the energy of the system. However, the MC method only considers the potential energy of the system and, due to its stochastic nature, cannot provide information about the real dynamics of the system. On the other hand, molecular dynamics is a deterministic method that numerically solves Newton's equations of motion for a system of particles, atoms, or molecules, taking into account both kinetic and potential contributions in energy. In this way and by integrating the differential equations of motion in a discrete step-by-step pattern, the MD simulation tracks the evolution of the system in time and, consequently, provides dynamic information. However, the simulation of a real system by massively parallel state-of-the-art MD algorithms cannot exceed a few hundred or, at most, thousands of nanoseconds. Thus, molecular dynamics is too slow to reach the required observation time to study phenomena with slow dynamics, such as happens for example in polymer melts of high molecular weight. While MC does not offer dynamical information for long chains, it can provide rapid equilibration due to its stochastic nature and the underlying frequently unphysical but robust algorithms. Therefore, the choice of molecular simulation method is based on the system or phenomenon to study, its characteristics, the processing conditions, and the properties of interest. Molecular dynamics is generally used when dynamical properties or temporal evolution are of interest. Monte Carlo is instead employed to analyse equilibrium structural properties or as a method to provide a long sequence of equilibrated system configurations, which can be successively studied through MD. As an intermediate approach, Kinetic Monte Carlo methods provide a reasonable connection with time evolution when the rates of individual events are known a priori [83].

2.2 Random Packing and Chain Structure

As has been mentioned previously, understanding the connection between microscopic structure and macroscopic properties is of paramount importance for the design of novel materials and the advancement of technology and science [84, 85]. Numerous factors, such as chemical constitution, molecular weight, chain architecture, concentration, processing conditions, etc., affect microscopical behaviour. One of those factors is the concentration or density, which further affects how atoms, particles, and molecules are packed together. Packing has been a research field of interest since early times for multiple disciplines, such as mathematics, physics, chemistry, biology, and engineering [86, 87]. For general atomic and particulate systems, packing is intimately related to the phase behaviour and self-organisation

of the system and is an important factor in applications and processes related to microgels, granular and colloid media, liquids, glasses, biomaterials, etc. [88].

The description of complex general atomic and particulate systems is not an easy task for analytical methods, especially when polymer configurations and conformations are addressed at the atomistic detail. The simplicity of colloidal or granular systems makes them amenable to studying monomeric and polymeric systems at the atomic level. Although they lack the chemical details of their realistic counterparts, colloidal or granular polymers have provided significant insights into the packing and phase behaviour of these systems with theoretical analysis [89-94] and experimental techniques because of their larger size than traditional polymers, which provides more tractable synthesis and characterisation [56-64]. Furthermore, the statistical description of molecular simulation [2, 13, 65-69] provides a strong alternative to theoretical and experimental methods. In molecular simulation, hard colloidal or granular polymers can be straightforwardly implemented by employing rather idealised models for the description of the interactions between monomers.

Packing efficiency and maximum packing density have been extensively studied for ordered and random systems of hard spheres in three dimensions under periodic boundary conditions. In the 17th century, Kepler conjectured that the densest possible arrangement of hard congruent spheres in a 3D Euclidean space corresponds to the packing of the face-centred cubic (FCC) crystal. This conjecture was only recently proved by Hales *et al.* [95-97]. Thus, the densest packing of spheres in three dimensions corresponds to the face-centred cubic (FCC) or hexagonal close-packed (HCP) crystals, with the corresponding packing density being $\varphi^{FCC} = \varphi^{HCP} \approx 0.74048$ [87], where packing density is the ratio of the total volume of bodies in a space to the volume of the space. Analogously, in two dimensions, the maximum packing of disks on a plane corresponds to the hexagonal crystal of the $p6m$ wallpaper group (in this work, it is termed triangular, TRI, to distinguish it from the 3D hexagonal crystal, HEX), with a calculated surface coverage of $\varphi_{sup}^{TRI} \approx 0.907$, where surface coverage is the area occupied by bodies over a surface. Recently, the sphere-packing problem has also been solved in spaces of higher dimensionality (8 and 24 dimensions) by Viazovska *et al.* [98, 99].

Starting from dilute conditions, denser sphere configurations can be generated by gradually compressing a container in experimental setups or an infinitely repeated periodic cell in computer simulations employing shrinkage algorithms [100-103]. However, the maximum density of ordered packings (FCC or HCP) cannot be reached through a standard compression process; rather, the system stops at a lower density than the maximum ordered due to the onset of jamming [104-112]. Thus, given enough stirring and shaking, a random assembly of spheres always settles on an upper limit of maximum density, which is lower than the maximum ordered packing density, which lies in the range of 0.635–0.650 and is termed the Random Close-

Packed (RCP) limit [113-115]. In general, the creation protocol or compression algorithm strongly influences the value of RCP for a given system [104].

In two dimensions, the random close-packed (RCP) limit has also been studied for systems of disks on a plane. Through theoretical studies [116-118], the RCP limit for disks has been established in the range between 0.853 [117] and 0.887 [118]. As for the RCP state in three dimensions, the densest structure and its degree of ordering strongly depend on the adopted creation/compression protocol. Thus, the compression of disk systems from dilute conditions generally leads to the eventual formation of compact, ordered triangular configurations and to an RCP state that is closer to one of the maximum densities, compared to three dimensions.

Nevertheless, the definition of the random close-packed (RCP) state is rather not quantitatively precise. Torquato *et al.* improved the concept of the RCP state with the more rigorous statistical-mechanical definition of the Maximally Random Jammed (MRJ) state [119]. The MRJ corresponds to the state of maximum disorder (or minimum order) of all configurations that correspond to a given jammed system. According to Torquato *et al.* [119], a particle is considered jammed if it cannot be translated when the positions of the other particles of the system are fixed, and the concept can be extended to groups of jammed particles. Thus, an ideal random packing is considered jammed if every hard sphere of the system is jammed. Although the theoretical determination of the packing density in the MRJ state is complex, in a first approach through simulations based on the Lubachevsky-Stillinger algorithm [100], the packing density at the MRJ state of hard spheres was calculated as $\phi^{MRJ} \cong 0.64$ [120]. Later, other studies, through both experiments and simulations, also converged on the established value of packing density for single spheres at the MRJ state [121-124]. Moreover, theoretical, experimental, and simulation studies on random packings in 3D have been extended to more complex, non-spherical elements [125-132], such as ellipsoids, fibres, superballs, etc.

Although the analysis of jamming is more complex in two dimensions due to the general tendency to form triangular configurations during compression, monodisperse jammed disk packings can be obtained through the appropriate algorithm and fine-tuning of the corresponding parameters [133]. That way, the MRJ state for monodisperse disk packings was determined at a surface coverage $\phi_{sup}^{MRJ,2D} \cong 0.826$ [133], which lies at a lower concentration than the packings in the RCP limit [117, 118]. These jammed packings are isostatic, as in 3D, and are more disordered than RCP packings generated by typical protocols [133]. Besides, jamming in 2D is also observed for packings of other types of objects and systems, such as binary disks or polygons, where the shape and symmetry of the objects affect the melting transition and the structural characteristics [104, 129, 134-142].

One interesting question is how the RCP limit and the MRJ state are affected when the hard spheres are connected through chemical bonds or mechanical links to form long linear

chains. One has then to further study how additional factors like chain length, chain architecture, and bond geometry (in the form of bond lengths, bending and torsion angles) affect the ability of the hard-sphere systems to pack. Among them, the simplest possible polymer model corresponds to freely-jointed chains of tangent hard spheres, considered the second type of ideal amorphous solids [143]. Despite the simplicity of the underlying model, there existed an initial inability to explore volume fractions comparable to the established MRJ state for individual hard spheres, due to the difficulty in constructing experimental mechanical models and the computational complexity of generating polymer configurations at these concentrations. Eventually, Karayiannis and Laso identified and thus analysed the MRJ state for assemblies of freely-jointed chains of tangent hard spheres in 3D through extensive off-lattice MC simulations [13]. They determined that linear and fully flexible chains of tangent hard spheres can randomly pack as efficiently as assemblies of individual hard spheres and reach their MRJ state, within statistical uncertainty, at the same packing density ($\varphi_{spheres}^{MRJ} = \varphi_{chains}^{MRJ} \approx 0.639 \pm 0.004$), regardless of the chain length [14, 16, 33]. For both monomeric and polymeric systems, the structure of the MRJ state shares similar properties, like for example the contact network [17], despite the characteristic topological constraints, in the form of entanglements and knots, at the level of chains and the ones imposed by the bond geometry at the level of monomers, which are not present in individual hard spheres [15, 16, 33]. Afterwards, analogous conclusions on the packing of individual hard spheres and hard-sphere chains have been described by other independent studies in three dimensions [144-146].

In addition, by exploring, through extensive simulations, the entire volume fraction range from very dilute conditions to the MRJ state, the global size of hard-sphere chains, as quantified by the end-to-end distance and radius of gyration, is demonstrated to depend strongly on the packing density [16, 33]. Thus, fully flexible hard-sphere chains display a universal static scaling behaviour [45, 147] with increasing packing density, in agreement with theoretical predictions [34, 45, 147, 148], as a consequence of the long- and short-range conformational changes produced as the packing density increases and eventually approaches the MRJ state. Specifically, four distinct scaling behaviours are observed with increasing packing density: 1) dilute, 2) semi-dilute, 3) marginal, and 4) concentrated. Quantifying chain size by the characteristic ratio $C_N = \langle R^2 \rangle / (N - 1)l^2$, where $\langle R^2 \rangle$ is the mean square end-to-end distance, N is the chain length (measured in number of monomers/spheres), and l is the bond length, the four scaling regimes are characterised by a power-dependence of the chain size on the volume fraction ($C_N \sim \varphi^n$), where n is the scaling exponent for each regime [16, 33]. These regimes, the scaling exponents n and the transition thresholds are summarised as follows [16, 33]:

- 1) **Dilute:** $n = 0.0 \pm 0.1$, $0 \leq \varphi \leq \varphi^{*,\text{semi}}$.
- 2) **Semi-dilute:** $n = -0.23 \pm 0.003$, $\varphi^{*,\text{semi}} \leq \varphi \leq \varphi^{*,\text{marg}}$, $\varphi^{*,\text{semi}} \approx N^{-0.764}$ [147].
- 3) **Marginal:** $n = -1.0 \pm 0.1$, $\varphi^{*,\text{marg}} \leq \varphi \leq \varphi^{*,\text{conc}}$, $\varphi^{*,\text{marg}} \cong \varphi^{MRJ}/2 \cong 0.32$ [34].

4) **Concentrated:** $n = 0.0 \pm 0.1$, $\varphi^{*,\text{conc}} \leq \varphi \leq \varphi^{\text{MRJ}}$, $\varphi^{*,\text{conc}} \cong 0.59$ [34].

All scaling exponents and crossover packing densities between high-concentration regimes, i.e. semidilute to marginal ($\varphi^{*,\text{marg}}$) and marginal to concentrated ($\varphi^{*,\text{conc}}$), are independent of chain length. In contrast, the crossover packing density between the dilute and semi-dilute regimes is strongly dependent on the chain length [16, 33]. The four scaling regimes of chain size with increasing packing density and the crossover transitions are displayed in Figure 2.2 [16].

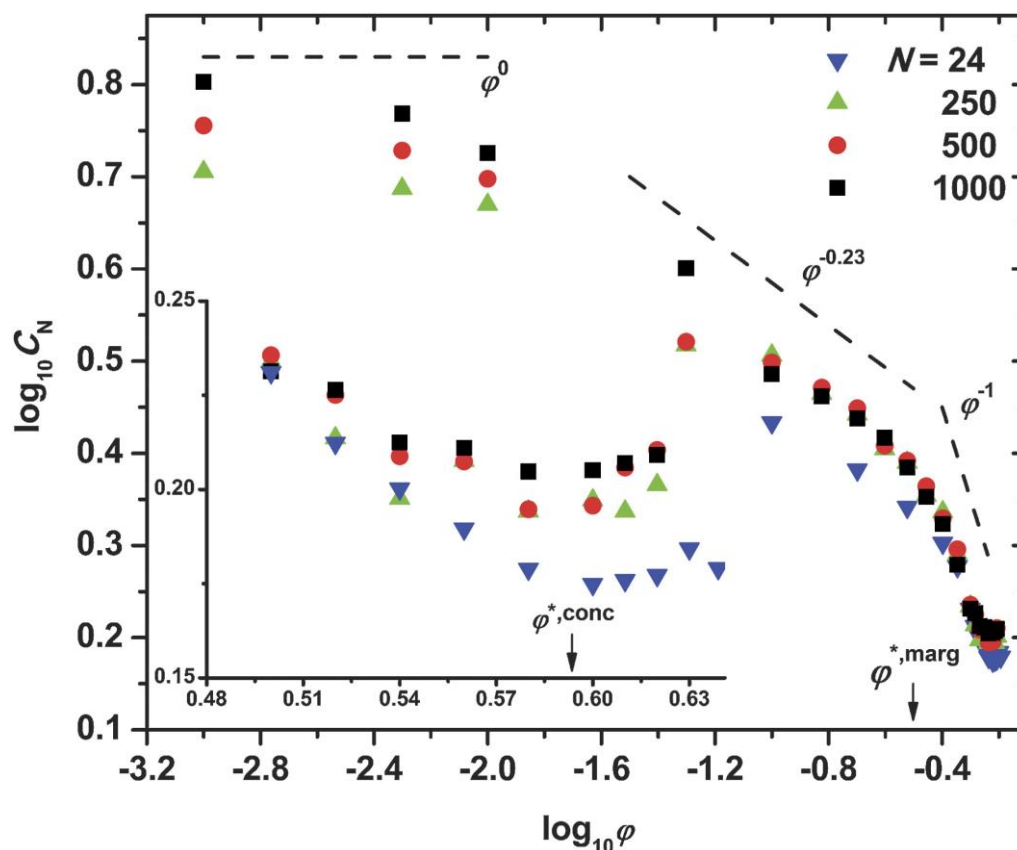


Figure 2.2: Double logarithmic plot of the characteristic ratio, C_N , as a function of packing density, φ . Lines with characteristic slopes are drawn as a guide to the eye. Inset: logarithm of characteristic ratio *versus* (linear) packing density in the marginal and concentrated regimes: $\varphi^{*,\text{marg}}$ and $\varphi^{*,\text{conc}}$ mark the predicted [34] crossovers for the transitions from semi-dilute to marginal, and from marginal to concentrated regimes, respectively.

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In parallel to the scaling behaviour, the structure of freely-jointed, hard-sphere chains due to the connectivity (chain conformation) also presents a strong dependence on packing density, especially near the MRJ state [15]. As a cause for the decrease in the chain size described by the scaling regimes [16, 33], chains collapse adopting more compact (coiled) conformations to efficiently pack at higher packing densities. The collapse continues until the most compact chain conformations are reached in the MRJ state. Thus, the arrangement of hard spheres in locally compact (tetrahedral) structures gives rise to prominent peaks in the local structure, as reflected by the bending and torsion angle distributions of Ref. [15].

Therefore, motivated by the past results on fully flexible chains, the present thesis studies the effect primarily of packing density and secondarily of chain length on the local and global structure of semi-flexible chains of tangent hard spheres in two and three dimensions. For that objective, semi-flexible polymer systems of various equilibrium angles are first generated and then equilibrated in the entire volume fraction, following the four different scaling regimes, and the corresponding behaviour is compared against the one of freely-jointed (fully flexible), hard-sphere chains from Ref. [15].

2.3 Crystallisation of Polymers

Crystallisation is another important research field of interest, strongly related to the packing of atoms and particles, to understand the connection between local (microscopic) structures and macroscopic properties of end materials. In materials science and physics, crystallisation corresponds to the formation of periodic ordered structures, minimising the free energy of the system. Thus, crystallisation is an important physicochemical process in various industrial processes and applications [84, 85]. Although many aspects of the phase behaviour and self-organisation of complex systems remain unknown or poorly understood, specifically when macromolecular systems are tackled, advances in theoretical, experimental, and simulation methods continually enrich our understanding of the phenomenon [149-153].

The nature of crystallisation is governed by both kinetic and thermodynamic factors. During the crystallisation, monomers or molecules are geometrically arranged in periodic, highly ordered structures, denominated crystals. The process generally consists of two steps: crystal nucleation and growth. Crystal nucleation corresponds to the formation of crystal seeds or nuclei when dispersed atoms or molecules gather to form isolated, ordered clusters. Then, the crystal nuclei grow through the addition of new atoms or molecules until they reach a critical size. Crystal growth is thermodynamically driven by the fact that the inner atoms are more stable than the surface atoms, following the Ostwald ripening. This mechanism of crystallisation is initiated by the effect of thermodynamic forces that drive the ordering.

As mentioned above, crystallisation is driven by the minimisation of the free energy of the system, i.e. the combined influence of enthalpy and entropy. Thus, a crystal is formed if the change in free energy is negative. According to the Gibbs equation, for thermal systems, crystallisation is initiated when the minimum energy state of the crystal, owing to internal and/or external forces, can compensate for the loss of entropy from the transition from the amorphous to the ordered states. For a system of constant enthalpy, an increase in the entropy of the system can also initiate crystallisation. In the case of polymers, the entropy is practically considered as the sum of translational entropy, related to the movement of monomers in their

accessible volume, and configurational entropy, related to the number of possible chain conformations.

In a similar way to the study of random packing, the hard-sphere model is frequently used to study crystallisation because of its simplicity and athermal nature. Early and pioneering works have reported the entropy-driven crystallisation of hard spheres through Molecular Dynamics simulations [54, 154] once the melting point is reached and given a sufficiently long observation time [155, 156]. The freezing ($\phi_{monomers}^F \approx 0.495$) and melting ($\phi_{monomers}^M \approx 0.545$) packing densities for systems of monoatomic hard spheres were determined by Hoover through Monte Carlo simulations [157]. Although the expected crystal for monoatomic hard spheres should be the face-centred cubic (FCC), as it is thermodynamically slightly more stable than the hexagonal close-packed (HCP) one [158-160], extensive experimental [161-166] and simulation studies [155, 167-171] studies have clearly shown the difficulty of obtaining a perfect FCC crystal. Instead, random hexagonal close packing (rHCP) is almost always observed because of the small free energy of stacking faults [172]. Even for monoatomic hard-sphere systems and starting from a predominantly amorphous initial configuration, crystal perfection in the form of a defect-free pure FCC crystal is rarely encountered in constant-volume computer simulations [23, 173, 174], as the system becomes trapped in the rHCP morphology, with the transition to the stable FCC structure being too slow to be observed [174-177].

For macromolecular systems, the complexity of the mechanism of crystallisation increases because of the extra restrictions related to the connectivity of the chains and the sluggish motion of the entangled polymers. It is necessary to further take into account that the crystallisation mechanism of hard colloidal polymers [19-23, 29, 30, 178, 179] differs substantially from that of traditional polymers, as revealed in x-scattering studies [180-182] and molecular simulations [179, 183-187], including simulations with realistic, all-atom interaction potentials [188-197].

Just as for monomeric packings, off-lattice MC simulations have shown that random packings of freely-jointed chains of tangent hard spheres are able to crystallise once a critical volume fraction is reached [19-21, 23, 29]. This crystallisation follows an entropy-driven mechanism, very similar to that of the monomeric analogues, due to an increase in the translational entropy of the system that compensates for the loss of conformational entropy. In short MC simulations, crystallisation primarily gives rise to an rHCP phase, which is composed of layers of FCC and HCP character with a unique stacking direction and which is free of fivefold defects [19-21]. Extending such simulations to very long observation times (measured in number of MC steps), the rHCP polymorph transits to an almost perfect FCC crystal. This is further supported by thermodynamic arguments which show that the FCC crystal is the most stable polymorph in the case of fully flexible chains of tangent hard spheres [23, 24].

In spite of the similarities to their monomeric counterparts, athermal polymer crystallisation exhibits unique characteristics due to the effect of chain connectivity. First, the critical volume fraction for the phase transition (melting point) for the freely-jointed chains of tangent hard spheres ($\phi_{chains}^M > 0.56$) is higher than the value for individual hard spheres ($\phi_{monomers}^M \approx 0.545$). Second, while monomeric systems present diverse crystal morphologies ranging between single FCC or HCP structures and close-stacked packings with random directions where twin defects kinetically frustrate crystallisation [198, 199], both the FCC and rHCP crystals of tangent hard-sphere chains are usually free of twin defects due to a conformational entropic barrier [200]. These twin defects, regularly absent in the case of polymers, are associated with the formation of structures of fivefold (FIV) symmetry [198-200]. The phase transition and the ordered morphologies of hard-sphere chains are affected insignificantly by chain length but are sensitive to other factors, such as gaps in bond lengths [22, 201], the presence of surfaces/confinement [6, 29, 30, 202], and chain stiffness [5, 203-206]. Among these factors, the present doctoral thesis focuses on analysing the effect of chain stiffness, specifically the equilibrium bending angle, on the entropy-driven self-organisation and the resulting crystal morphologies.

2.4 Chain Stiffness and Semi-flexible Polymers

As has been mentioned in the Introduction, the main focus of this doctoral thesis is the study of the effect of chain stiffness on the chain conformations and the phase behaviour (crystallisation) in athermal packings of linear polymers.

The simplest, non-trivial polymer model is the freely-jointed (FJ) chain, whose bond lengths are fixed while bending and torsion angles can fluctuate freely. Thus, freely-jointed chains effectively represent a fully flexible model. Another frequently used chain model is the freely-rotating (FR) one, whose bond lengths and bending angles are fixed, while torsion angles are still allowed to fluctuate freely. This way, the freely-rotating model provides an inherent degree of rigidity to the polymer chains as the result of the inclusion of rigid bending angles.

Semi-flexible polymers show a certain degree of bending stiffness. Fluctuations in bending angles and, accordingly, in the rigidity of the polymers are due to the thermal motion of the constituent monomers. Thus, semi-flexible polymers fall practically between the FJ and the FR limits. One example of semi-flexible polymers is the double-chained DNA [207-209].

In molecular simulation, chain stiffness is generally represented via a bending potential [210-216], which controls the angle formed between two consecutive bonds, and/or a torsional potential, which controls the angle formed between three successive bonds [210]. A common bending potential model is the cosine angle (CA) potential [216], which favours the conformation of straight trimers, as seen in Equation (2.1) where constant (k_θ) controls the

fluctuations. This model allows for the representation of a common description of rigid and semi-flexible polymers: the worm-like chain (WLC) model, suggested by Kraftky and Porod [217]. WLC is an appropriate model to describe very stiff polymers (“hard rods”), whose flexibility is due to fluctuations in the chain contour length ($R_{max} = (N - 1)l$), deviating from a straight line rather than from trans-gauche bond rotations.

$$U_{bend}(\theta) = k_{\theta}(1 - \cos \theta) \quad (2.1)$$

Semi-flexible polymers have been studied through Molecular Dynamics [204, 218-222] and Monte Carlo simulations, in lattice [211-213, 223-225] and off-lattice [215] realisations. Lattice simulations place atoms in specific positions in the simulation cell, which consists of discrete points, usually corresponding to the sites of a specific crystal. The most common is the simple cubic lattice model (SCLM), where the bond length is equal to the lattice spacing and the bending angle, by respecting the topology of the lattice, can adopt two values: 0 or $\pi/2$. Other lattice models are the Larson-type bond fluctuation model (L-BFM) and the bond fluctuation model (BFM), which allows for a larger selection of discrete bending angles [223]. These lattice models have been frequently used to study the worm-like chain model and the characterisation of the persistence length through the chain stiffness [213, 214, 223, 224].

The effect of chain stiffness on the local and global structure of athermal polymer packings has not been studied extensively in the literature, albeit the direct connection to hard colloidal experimental realisations. This is because advanced modelling techniques are required to generate and subsequently equilibrate dense or nearly jammed polymer packings, especially once chain stiffness is introduced. Recent MD simulations by Hoy *et al.* have studied the jamming and solidification of semi-flexible polymers employing the freely-rotating model, varying the fixed bending angle [218-220]. Through those simulations, they studied the mechanisms of solidification as a function of the equilibrium bending angle and the chain length. Thus, it was determined that the packing density at jamming for FR chains is directly proportional to the bending angle, being minimal for rod-like (strictly straight) chains, and inversely proportional to the chain length [218]. During the solidification process, freely-rotating polymers [220] and semi-flexible trimers [219] show two discrete transitions in all systems: first, an entanglement transition; and second, a jamming transition, which is produced at a packing density higher than the entanglement one.

A general topic of study about the phase behaviour of semi-flexible polymers is the orientational (nematic) ordering of the chains. As stated theoretically in the seminal work by Onsager, thin, infinitely long rigid rods undergo a transition from the isotropic to the nematic phase. This transition is driven by entropy as a result of the competition between translational and orientational ordering [226]. Tracing the factors that influence the Onsager transition, Bolhuis and Frenkel mapped out the complete orientational phase diagram of hard

spherocylinders as a function of shape anisotropy [227]. Similarly, Khokhlov and Semenov established that the long-range, nematic order in solutions of semi-flexible polymers also depends on the size ratio of the chain [228-230]. For the rod limit, the isotropic-to-nematic transition occurs at high concentrations but still occurs at lower concentrations compared to the solidification of the system [231, 232]. Therefore, diverse theories have been developed [233-236] and studies have been conducted [237-242] under various conditions on the isotropic-to-nematic transition of semi-flexible chains, such as the effect on the nematic order and the phase separation of different types of mixtures employing experimental studies [243-245] and computer simulations [237, 246-249].

For the case of systems in two dimensions, the orientational ordering presents a more complex behaviour due to the reduction of dimensionality. This leads to anisotropic hard bodies presenting, under specific conditions, a stable or unstable long-range orientational order while higher-order symmetries can also prevail in the form of tetratic, sexatic, or octactic phases [250-255]. The singular long-range phase behaviour in two dimensions has been theoretically predicted and further explored by simulations and experiments. Thus, these works have further gauged systematically the effect of aspect ratio and local geometry of the particles and of coverage and curvature of the surface [135, 256-266]. Different hard-body realisations, such as zig-zag [267], rod [255, 257], general-shape [251, 268, 269] objects, bend-core trimers [270], and semi-flexible polymers [271], have also been studied. Concerning rod-like systems, Bates and Frenkel demonstrated that the establishment of the nematic phase for spherocylinders confined to a plane depends on the aspect ratio L/D [257], where L is the length and D the diameter (the limit of $D \rightarrow 0$ corresponding to needles [256]). Thus, rods shorter than a threshold show an isotropic phase where chains are aligned either side-by-side or perpendicular to each other [257]. Moreover, the rod length dispersity, analysed through infinitely thin rods (needles), significantly affects the phase behaviour of the system, with long and short rods stabilising and weakening, respectively, the nematic phase [256].

In addition, crystallisation and glass formation of semi-flexible polymers has been another topic of interest for study. Building on this, Bulacu and van der Giessen determined the glass transition temperature (T_g) in amorphous polymers for different types of chain stiffness (bending and torsion potential) [210]. Nguyen *et al.* studied the effect of chain stiffness and temperature on the competition between crystallisation and glass formation for unentangled semi-flexible polymer melts [203, 204]. In the same year, Zierenberg *et al.* provided an overview of the collapse and aggregation transitions of self- and mutually attractive dilute semi-flexible polymers [215]. Other recent works are the studies by Shakirov and Paul on the crystallisation in melts of short, semi-flexible hard-sphere chains employing Monte Carlo simulations [205, 206]. In their works they established that rod-like polymer melts undergo a first-order crystal transition at a density lower than a melt of monoatomic hard spheres or fully

flexible hard-sphere chains [205]. During crystallisation, the orientational ordering (nematic) transition is accompanied by a 2D translational ordering on the plane perpendicular to the chains. Thus, these orderings induce the formation of hexagonal crystal planes [272]. Furthermore, to obtain a fundamental understanding of glass formation and crystallisation, the influence of chain stiffness has been studied on some theories, such as the classical nucleation theory (CNT) or the generalised entropy theory (GET) [273, 274].

A better understanding of the phase behaviour, both at the local (crystallisation and glass formation) and global (orientational ordering) levels, and the spectrum of variables that have an influence on it will be imperative to eventually establish a connection between the microscopic behaviour and the macroscopic properties of end materials. We should note that the design of crystals made of soft or hard colloidal polymers and molecules [275, 276] is currently an imposing challenge. Still, computer simulation can be used to provide aid in such efforts by exploring exhaustively the effect of chain stiffness, molecular architecture and other parameters [275, 277-279] on the establishment of specific structures. This computer-aided, fine-tuning of structural behaviour [205, 220, 280-282] can be considered as another step to develop novel materials with enhanced characteristics and effectively guide the corresponding synthesis and characterisation through equally advanced experimental techniques[62, 277-279, 283-285].

Chapter 3: METHODOLOGY

The main theoretical and technical aspects of the methodology of this doctoral thesis are addressed in this chapter. Numerous systems of linear chains of tangent hard spheres are equilibrated and analysed through molecular simulations. Hence, the core of the methodology is the simulation software. The *Simu-D* simulator-descriptor suite [2] is, as its name suggests, composed of two distinct parts: the simulator and the descriptor. The first (simulator) carries out the Monte Carlo (MC) simulations of general systems based on polymers and is applied here to semi-flexible chains. *Simu-D*, developed by the Laboratory of Simulation of Materials (LSM), is based on advanced Monte Carlo algorithms (moves) to equilibrate polymer-based systems under a wide range of conditions, including extreme ones. Furthermore, the descriptor part of *Simu-D* allows the identification of the local structure of atomistic systems employing the Characteristic Crystallographic Element (CCE) norm [3, 4].

The results of this research have been obtained through a methodology that consists of three major sequential steps. This methodology is based on the basic principles of computer-assisted research, as described in detail in the reference book by Allen and Tildesley [65].

- 1) **Creation of Initial Configurations:** The simulation cell is created according to the characteristics required for the system: periodic boundary conditions, confinement, nanofillers, system composition, number of dimensions, chain length, relative concentrations, presence of interfaces/surfaces, etc. Then, monomers and polymer chains are randomly inserted inside the simulation cell at dilute conditions, following the characteristics and restrictions of the system, such as chain lengths, chain connectivity, and chain stiffness. Later, employing a shrinking algorithm of *Simu-D*, simulation cells are compressed at regular intervals to produce progressively denser initial configurations until the desired volume fraction is reached. For the case of 2D systems, an initial dilute 3D configuration is confined in one dimension, and through tuning of the interactions between the confining agent and the monomers in the system, a monolayer is formed through an adsorption procedure. These 2D systems are further compressed into denser systems until a specific surface coverage is reached or until no further compression is possible. Initial configurations are not required to

represent an equilibrated state as, if the sampling methodology is robust, the final state of equilibrium should not depend on the choice of the initial configuration.

- 2) **Equilibration Simulations:** Once the desired initial configuration is created at the corresponding packing density, simulations are performed under isochoric (*NVT*) or isobaric-isothermal (*NPT*) conditions of the order of hundreds of billions of iterations (or MC steps). Every move (step or iteration) corresponds to an attempt to execute a specific Monte Carlo move. The system is led, within fluctuations, towards the equilibrium state or state of minimum energy, in terms of statistical physics [1], generating a collection of uncorrelated microstates or system configurations. This sequence of transitions should respect microscopic reversibility (the reverse transition should always be possible) and ergodicity (all possible microstates corresponding to the ensemble should be accessible) [65]. System configurations are periodically recorded (called “frames”), storing information about atomic coordinates, chain connectivity, thermodynamic properties, and statistics.
- 3) **Post-processing:** Huge data files, called simulation trajectories, are produced that contain every frame recorded during the simulation. Raw binary data are processed to extract physical parameters as ensemble averages in this step, which is as important as the simulation itself. Moreover, advanced analysis of the trajectories can provide information about the local structure and phase behaviour of the system with the CCE norm descriptor or the global order with the orientational, Long-Range Order (LRO) parameter, among other analyses.

Every simulation directed to study phase behaviour at very high concentrations requires a very long execution time and large processing capacities, so they cannot be performed on personal computers. Consequently, all simulations are carried out on single cores of high-performance workstations owned and operated by the LSM, and on the High-Performance Computing (HPC) cluster of the UPM called “Magerit3”, operated by the Centro de Supercomputación y Visualización de Madrid (CeSViMa).

When considering the complexity of the approach, the very wide range of distinct systems to be simulated, and the frequently enormous times required to observe the crystallisation of athermal polymers, an important aspect is the automatization of the process. The high frequency of task repetition and the creation and management of large amounts of files make it difficult to perform these tasks manually. Thus, the usage of scripting was implemented here to create automatic processes in the different steps of the methodology, for example, simulation initialisation, simulation execution, file transfer, post-simulation analysis, and data storage and representation, including visualisation.

In the following sections of this chapter, basic theoretical concepts of statistical physics and the Monte Carlo method are explained first. Then, the molecular model and the simulation

cell used for the *Simu-D* suite are presented, together with the systems to be studied. An explanation of the Monte Carlo algorithms used by *Simu-D* is also included. Finally, the advanced post-simulation analyses used for this research, the Characteristic Crystallographic Element (CCE) norm and the global orientational, Long-Range Order (LRO), are described in detail.

3.1 Theoretical Framework

Simulation is a scientific tool for predicting and studying the evolution and behaviour of physical systems through mathematical models. Mathematical models define the laws of nature in a series of equations to represent real-world and physical phenomena, processes, and general systems. The mathematical model is subsequently solved, generally by computer simulations, to produce an output as close as possible to the reality captured by the model. However, the complexity of the physical system under study can make the model evolve slowly or be too difficult to represent by equations. For this reason, assumptions and approximations are required in order to produce a faster and simpler output. Thus, a trade-off between desired accuracy and model complexity is considered to arrive at such approximations. The results of the simulations should then be compared with the experimental results to validate the accuracy and robustness of the model and the simulation method.

For the study of systems and phenomena at the atomic and molecular level, these are composed of an enormous number of atoms and corresponding degrees of freedom; so, they are dealing with many-body problems. Molecular simulation is the tool to solve and analyse these problems, which are not amenable to analytical solutions. The heart of molecular simulation is statistical physics, which is a scientific field in physics that deals with the treatment of many-body systems. Thus, thanks to statistical physics, it is possible to analyse the self- or directed-organisation and behaviour of monomers and chains and, eventually, to link the microscopic description, obtained by molecular simulation, to the macroscopic properties of the end material.

In the present doctoral thesis, the Monte Carlo method is employed to simulate semi-flexible systems. Monte Carlo is a stochastic methodology that allows one to generate and successively equilibrate polymer-based systems by employing a set of properly selected “moves” that rapidly explore the phase space. However, the main drawback of the MC method is that it does not offer dynamic information about the system due to its stochastic nature, especially when highly unphysical moves are included.

3.1.1 Statistical Physics

Statistical Physics is a scientific field that applies mathematical probability methods and statistics to treat many-body physical problems. Therefore, statistical physics is at the heart of molecular simulation, which requires handling systems of many-body elements at the level of atoms or particles. For this reason, it is possible to determine the macroscopic properties of a system through the information at the microscopic level obtained by molecular simulation [65].

Unlike Classical Thermodynamics, which defines macroscopic systems and their laws through macroscopic quantities (volume V , temperature T , pressure P , etc.), Statistical Physics employs a microscopic definition (atomic constitution and microscopic properties) to derive the macroscopic properties and laws. Gibbs established in 1902 the premise behind statistical physics, which asserts that the macroscopic observables can be calculated as the statistical average over microscopic properties.

The state of a macroscopic system defined by a small set of macroscopic parameters is the macrostate. Using the equations of state and the fundamental equations of thermodynamics, other macroscopic properties can be derived from the macrostate and a small set of macroscopic constraints. On the other hand, the microstate is the state of the system microscopically defined, and all microstates follow constraints imposed by macroscopic variables that define the system. The microstate of a specific system is described by the coordinates, $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}, \mathbf{r}_N)$, and momenta, $\mathbf{p} = (\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_{N-1}, \mathbf{p}_N)$, of their constituent atoms through the Hamiltonian, $\mathcal{H}(\mathbf{r}, \mathbf{p})$, which contains the potentials of position (dynamic energy, $\mathcal{V}(\mathbf{r})$) and motion (kinetic energy, $\mathcal{K}(\mathbf{p})$).

$$\mathcal{H}(\mathbf{r}, \mathbf{p}) = \mathcal{K}(\mathbf{p}) + \mathcal{V}(\mathbf{r}) \quad (3.1)$$

The set of positions and momenta that can be thought of as coordinates in a multidimensional space is called phase space. Besides, the set of all different points in phase space, all subjected to the same specific macroscopic constraints, corresponds to the statistical ensemble. Thus, a statistical ensemble is a large discrete number of microstates (system configurations) that have the same macroscopic constraints (see Figure 3.1). According to the premise of Gibbs, a macrostate can be defined as the average over a statistical ensemble.

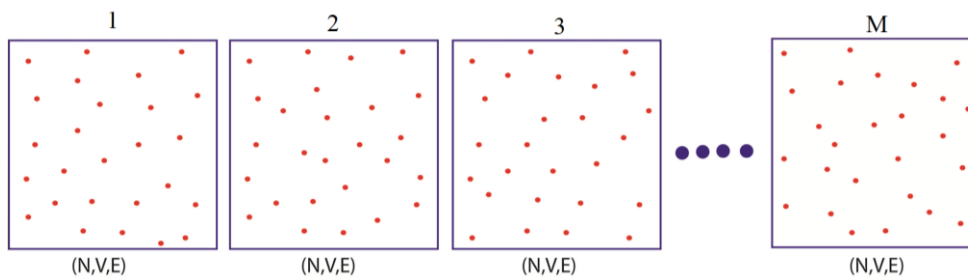


Figure 3.1: Statistical ensemble. M different microstates are subjected to the same macroscopic constraints (number of atoms N , volume V , and energy E).

Through statistical physics, we can obtain the value of a macroscopic variable as the average of its values in the microstates. For an N -atoms system, the phase space has $6N$ dimensions. In the following, we consider Γ a particular point in the phase space and $\mathcal{A}$ the instantaneous value of some property. Then, $\mathcal{A}$ is a function of the phase space: $\mathcal{A}(\Gamma)$. If the system evolves over time, t , the particular point in the phase space, $\Gamma(t)$, changes and so does $\mathcal{A}(\Gamma(t))$. Hence, the experimentally observable macroscopic property $\mathcal{A}_{\text{obs}}$ can be calculated as the time average during a long-time interval of $\mathcal{A}(\Gamma)$.

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{time}} = \langle \mathcal{A}(\Gamma(t)) \rangle_{\text{time}} = \lim_{t_{\text{obs}} \rightarrow \infty} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} \mathcal{A}(\Gamma(t)) dt \quad (3.2)$$

Newton's equation of motion in a simple classical system governs the time evolution of the system in phase space. In Molecular Dynamics, this system of ordinary differential equations can be solved by integrating over sufficiently long but practically finite time t_{obs} using a step-by-step discretization method, where a finite but large succession of steps τ_{obs} of length dt replaces the integral by converting it to summation over the number of time steps:

$$dt = \frac{t_{\text{obs}}}{\tau_{\text{obs}}} \quad \mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{time}} = \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} \mathcal{A}(\Gamma(\tau)) \quad (3.3)$$

On the other hand, the time average can be substituted by the ensemble average, the approach pioneered by Gibbs. If the ensemble represents all possible points in the phase space, the system is ergodic. The points in phase space are distributed according to a probability density $\rho_{\text{ens}}(\Gamma)$, which is a function of the macroscopic constraints. In Equation (3.4), the probability density of the phase space $\rho_{\text{ens}}(\Gamma)$ is defined, where w_{ens} is the weight function of the phase space (a non-normalised form of the probability density) and Z_{ens} is the partition function of the ensemble, which is the summation over the ensemble. In an ensemble, each point represents the system at any particular instant of time, and, if each system evolves in time independently according to the equations of motion, the probability density of the phase space $\rho_{\text{ens}}(\Gamma)$ changes with time. So, for an ergodic system, the average time of the evolution of a system can be replaced by the average of all microstates of an ensemble in a particular instant of time, where each microstate can be thought of as a different instant of the time evolution of a system. Applying the approach of Gibbs, the macroscopic observable property $\mathcal{A}_{\text{obs}}$ can be determined through ensembles according to Equation (3.5).

$$\rho_{\text{ens}} = \frac{w_{\text{ens}}(\Gamma)}{Z_{\text{ens}}} = \frac{w_{\text{ens}}(\Gamma)}{\sum_{\Gamma} w_{\text{ens}}(\Gamma)} \quad (3.4)$$

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{time}} = \langle \mathcal{A} \rangle_{\text{ens}} = \sum_{\Gamma} \mathcal{A}(\Gamma) \rho_{\text{ens}}(\Gamma) \quad (3.5)$$

As was mentioned, the statistical ensembles are imposed by macroscopic constraints. The main constraints used by the most common ensembles are the number of interacting sites (atoms or particles) (N_{at}), volume (V), pressure (P), energy (E), temperature (T), and chemical potential (μ). The probability density of the ensemble $\rho_{\text{ens}}(\mathbf{\Gamma})$ is a function of the fixed macroscopic constraints that fully define the ensemble. The most common statistical ensembles, their constant constraints and the relationship between the constraints and the probability density $\rho_{\text{ens}}(\mathbf{\Gamma})$ are the following ones, where k_B is the Boltzmann constant:

- Microcanonical ensemble (NVE) $\rho_{NVE}(\mathbf{\Gamma}) \sim \delta(\mathcal{H}(\mathbf{\Gamma}) - E)$
- Canonical (NVT) $\rho_{NVT}(\mathbf{\Gamma}) \sim \exp\left(-\frac{\mathcal{H}(\mathbf{\Gamma})}{k_B T}\right)$
- Isobaric-isothermal (NPT) $\rho_{NPT}(\mathbf{\Gamma}) \sim \exp\left(-\frac{(\mathcal{H}(\mathbf{\Gamma}) + PV)}{k_B T}\right)$
- Grand Canonical (μVT) $\rho_{\mu VT}(\mathbf{\Gamma}) \sim \exp\left(-\frac{(\mathcal{H}(\mathbf{\Gamma}) - \mu N)}{k_B T}\right)$

Finally, an important concept is the state of equilibrium, which is the state towards which an isolated system tends to evolve if left alone. In that state, the gradients and differences in the macroscopic properties of the system are eliminated. The time to reach the state of equilibrium is called the relaxation time and depends on the corresponding process. The state of equilibrium is fully defined by a few macroscopic variables which are independent of time. These variables are called state functions and can determine all the macroscopic properties of the system. Furthermore, if an ensemble is in equilibrium, the time-dependence of the probability density of the phase space $\rho_{\text{ens}}(\mathbf{\Gamma})$ is eliminated, so that $\frac{\partial \rho_{\text{ens}}}{\partial t} = 0$. Related to the state of equilibrium, two postulates of statistical physics are exhibited [286]:

- 1) The probabilities of microstates that correspond to the same macrostate are equal.
- 2) Equilibrium is the state of maximum probability; it corresponds to the maximum statistical weight.

Thus, the most probable values correspond to the equilibrium, and so the macroscopic observable property would be accurately obtained as the average over the microstates at equilibrium. For that reason, Monte Carlo, whose stochastic approach can accelerate the process to reach equilibrium, is the simulation method employed in this doctoral thesis instead of Molecular Dynamics, which may require a large number of steps τ_{obs} to efficiently explore the phase space. Especially, for example, when the focus of the simulations is on rare or slow events, such as the relaxation of entangled polymer melts or the crystallisation of athermal chain systems at very high concentrations.

3.1.2 Monte Carlo

The Monte Carlo (MC) method was proposed by Metropolis, Ulam, and collaborators in 1953 [1] as a methodology of molecular simulation to study the diffusion of neutrons in

fissionable material. Monte Carlo is a stochastic method that relies heavily on the generation of random numbers (for that reason, it receives its name from the casinos in Monte Carlo) to calculate a trajectory of points in the phase space Γ (microstates) according to a statistical ensemble and its ensemble probability density, $\rho_{\text{ens}}(\Gamma)$. Since Monte Carlo does not require the solution of the equations of motion and thus is not related to time, the momenta of the atoms are not taken into account and the points of the phase space (Γ) can be reduced to the position of the atoms ($\mathbf{r}$).

Monte Carlo can be used as a numerical method of multidimensional integration: The sample mean integration is, for example, based on the mean value theorem. It consists of integrating over a random sampling of points instead of over a regular array of points. So, an arbitrary probability function, $\rho(x)$, is selected to rewrite the integral of a function $f(x)$ as Equation (3.6). Then, a number of trials, N_{trials} , are performed choosing a random number ζ from the probability distribution in the interval (x_1, x_2) . Thus, the integral F of a function $f(x)$ can be calculated as the average over all trials.

$$F = \int_{x_1}^{x_2} f(x) dx = \int_{x_1}^{x_2} \left(\frac{f(x)}{\rho(x)} \right) \rho(x) dx \quad (3.6)$$

$$F = \left\langle \frac{f(x)}{\rho(x)} \right\rangle_{N_{\text{trials}}} \approx \sum_{i=1}^{N_{\text{trials}}} \frac{f(\zeta_i)}{\rho(\zeta_i)} \quad (3.7)$$

If the mean value theorem is applied to the uniform probability function of Equation (3.8), the integral F can be estimated according to Equation (3.9).

$$\rho(x) = \frac{1}{x_2 - x_1} \quad x_1 \leq x \leq x_2 \quad (3.8)$$

$$F = \int_{x_1}^{x_2} f(x) dx \cong \frac{x_2 - x_1}{N_{\text{trials}}} \sum_{i=1}^{N_{\text{trials}}} f(\zeta_i) \quad (3.9)$$

The mean value theorem can be employed to calculate macroscopic properties according to statistical physics. If the expression of Equation (3.9) is applied to the approach of Gibbs of Equation (3.5), macroscopic observable properties are obtained as an ensemble average according to the following expression.

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{ens}} = \frac{\int \mathcal{A}(\mathbf{r}) \rho_{\text{ens}}(\mathbf{r}) d\mathbf{r}}{\int \rho_{\text{ens}}(\mathbf{r}) d\mathbf{r}} = \frac{\sum_{i=1}^{N_{\text{trials}}} \mathcal{A}(i) \rho_{\text{ens}}(i)}{\sum_{i=1}^{N_{\text{trials}}} \rho_{\text{ens}}(i)} \quad (3.10)$$

However, the use of a uniform probability density becomes impractical for systems of large dimensionality, such as molecular systems, because the contribution of the number of

trials to the ensemble average will be very limited. To solve this problem, importance sampling is applied. This scheme chooses random numbers from a non-uniform distribution $\rho(x)$ which allows concentrating the sampling of microstates to regions of phase space that make important contributions to the integral. Considering the second postulate of statistical physics, these regions correspond to microstates close to and at equilibrium.

Towards this, the Markov Chain algorithm [65] generates a sequence of random states towards the equilibrium, so that at the end of the Monte Carlo simulation each microstate has occurred with the appropriate probability. This scheme produces a stochastic sequence of trials that satisfies two conditions:

- 1) The outcome of each trial belongs to a finite set of outcomes.
- 2) The outcome of each trial depends only on the outcome that immediately precedes it.

The probability of moving from one state Γ_m to another state Γ_n is the transition probability P_{mn} . Because Markov Chain possesses a very short-lived memory (one step back) due to the second condition, the transition probability P_{mn} depends only on the aforementioned two states (“old” m and “new” n). The transition probabilities between all possible states Γ_m and Γ_n are collected in the transition matrix. Due to short memory, the probability distribution $\rho(x)$ only depends on the transition matrix. Consequently, the equilibrium of the system and its corresponding thermodynamic properties are independent of the initial conditions.

For molecular systems, the transition matrix should be ergodic and stochastic. Although the elements of the matrix are unknown, the probability distribution is $\rho_m = \rho_{\text{ens}}(\Gamma_m)$ for each point in the phase space. Metropolis proposed a transition probability $P_{mn} = \min(1, \rho_n/\rho_m)$ for $m \neq n$ [65].

For the canonical ensemble (NVT) and only with respect to position $\mathbf{r}$, the probability density ρ_{NVT} follows the expression of Equation (3.12), where the partition function Z_{NVT} is :

$$Z_{NVT} = \sum_{\mathbf{r}} \exp\left(-\frac{\mathcal{V}(\mathbf{r})}{k_B T}\right) \quad (3.11)$$

$$\rho_{NVT}(\mathbf{r}) = \frac{\exp\left(-\frac{\mathcal{V}(\mathbf{r})}{k_B T}\right)}{\sum_{\mathbf{r}} \exp\left(-\frac{\mathcal{V}(\mathbf{r})}{k_B T}\right)} = \frac{\exp(-\beta \mathcal{V}(\mathbf{r}))}{Z_{NVT}} \quad \beta = \frac{1}{k_B T} \quad (3.12)$$

$$\frac{\rho_n}{\rho_m} = \frac{\frac{\exp(-\beta \mathcal{V}_n)}{Z_{NVT}}}{\frac{\exp(-\beta \mathcal{V}_m)}{Z_{NVT}}} = \frac{\exp(-\beta \mathcal{V}_n)}{\exp(-\beta \mathcal{V}_m)} = \exp[-\beta(\mathcal{V}_n - \mathcal{V}_m)] = \exp(-\beta \Delta \mathcal{V}_{nm}) \quad (3.13)$$

Finally, the transition probability for a canonical ensemble between microstates m and n is calculated according to the Metropolis criterion as in Equation (3.14) and depends only on the energy difference of both microstates, $\Delta\mathcal{V}_{nm}$.

$$P_{mn} = \min(1, \exp(-\beta\Delta\mathcal{V}_{nm})) \quad (3.14)$$

During the Monte Carlo simulation, moves that attempt transitions between microstates are performed. According to the transition probability P_{mn} for the canonical ensemble, these moves (transitions) are accepted or rejected following the two possible cases:

- $\mathcal{V}_n \leq \mathcal{V}_m \Rightarrow \Delta\mathcal{V}_{nm} \leq 0$: “Downhill transition”. The energy of the system decreases and the transition $m \rightarrow n$ is always accepted.
- $\mathcal{V}_n > \mathcal{V}_m \Rightarrow \Delta\mathcal{V}_{nm} > 0$: “Uphill transition”. The energy of the system increases and the transition $m \rightarrow n$ is accepted if $P_{mn} > \zeta$, where ζ is a random number in the interval $[0,1)$. In the contrary case, it is rejected.

If the transition $m \rightarrow n$ is rejected, then the system remains in the microstate m and it is counted again in the calculation of average values.

For the isobaric-isothermal ensemble (NPT), the Metropolis criterion is implemented similarly to the canonical ensemble (NVT) ensemble by generating a Markov chain with the probability distribution ρ_{NPT} of Equation (3.16), where N is the sum of all elements in the system, V is the volume, and P is the constant pressure of the system.

$$Z_{NPT} = \sum_{\mathbf{r}} \exp\left(-\frac{\mathcal{V}(\mathbf{r}) + PV}{k_B T} + N \ln V\right) \quad (3.15)$$

$$\rho_{NPT}(\mathbf{r}) = \frac{\exp\left(-\frac{\mathcal{V}(\mathbf{r}) + PV}{k_B T} + N \ln V\right)}{\sum_{\mathbf{r}} \exp\left(-\frac{\mathcal{V}(\mathbf{r}) + PV}{k_B T} + N \ln V\right)} = \frac{\exp(-\beta(\mathcal{V}(\mathbf{r}) + PV) + N \ln V)}{Z_{NPT}} \quad (3.16)$$

$$\frac{\rho_n}{\rho_m} = \frac{\frac{\exp(-\beta(\mathcal{V}_n + PV_n) + N \ln V_n)}{Z_{NPT}}}{\frac{\exp(-\beta(\mathcal{V}_m + PV_m) + N \ln V_m)}{Z_{NPT}}} = \exp\left(N \ln \frac{V_n}{V_m} - \beta\Delta\mathcal{V}_{nm} - \beta P(V_n - V_m)\right) \quad (3.17)$$

Therefore, the transition probability P_{mn} in the isobaric-isothermal ensemble is expressed as

$$P_{mn} = \min\left[1, \exp\left(N \ln \frac{V_n}{V_m} - \beta\Delta\mathcal{V}_{nm} - \beta P(V_n - V_m)\right)\right] \quad \beta = \frac{1}{k_B T} \quad (3.18)$$

where $\Delta\mathcal{V}_{nm}$ is the total energy difference in the transition $m \rightarrow n$, and V_n and V_m are the volumes of the system in the state n and m , respectively. Unlike the NVT ensemble, the NPT

ensemble depends not only on the energy difference of the system but also on the variation of the volume between both microstates. Following the Metropolis criterion, the transition will be accepted as in the canonical ensemble, by generating a random number ζ and comparing it against the transition probability P_{mn} .

Therefore, for the original and simplest implementation of the Metropolis Monte Carlo scheme for a system of individual atoms, a single atom is selected randomly and then a displacement of random amplitude is attempted. Energies are calculated for the initial and final states, and so the move is accepted or rejected according to the scheme presented above, whereas the possible new microstate should respect the restrictions imposed by the employed statistical ensemble. This displacement attempt continues to create very long Markov chains of MC events, sampling the microstates of the enforced statistical ensemble.

However, in the case of complex molecular systems like those of flexible or rigid macromolecules, the realisation of a trial move and the transition matrix should consider not only the restrictions of the statistical ensemble but also the geometric constraints due to, for example, the bonds between two successive atoms, and the bending angles among three successive atoms along the chain backbone. Furthermore, different moves should target different parts of the chain (ends, inner segments, etc.) so that the system evolution is ergodic.

3.2 Molecular model

The first step in performing a molecular simulation is to define a model. The interaction potential model controls all interactions between all elements conforming the molecular system to simulate, such as atoms, molecules, monomers, chains, nanofillers, or layers. These elements are placed inside a specific volume (in three dimensions) or on a surface (in two dimensions), which is called simulation cell. Thus, the simulation cell corresponds to the environment that hosts the elements of the molecular system. Special care should be taken to describe the conditions that occur at the boundaries of the simulation cell.

Simu-D software is designed to handle mainly atomistic polymer-based systems under an extensive variety of conditions. This section explains the types of interaction potential models (force field) and simulation cells that can be handled through *Simu-D*. In addition, the semi-flexible systems to be studied and their specific molecular model are presented at the end of the current section.

3.2.1 Interactions

The interaction potential model or force field governs all interactions between all elements of the molecular system, i.e. atoms, molecules, chains, particles, layers, walls, nanofillers, etc. Therefore, the potential model constitutes the basis for molecular simulation.

These interactions can be classified as bonded interactions and non-bonded ones. Bonded interactions are related to the bond geometry and connectivity of the chain (mainly bond length, bending angle, and torsion angle). Non-bonded interactions are pairwise interactions between monomers in different chains or in the same chain if they are separated by at least three bonds. The interactions are generally represented in atomistic simulations as corresponding terms of the total potential that describes all the interactions between elements.

Currently, *Simu-D* allows the simulation of the following elements: (1) individual monomers, atoms, or particles, (2) linear chains of monomers of varied stiffness and length, (3) nanofillers of different sizes, shapes, and concentrations, such as spheres of varied diameter or cylinders of infinite length and varied diameter, and (4) chains terminally anchored onto spherical nanoparticles. Atomistic systems are composed of N_{at} spherical monomers, which can be part of macromolecules or exist as individual entities. So, in the general case, a polydisperse system can be formed by N_{ch} chains of average length N_{av} (each chain i being characterised by its length N_i) and N_s individual monomers with $N_{ch} \times N_{av} + N_s = N_{at}$. In addition, the system can further include N_{part} spherical nanoparticles and N_{cyl} cylinders of infinite length, with the total number of entities present in the system being $N_{ent} = N_{at} + N_{part} + N_{cyl}$.

Bonded interactions are interactions corresponding to chemical bonds between covalent atoms. For polymer chains, they depend on the arrangement and connectivity of the monomers in the chain. The chain conformation is the way that the monomers are arranged and connected in space, and so it is dominated by the bond geometry and the non-bonded interactions. In *Simu-D*, all monomers are considered spheres of diameter (σ), which is also the characteristic length of the system, and polymers are modelled as linear sequences of monomers with variable chain stiffness. The bond geometry of a chain can be univocally constructed by defining the geometric variables shown in Figure 3.2. The terms that define the bond geometry are as follows:

- Bond length (l): Distance between two successive atoms (dimer) along the chain backbone.
- Bending angle (θ): Angle formed by two successive bond vectors defined by three successive atoms (trimer). For example, the bending angle for straight trimers is zero.
- Torsion angle (ϕ): Angle between two planes defined by a sequence of four atoms (quartet) along the chain backbone.

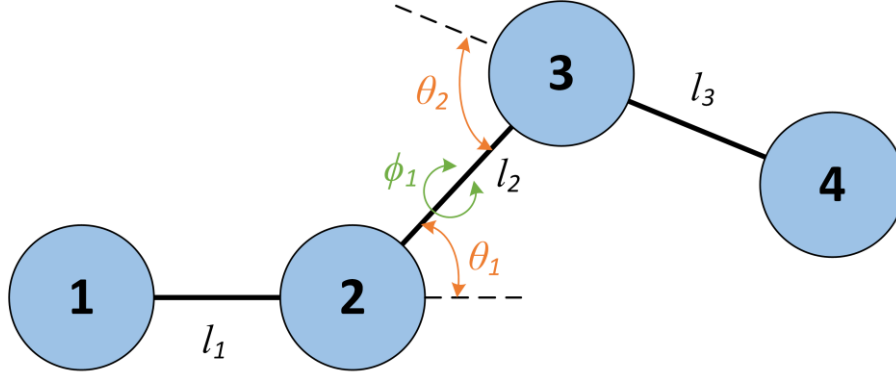


Figure 3.2: Scheme of the bond geometry of a linear sequence of four monomers. Bond lengths l (1-2 interactions), bending angles θ (1-3 interactions), and torsion angle ϕ (1-4 interaction) are represented.

Simu-D allows for a small degree of flexibility for bond lengths between consecutive monomers of a chain. Therefore, bond lengths can be longer (bond gaps), equal (bond tangency), or shorter (fused spheres) than the collision distance (σ). For bond gaps, the length of any bond (l) can vary depending on a tuneable bond tolerance/gap (dl) in the interval $l \in [l_{min}, l_{max}]$. If the allowed bond gap tends to zero ($dl \rightarrow 0$), subject to numerical precision, the bonded monomers are considered strictly tangent. For the modelling of bond lengths, currently, no energetic potential is considered, allowing them to fluctuate freely. However, implementation of the harmonic-type of potential for the bond lengths is rather straightforward given that the bond lengths are constantly calculated in the MC transitions and such a potential is already available for the more complicated bending angles. In the past, publications of the LSM have demonstrated that bond gaps or tangency have a profound effect on the ability of HS chains to crystallise [22].

$$l_{min} = \sigma \quad l_{max} = \sigma + dl \quad (3.19)$$

Chain stiffness is determined through a harmonic-spring potential that governs the bending angle (θ) according to:

$$U_{bend}(\theta) = k_{\theta}(\theta - \theta_0)^2 \quad (3.20)$$

where k_{θ} is the bending constant and θ_0 is the equilibrium bending angle, which can vary from fully extended ($\theta_0 = 0^\circ$) to fully compact ($\theta_0 = 120^\circ$) configurations of triplets in the case of non-overlapping hard spheres. The stiffness of the bending angle is determined by the bending constant k_{θ} . For fixed bond lengths, freely-jointed (FJ) chains are modelled by setting $k_{\theta} = 0$. In contrast, freely-rotating (FR) chains are modelled setting the opposite limiting case of $k_{\theta} \rightarrow \infty$. Figure 3.3 represents schematically i) the freely-jointed chain model, which corresponds to linear fully flexible chains with uniform bond lengths while bending and torsion angles can adopt all possible conformations with equal probability, and ii) the freely-rotating model, whose bond lengths and bending angles of linear chains are fixed to specific values while torsion angles are allowed to fluctuate freely.

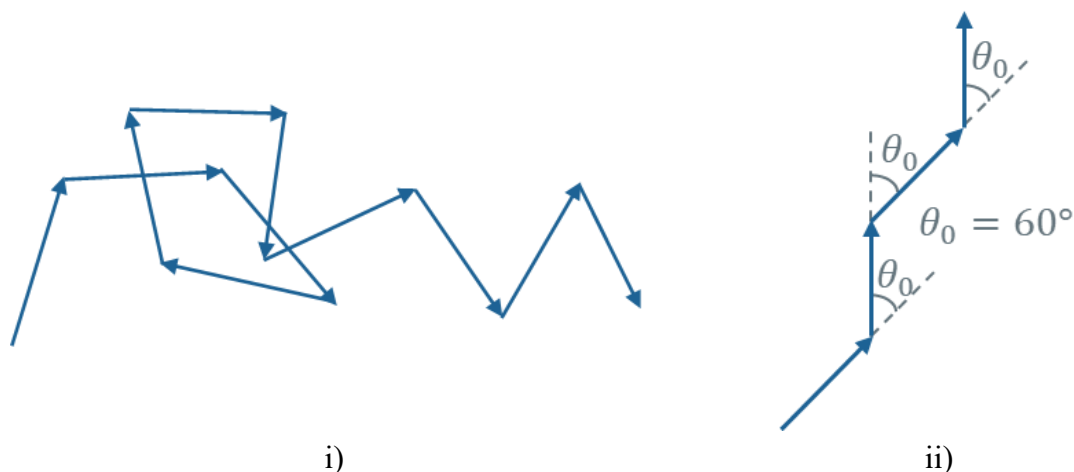


Figure 3.3: Schematic representations for ideal chain models: i) freely-jointed chain and ii) freely-rotating chain.

Currently, no potential exists for torsion angles (ϕ) in *Simu-D*, which are thus allowed to fluctuate freely. Consequently, chain stiffness is only governed by the bending potential. However, future updates of the *Simu-D* suite will implement an energetic potential controlling the torsion angle, $U_{tor}(\phi)$, to model polymers with inherent torsional hindrance and ideal chains corresponding to the Porod-Kratky, worm-like model.

Non-bonded interactions are pairwise atomic interactions that can have short or long ranges. For polymers, the non-bonded interactions correspond to the same (intramolecular) or different (intermolecular) chains. Short-range, non-bonded interactions have a repulsive part due to the Pauli principle of exclusion of electron orbitals and an attractive part which is produced by Van der Waals or London forces. Long-range interactions are due to electrostatic interactions (Coulombic forces) for charged molecules. There are different models for representing interatomic interactions, ranging from highly idealised models to very detailed ones.

The simplest pair-wise, non-bonded potential model is the Hard-Sphere (HS). This is a highly idealised model that considers neither long-range interactions nor short-range ones, being limited only to the concept of excluded volume. Thus, due to the lack of energy in the model, the corresponding systems are athermal, i.e. the temperature is not present. Such athermal systems are well suited to study entropy-driven phenomena, including crystallisation, melting, and self-organisation. The model is defined as:

$$U_{HS}(r_{ij}) = \begin{cases} \infty, & r_{ij} < \sigma \\ 0, & r_{ij} \geq \sigma \end{cases} \quad (3.21)$$

where r_{ij} is the distance between the centres of atoms i and j and σ is the hard-sphere or collision diameter of monomers. The hard-sphere model shows a discontinuous function of energy, as Figure 3.4 shows, at $r_{ij} = \sigma$. If r_{ij} is smaller than σ , there is an energetic overlap (infinite energy). Although this potential is highly idealised and therefore it is not suitable for

simulations when chemically realistic molecular systems are needed, its simplicity provides an efficient model, which requires few computational resources and guarantees rapid execution. Moreover, it can be directly compared against well-established theories that account only for the concept of excluded volume. Consequently, due to its simplicity and efficiency, it has very extensively been used in numerous studies to compare experimental data from granular or colloidal systems and theoretical models.

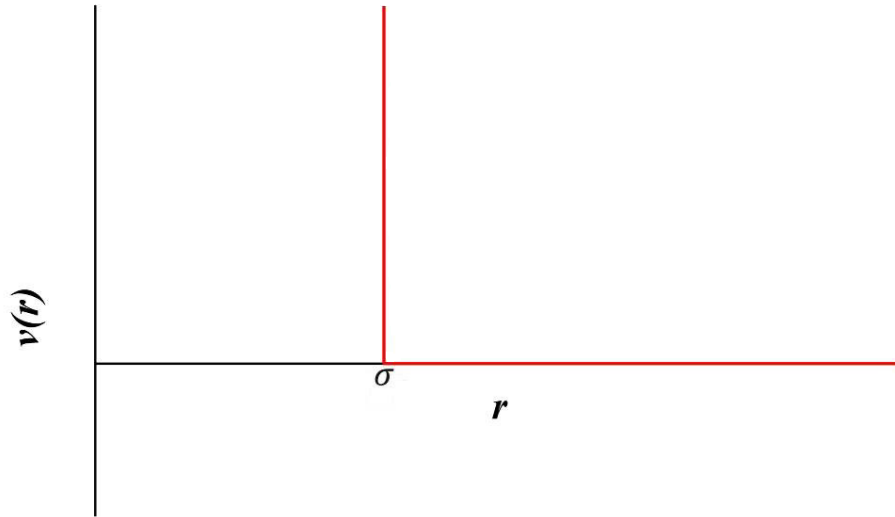


Figure 3.4: Pairwise interaction potential as a function of distance according to the Hard-Sphere (HS) model.

A more complex pair-wise, non-bonded model is the Square-Well/Shoulder (SW/SS). Unlike the hard-sphere model, this model accounts for repulsive (SS) and attractive (SW) interactions, in addition to the non-overlapping condition, through two additional parameters: the interaction intensity (ε) and interaction range (σ_2). Including an energetic intensity, the model simulates a thermal system, in contrast to the athermal HS model. The following set of equations mathematically represents the SW potential, where, like HS potential, r_{ij} is the distance between the centres of atoms i and j and σ_1 is the collision diameter:

$$U_{SW/SS}(r_{ij}) = \begin{cases} \infty, & r_{ij} < \sigma_1 \\ \varepsilon, & \sigma_1 \leq r_{ij} \leq \sigma_2 \\ 0, & r_{ij} \geq \sigma_2 \end{cases} \quad (3.22)$$

Although the SW model is more complex than the HS potential, it is also an ideal model whose pairwise energy is discontinuous at two distances: $r_{ij} = \sigma_1$ and $r_{ij} = \sigma_2$ (see Figure 3.5). The interval between both points is the region where the energy has a finite, continuous value corresponding to intensity ε . Negative intensities ($\varepsilon < 0$) produce attraction between atoms, while positive intensities ($\varepsilon > 0$), repulsion. In the case of the distance being lower than the collision diameter, there is an energetic overlap, like the HS model, leading to infinite energy and thus zero probability of occurrence. If the distance is longer than the interaction range, the atoms have zero pair energy. The SW model can be easily transformed into the HS model if we

set $\varepsilon = 0$ and $\sigma_2 = \sigma_1$. Thus, it is possible to work with any of the two models in the *Simu-D* suite and the HS model can be selected as a specific case of the SW model by proper tuning of the corresponding parameters.

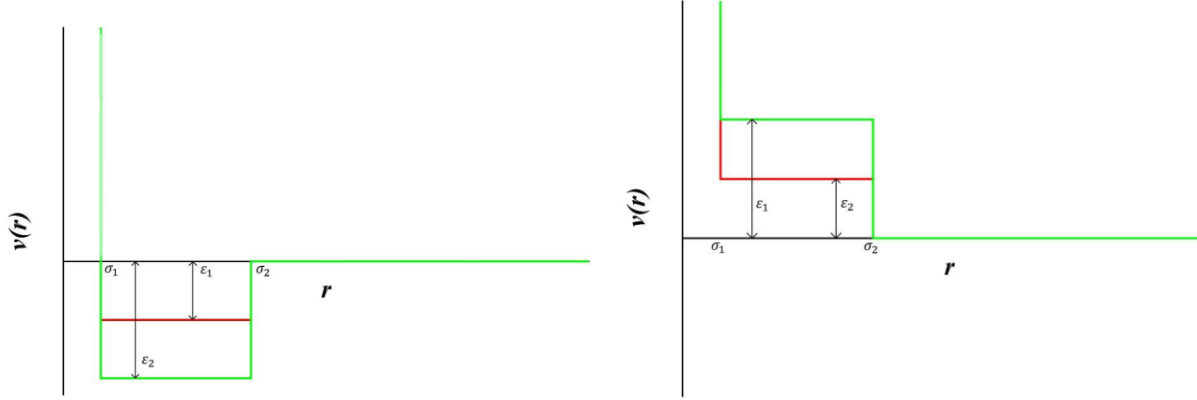


Figure 3.5: Pairwise interaction potential as a function of distance according to the, on the left, Square-Well (SW) and, on the right, Square-Shoulder (SS) models.

The SW/SS model is a very idealised model, where the intensity of the potential within the interaction range is constant and does not depend on the distance between atoms. In spite of this fact, it can be employed to study glass transition versus crystallisation in the case of attractive chains [31] and the richness of the established morphologies (including quasi-crystals) by tuning the interaction range [287] under very dilute conditions.

In parallel, a more complex and realistic model, such as the 12-6 Lennard-Jones potential, can be adopted to represent chemically realistic systems. Unlike previous models, the Lennard-Jones (LJ) potential, which is described by Equation (3.23), is a continuous model as a function of the distance between the centres of the atoms (see Figure 3.6). The model consists of a repulsive part based on the exclusion of electron orbitals of the Pauli principle and an attractive part due to Van der Waals or London forces. The repulsive part allows a pair of spheres to be fused (overlapping).

$$U_{LJ}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (3.23)$$

Because the calculation of energy is the most demanding step in molecular simulation, the selection of the non-bonded interaction model is an important decision that requires a balance between accuracy and simplicity. Furthermore, many potential models function accurately only under specific conditions (non-transferable potentials). So, the HS model is the most computationally efficient but also the least representative of “real” polymers (at least with respect to traditional ones) due to the lack of attractive/repulsive phenomena, while the LJ model provides more accurate results at the cost of greater time consumption. The SW/SS model provides a balanced alternative, standing between the HS and LJ models.

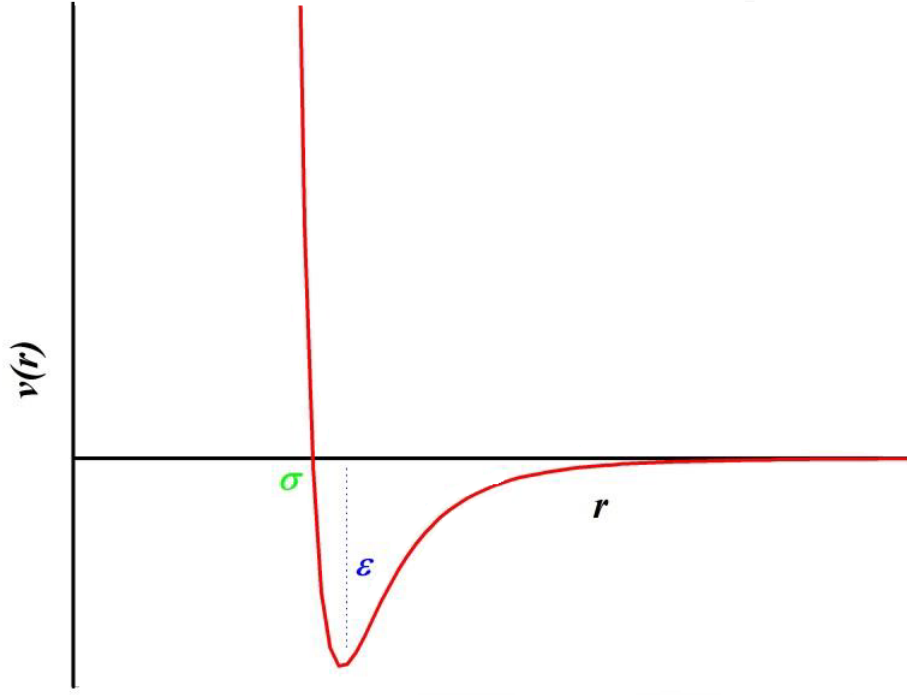


Figure 3.6: Pairwise interaction potential as a function of distance according to the 12-6 Lennard-Jones (LJ) potential.

The summation of all pre-described bonded and non-bonded interactions defines the total energy of the system, which governs the stochastic evolution of the Monte Carlo simulation. Moreover, the force field can also include pairwise interactions between monomers and other elements in the system, such as nanofillers (particles and cylinders) or layers for polymer nanocomposites (PNC) and confining walls for nanoconfinements. Thus, the total energy of the system can be calculated according to Equation (3.24). The first term is the monomer-monomer interactions (N_{at} being the total number of monomers), the second term is the monomer-wall interactions (W being the number of walls), the third term is the monomer-nanofiller interactions (F being the number of nanofillers), and the last term is the total bending potential ($N_{\theta} = (N_{at} - N_s) - 2N_{ch}$ being the number of bending angles). We should mention here that, in general, the different entities could further interact among themselves, for example, one nanoparticle with another or with a confining surface. Such a case is not considered in the present project.

$$\mathcal{V} = \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} U(r_{ij})_{M-M} + \sum_{i=1}^{N_{at}} \sum_{w=1}^W U(r_{iw})_{M-W} + \sum_{i=1}^{N_{at}} \sum_{f=1}^F U(r_{if})_{M-F} + \sum_{b=1}^{N_{\theta}} U(\theta) \quad (3.24)$$

3.2.2 Simulation cell

The simulation cell is the volume (3D) or surface (2D) where all elements of the simulation (monomers, chains, particles, walls, etc.) are inserted. The number of monomers and the dimensions (lengths of edges) of the simulation cell depend on the system size, so the selection of the system size is an important question to address before starting a simulation. Although a large system size is always closer to reality (1 mole contains $6.022 \cdot 10^{23}$ particles, the Avogadro number), it requires significant computational resources and simulation time. Thus, the smaller the system size, the less demanding the simulation. However, small system sizes could potentially introduce artificial results (system size effects) such as atoms interacting with their images/clones. Also, physical quantities that depend on distance cannot exceed the limits imposed by the cell size. Consequently, selecting the size of the system requires a trade-off between the accuracy of the results and the resources available and time required.

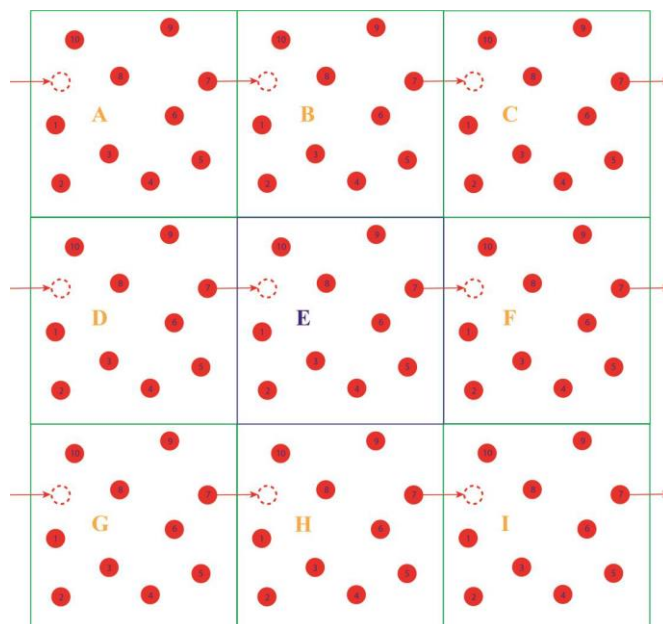


Figure 3.7: Schematic representation of a two-dimensional simulation cell (represented with the letter E) under Periodic Boundary Conditions (PBCs), represented by exact replicas surrounding the main cell.

A way to avoid surface or interfacial effects in bulk systems is to apply Periodic Boundary Conditions (PBCs), which consists of creating an infinite lattice by replicating the original box in all dimensions. Such an action would require infinite calculations of the potential energy, but by taking the minimum image convention it is possible to avoid unnecessary energetic calculations of pairwise interactions that lie far apart using a smaller system that does not suffer surface effects. According to the PBCs, exact replicas surround the simulation cell and, when an atom moves out of the cell, another identical atom appears on the exact opposite side of the cell (see Figure 3.7 for the schematic description of the PBCs). Practically, when the atom leaves the cell, the coordinates of the atom are “wrapped” inside the simulation cell, subtracting or adding the dimensions of the cell (L) from the corresponding coordinates. An example of the effect of PBCs on bulk systems is shown in Figure 3.8.

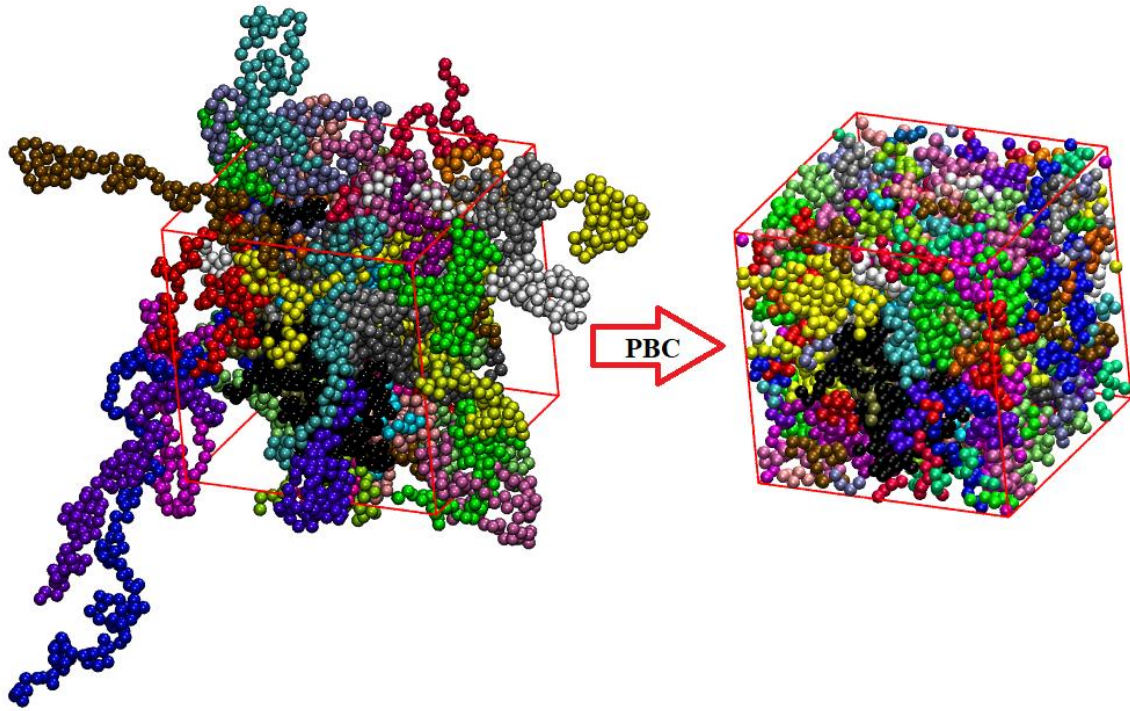


Figure 3.8: Example of the Periodic Boundary Conditions (PBCs) in a 3D simulation cell. On the left, the “unwrapped” (original) 48-chain system of average chain length $N_{av} = 100$ is represented. On the right, the same system is “wrapped” inside the simulation cell after applying PBCs.

In the case of simulating interfacial or surface phenomena such as confinement, the periodic boundary conditions are replaced by other boundary conditions. In the case of confinement, flat, impenetrable, and parallel surfaces are applied on the boundaries of the simulation cell on at least one dimension to inhibit the periodicity of the monomers. Furthermore, these surfaces may introduce attractive or repulsive potential to energetically interact with the elements of the system. Along with confinement, there is interest in studying systems with anisotropy, i.e. different sizes in one or two dimensions, instead of generally cubic cells (isotropic). The use of anisotropic confined cells allows the study of extreme confinement [27] as quasi-1D (tube-like) [26] or quasi-2D (plate-like) [28] confined simulation cells, which have direct applications in thin-film materials and nanowires. The current implementation of *Simu-D* allows the confinement as flat, parallel walls at least on one dimension or as curve surfaces. The former one always presents orthogonal simulation cells but can be anisotropic and have a different number of confined dimensions (d_{conf}), ranging from 0 (bulk cell with PBCs) to 3 (full confinement), as can be seen in Figure 3.9. Confined simulation cells with curved surfaces can take the form of spheres (full confinement) or cylinders with closed or open ends (subject to periodic boundary conditions), as shown in Figure 3.10. The intensity of the confinement is controlled by the distance between the confining surfaces (d_{wall}), i.e. the sphere or cylinder diameter, or the inter-wall distances for the orthogonal confinements (which in general can be different for different dimensions).

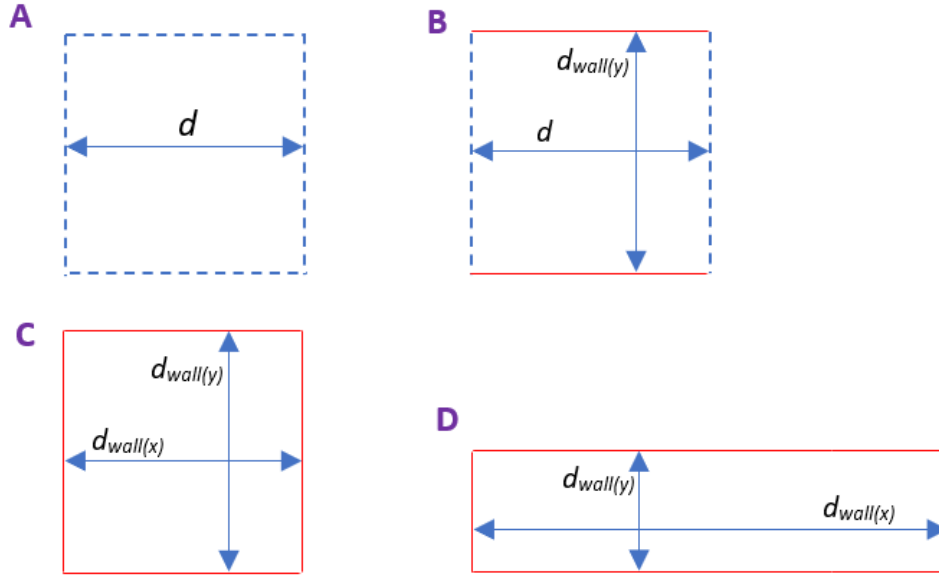


Figure 3.9: Schematic representations of different orthogonal simulation cells. For simplicity, all are represented in two dimensions. Isotropic bulk cell (A), cell confined in one dimension (B), fully confined isotropic cell (C), and fully confined anisotropic cell (D).

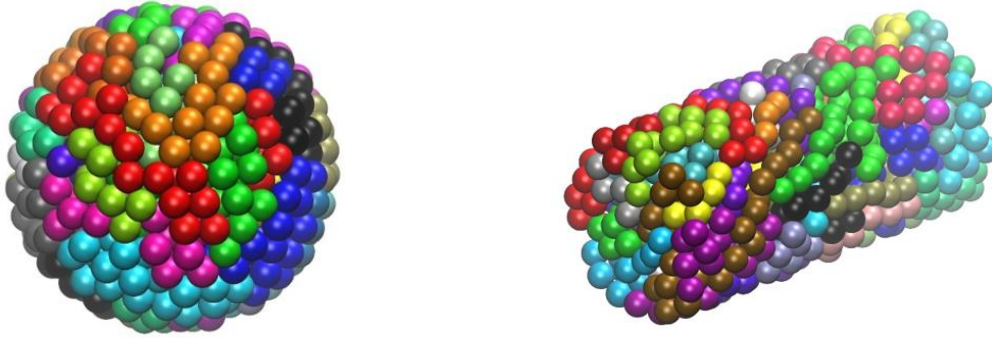


Figure 3.10: Examples of polymer systems under (left) spherical and (right) cylindrical confinement.

An important parameter related to the dimensions of the simulation cell and the size of the system is the packing density (φ) or volume fraction, especially for simulations of athermal systems where the main interaction is a non-overlapping condition (hard-sphere potential). The packing density is defined as the total volume of monomers over the volume of the simulation cell. For bulk systems of spherical monomers, it can be calculated as:

$$\varphi = \frac{V_{at}}{V_{cell}} = \frac{\frac{4}{3}\pi\left(\frac{\sigma}{2}\right)^3 N_{at}}{V_{cell}} = \frac{\pi N_{at}}{6V_{cell}}\sigma^3 \quad (3.25)$$

where V_{at} is the total volume occupied by monomers (from single monomers or a polymer chain), V_{cell} is the volume of the simulation cell and N_{at} is the total number of monomers of diameter σ .

In the case of two-dimensional systems, such as thin films of monolayers, the monomers are confined in a dimension with a size equal to the monomer diameter, so they cannot move in

the dimension of confinement. Therefore, for 2D systems, the parameter used is the surface coverage or superficial density (φ_{sup}) according to the following expression:

$$\varphi_{sup} = \frac{S_{at}}{S_{cell}} = \frac{\pi \left(\frac{\sigma}{2}\right)^2 N_{at}}{S_{cell}} = \frac{\pi N_{at}}{4S_{cell}} \sigma^2 \quad (3.26)$$

where S_{cell} is the surface area of the large faces in the dimension confined and S_{at} is the total surface occupied by monomers on the large faces.

For this doctoral thesis, two types of simulation cells are used: bulk 3D cells (PBCs in all dimensions) and 2D monolayer cells whose thickness along the confinement dimension is equal to the monomer diameter σ (plate-like thin films). Initial configurations for both kinds of systems are generated at very dilute configurations ($\varphi \leq 0.05$) in three dimensions utilizing fully flexible chains. Monomers and chains are randomly placed inside the three-dimensional cell according to the molecular model and other imposed restrictions that define the system. Under these conditions, the desired equilibrium bending angle (θ_0) and bending constant (k_θ) are activated, followed by a rapid constant-volume equilibration. From these dilute 3D initial configurations, denser 3D systems and polymer thin films are then generated at different packing densities and surface coverages, respectively. The reason to create these initial dilute configurations instead of directly denser configurations is the high inefficiency of the generation of denser configurations as a result of the low probability to find available space, without overlapping with other monomers previously placed on the cell.

The generation of denser packed systems from the dilute initial configurations involves the reduction of the volume of the simulation cell through a standard shrinkage algorithm. Following this shrinkage process, dense packings are generated, but no ordered morphologies at maximum density are reached due to jamming being triggered at lower packing densities, approximately 10% lower than the maximum achievable one [104]. However, this compression approach is able to reach packing densities very close to the maximally random jammed (MRJ) state and well above the value at the melting point of HS monomers [13, 14, 119].

The shrinkage algorithm uses a modified volume fluctuation move (explained later in Section 3.3.5) that only attempts isotropic shrinkages (compactions) of the cell accepting or rejecting the move considering only an overlap-free criterion for the resulting configuration. An MC simulation is performed under constant volume, through the application of the typical mix of moves, and a volume reduction is attempted with an established frequency. The modified volume fluctuation move affinely repositions all the chains and nanofillers of the system, while the bond geometry and connectivity of the individual chains remain unaltered. Clearly and especially at high concentrations, this shrinkage process can produce overlaps between the hard spheres, leading to the eventual rejection of the compression. Thus, NVT -MC moves are

performed between volume reduction attempts to realise structural rearrangements, accommodating the overlap-free distortion of all intermolecular distances. The MC simulation continues until it reaches a desired target density with an established accuracy (10^{-7}). The shrinkage algorithm is able to generate dense or nearly jammed system configurations under a variety of conditions in two and three dimensions. An example of the shrinkage process for a hard-sphere polymer chain system under PBCs is shown in Figure 3.11.

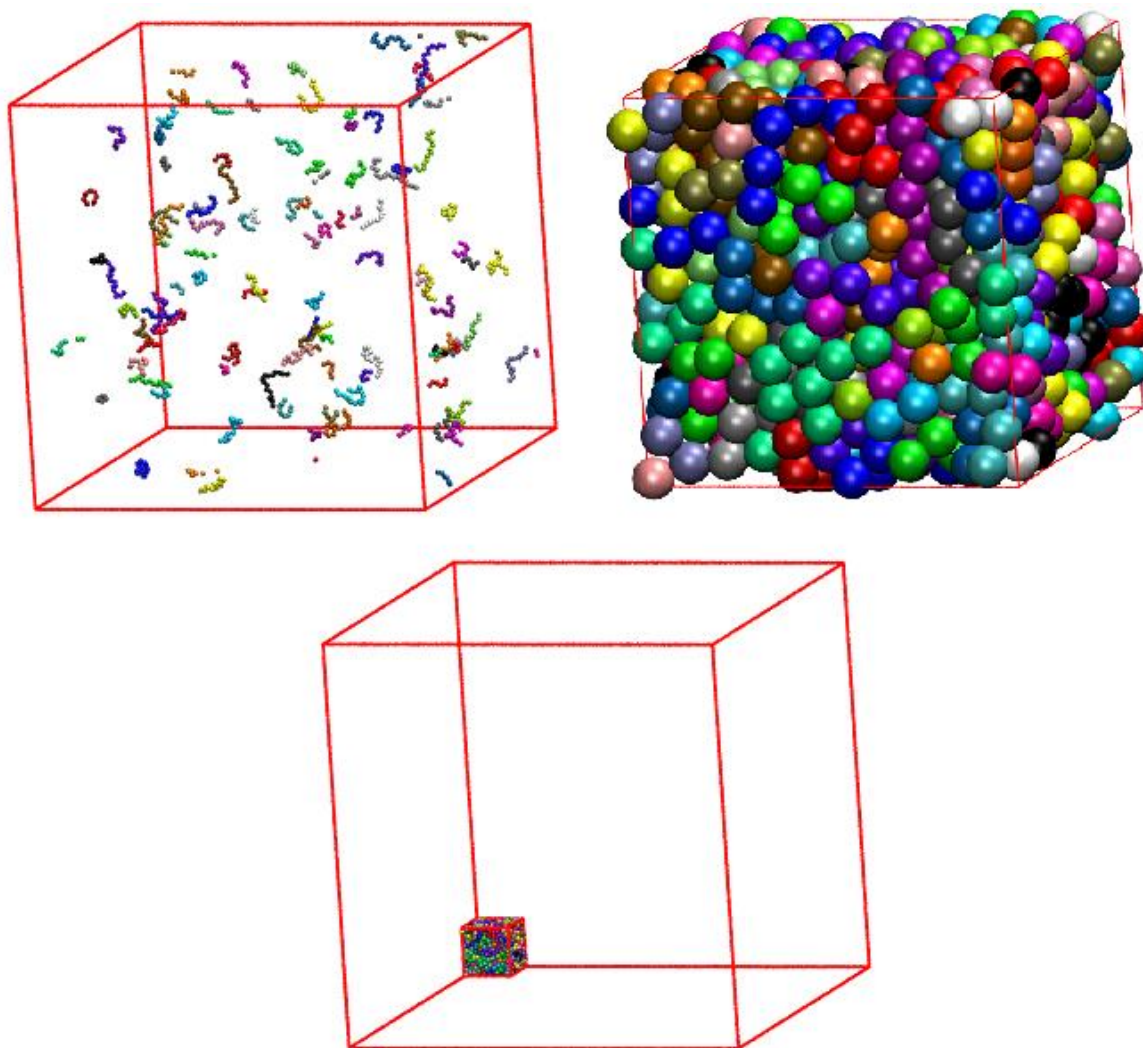


Figure 3.11: Examples of the shrinkage algorithm to create denser configurations. Top Left: Initial dilute configuration at $\varphi = 0.001$. Top Right: The same system at $\varphi = 0.60$ after employing the shrinkage algorithm. Bottom: Comparison of the dimensions of the simulation cell at $\varphi = 0.001$ and $\varphi = 0.60$.

For the creation of two-dimensional systems (polymer thin films) from very dilute three-dimensional configurations of the systems, confinement is employed in one dimension by introducing flat, parallel, and impenetrable walls. Then, an adsorption approach is employed to create a monolayer along the confined dimension. An attractive (square-well) potential is applied between the monomers and one of the flat surfaces, while an equivalent repulsive (square-shoulder) potential is enforced on the opposite wall, as shown in the scheme of Figure 3.12. The parameters of the two wall-monomer interaction potentials are adjusted until

eventually a single layer is formed on the attractive wall. Effectively, the simulation cell is converted into a polymer thin film with a thickness equal to the monomer diameter within a numerical tolerance of 10^{-5} .

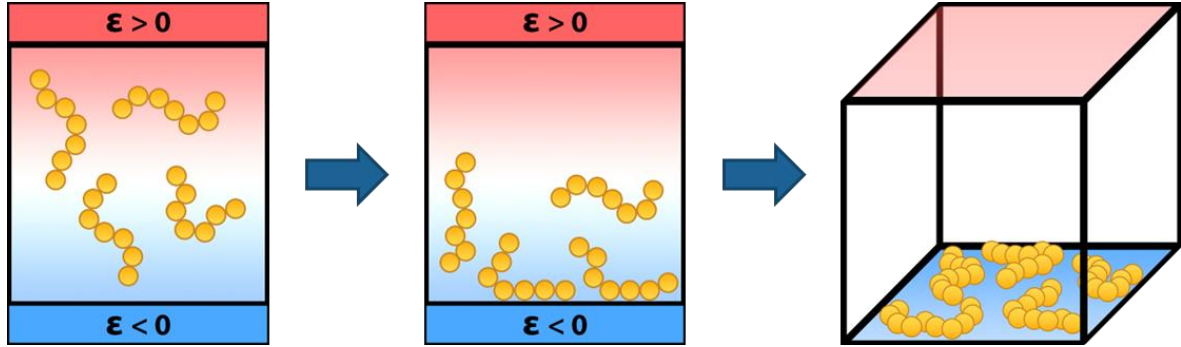


Figure 3.12: Schematic explanation of the adsorption process for the creation of 2D polymer thin films.

The thin-film systems are further isotropically compressed in the long dimensions of the simulation cell, generating the systems at the desired target surface coverages and/or until no further compaction is allowed. When a surface coverage of 0.70 is reached, cell shrinkage changes from isotropic (square) to anisotropic (rectangular), so that the dimensions can be compressed differently to accommodate specific geometric constraints imposed by compact crystals in two dimensions [6]. Accordingly, the final densest 2D cells present a very small value of anisotropy. Examples of the adsorption and shrinkage processes for the formation of polymer thin films are presented in Figure 3.13.

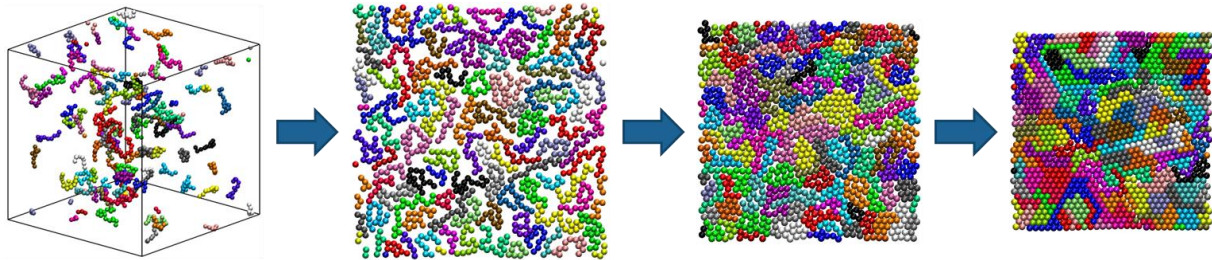


Figure 3.13: Process followed to create the densest polymer configurations of 2D polymer thin films of thickness equal to the monomer diameter ($d_{wall} = \sigma$) from an initial dilute 3D configuration. Spheres are coloured according to their parent chains.

3.2.3 Systems studied

We have dealt with two types of polymeric systems: bulk 3D systems and quasi-2D systems. These systems are entirely composed of polymer chains without the presence of single monomers or nanofillers. For all systems, polymer chains are modelled as linear chains of identical hard spherical monomers with a collision diameter σ , which is considered the characteristic unit length. Additionally, uniform dispersity is introduced in chain lengths through a dispersity index $\Delta = 0.5$, so lengths fluctuate within an interval $[N_{av}(1 - \Delta), N_{av}(1 + \Delta)]$.

The non-overlap condition of hard monomers is adopted by employing the Hard Sphere potential for all non-bonded interactions. For the bond lengths, tangency between bonded monomers is practically enforced by applying a bond gap $dl = 6.5 \times 10^{-4}$ (in units of σ) [22]. Regarding the chain stiffness of the semi-flexible polymers, the bending angle is controlled by the bending potential of Equation (3.20). Bending angles range from fully extended (rod-like) to fully compact (coiled) configurations of triplets. Specifically, five equilibrium bending angles are studied: 0° , 60° , 90° , 108° , and 120° . Schematic trimers of the bending angles studied are represented in Figure 3.14. Torsion angles ϕ are allowed to fluctuate freely.

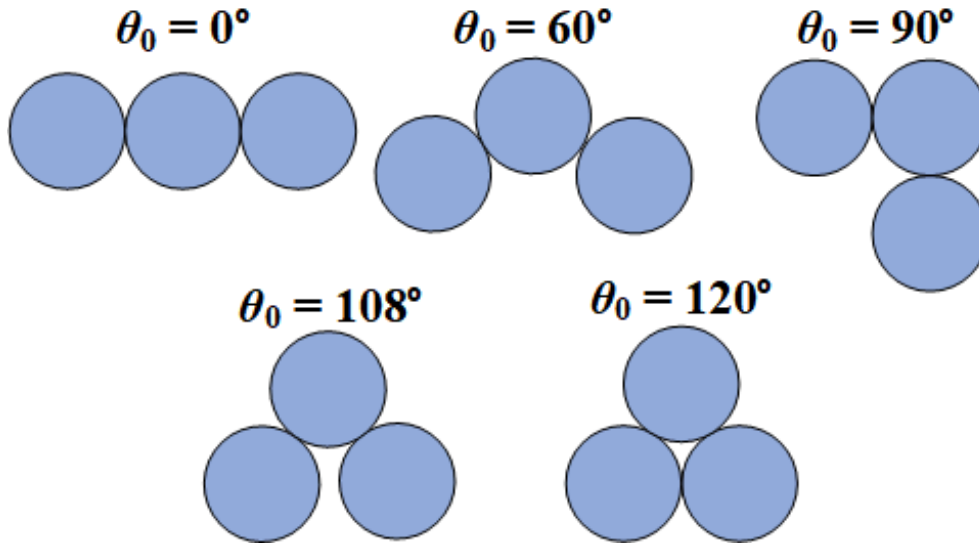


Figure 3.14: Schematic representations of trimers with the equilibrium bending angles (θ_0) studied in the present doctoral thesis.

For all simulated systems, the bending constant is set equal to $k_\theta/k_B T = 9 \text{ rad}^{-2}$ (for simplicity $k_\theta = 9$ hereafter), where k_B and T are the Boltzmann constant and temperature, respectively. The temperature for all simulations is constant and fixed to $T = 1/k_B$, so $\beta = 1/k_B T = 1$. The specific choice of the bending constant was made considering a trade-off between computational expediency and the accuracy of the model. The selected degree of stiffness limits the deviations from the equilibrium bending angles to, approximately, $\pm 20^\circ$, as shown in Figure 3.15, where the corresponding curves are compared with the resulting ones for a higher bending constant $k_\theta = 50$. Although angle distributions are wide under semi-dilute conditions, this range of bending constraints leads to orientational ordering for rod-like ($\theta_0 = 0^\circ$) chains, as demonstrated in Refs. [204, 206].

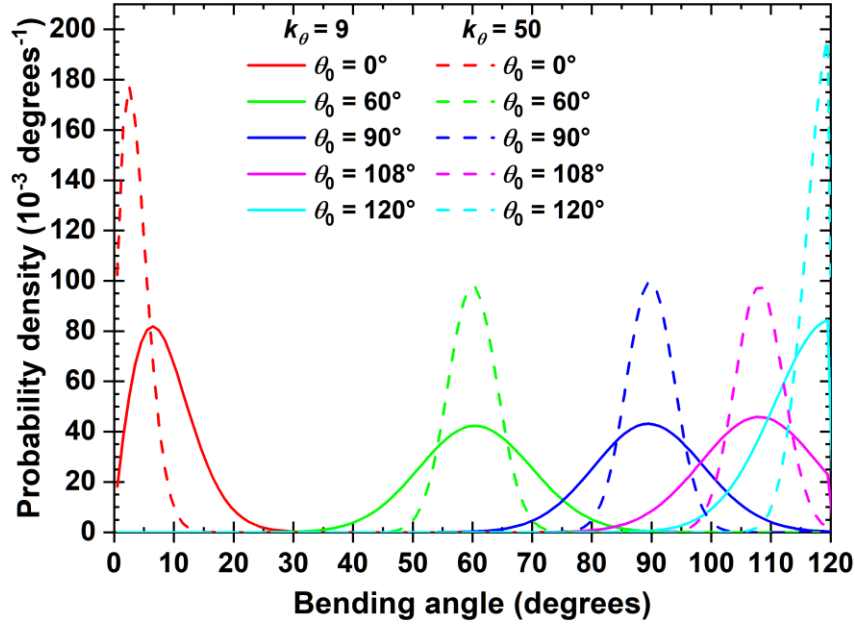


Figure 3.15: Distribution of bending angle (θ) of a three-dimensional, bulk 100-chain system of $N_{av} = 12$ at packing density $\varphi = 0.30$ for $k_\theta = 9$ (solid lines) and $k_\theta = 50$ (dashed lines) and different equilibrium bending angles (θ_0).

Systems of different sizes, both in terms of the number of monomers N_{at} , the number of chains N_{ch} , and the average chain length N_{av} , are studied in three dimensions (3D) for all the equilibrium bending angles indicated before. The average chain lengths of the systems range from 12 to 1000 monomers per chain. Table 3.1 summarises the types of 3D simulated systems together with the size parameters. From the initial very dilute conditions ($\varphi = 0.001$) to the densely packed configurations (in the vicinity of the MRJ state), a very wide range of volume fractions is explored through equilibrium NVT -MC simulations. All 3D systems are simulated under constant volume and temperature (NVT ensemble), employing Periodic Boundary Conditions (PBCs) in every dimension.

Table 3.1: Number of monomers N_{at} , number of chains N_{ch} , average chain length N_{av} , and minimum N_{min} and maximum N_{max} chain length (polydispersity distribution $\Delta = 0.5$) for the types of polymeric systems studied in three dimensions (3D).

System ID	N_{at}	N_{ch}	N_{av}	N_{min}	N_{max}
C12	1200	100	12	6	18
C24	1200	50	24	12	36
C100	4800	48	100	50	150
C500	10000	20	500	250	750
C1000	10000	10	1000	500	1500

In the case of two-dimensional (2D) systems, the simulated systems consist of freely-jointed (fully flexible) polymers and semi-flexible polymers, employing equilibrium bending angles of 0° , 60° , 90° , or 120° and the same bending constant as three-dimensional systems.

Polymeric systems in 2D are composed of $N_{at} = 1200$ hard spheres distributed into $N_{ch} = 100$ different chains with an average chain length equal to $N_{av} = 12$. Polymer thin films are formed under confinement in one dimension ($d_{conf} = 1$), as explained previously, while the other two dimensions employ PBCs. After the creation of the polymer thin films, the lower surface coverage φ_{sup} of the 2D systems is equal to 0.30 and the highest achieved surface coverage ranges from 0.7644 to 0.8387, depending on the equilibrium bending angle. All 2D systems are simulated under constant volume (surface coverage) in the canonical ensemble.

3.3 Simulation Algorithm: *Simu-D*

The core of the methodology relies on the execution of a series of Monte Carlo simulations of different average chain lengths, packing densities, and chain stiffness. All the simulations for this research are carried out using the *Simu-D* suite [2]. *Simu-D* is a Monte Carlo simulator-descriptor suite for the molecular modelling of polymer-based systems, specifically under extreme conditions. These “extreme conditions” denote a wide variety of conditions that represent a difficulty to reach equilibrium, such as very high concentrations, above the freezing transition for hard spheres and in the vicinity of the MRJ state [14, 119], extreme confinement (plates and tubes), where the distance between confining agents is approximately equal to the monomer size [6, 27, 28, 32], and/or the presence of nanofillers of very large relative sizes, such as particles, cylinders or terminally-grafted chains anchored on nanoparticles.

The simulator of *Simu-D*, which is the central component of the software, is the result of the accumulation over the years of successive expansions, modifications, and improvements in the original MC code, created by Karayiannis and Laso [288], for the simulation of dense and jammed athermal polymer-based systems in bulk. The expansions and improvements of the MC code, built in Fortran, allowed the simulation of progressively more complex and diverse systems, such as athermal polymers under confinement [25, 26], macromolecules whose monomers interact with the square-well (SW) or square-shoulder (SS) potential [31, 32], and systems in two dimensions (2D) as extremely thin films [6, 32]. The main goal of *Simu-D* is to create a general-purpose MC suite that is as efficient, general, and user-friendly for as many conditions as possible, taking into account the stochastic nature of the MC method and the inherent difficulty in making an MC scheme applicable on diverse physical systems dominated by chain connectivity and related constraints.

Currently, the *Simu-D* suite consists of a group of MC algorithms or moves which produce a collection of microstates following a sequence (Markov chain) according to the employed statistical ensemble. The moves permit the transition between microstates to the equilibrium state of the system respecting all restrictions imposed by the molecular model, microscopic reversibility, and ergodicity. Monte Carlo moves, used in *Simu-D*, are classified

as: (1) Standard Localised Moves (LMs) that displace a single or a sequence of monomers, (2) Chain-Connectivity-Altering Moves (CCAMs) [13, 14, 27] that delete and reconstruct bonds in a single chain or between a pair of chains, (3) cluster-based moves that displace or rotate a group of neighbour monomers by treating them as part of a rigid object (the cluster), (4) Identity Exchange Moves (IdExMs) that modify the identity of monomers in mixtures of chains and individual monomers, and (5) volume fluctuations moves. The first four types of moves are executed at a constant volume (NVT ensemble). In contrast, volume fluctuation moves, being the regular one or the MRoB algorithm [27], change, isotropic or anisotropically, the dimensions of the simulation cell, allowing cell shrinkage or NPT simulations.

The acceptance or rejection of transitions between microstates of all MC moves depends on the Metropolis criterion and the transition probability, P_{mn} , as explained in Section 3.1.2 and as modified for CCAMs [13, 50, 289, 290]. The transition probability depends on the statistical ensemble of the system and the employed move.

3.3.1 Standard Localised Moves

Standard Localised Moves or, to shorten, Local Moves (LMs) are algorithms that displace/reconstruct one or more atoms along the chain backbone. Described exhaustively in different molecular simulation works, Local Moves represent the real motion of polymer chains, similar to the ones performed in Molecular Dynamics simulations. Although they provide full-scale equilibration at low concentrations and short chain lengths, their efficiency diminishes in dense and highly entangled melts (high packing density). On one hand, high density leads to many transitions being rejected due to energetic overlaps; on the other hand, a displacement of a single monomer does not lead to long-range equilibration in a chain that consists of thousands of such monomers. Nevertheless, the local moves are considered of paramount importance, even at high packing densities and long-chain systems, because they provide a short-scale relaxation and an efficient re-arrangement of the local packing. Furthermore, they are required to render the MC simulation ergodic, and additionally, they work synergistically with the CCAMs to be explained later.

The simplest local move is the displacement of an individual monomer. The monomer is displaced to a random direction and length within a pre-defined maximum amplitude $l_{disp}(i)$, which can be different for each dimension i . For the chains, the corresponding LMs moves are: reptation, end-mer rotation, (internal) flip, intermolecular reptation, and end-segment re-arrangement (also known as continuum configurational bias, CCB, in Refs. [291, 292]). All local moves are attempted considering a constant volume simulation, so employing the transition probability P_{mn} for canonical ensemble (NVT) from Equation (3.14), including a modification to account for a possible configurational bias as explained later.

Reptation move displaces the chain moving one of the end monomers to the other extreme of the chain, so the move mimics the real “reptation” dynamics of polymer chains in melts. First, the move randomly selects one chain and one of its end monomers. The selected monomer is deleted and reconstructed using randomly selected bending and torsion angles at the other end of the chain. After the move is executed and, if accepted, the coordinates, bending angle, and torsion angle of the selected monomer are all changed (as can be seen in Figure 3.16).



Figure 3.16: Reptation local move.

Rotation move reconstructs one of the end monomers of the chain at a new coordinate without modifying the connectivity of the chain. As the reptation move, the move randomly selects one of the (two) ends of a random chain. The selected monomer is deleted and reconstructed on the same side with new coordinates, and so new bond length, bending, and torsion angle (as can be seen in Figure 3.17).



Figure 3.17: Rotation local move.

The internal flip move is similar to the previous rotation move. The flip move affects an inner monomer of the chain rather than an end monomer as the rotation move. After a random chain is selected, the move selects an internal monomer. Then, the monomer is rotated (modifying the torsion angle) in an increment within an interval from $-\Delta\phi$ to $+\Delta\phi$ (the typical value being $\Delta\phi = 20^\circ$). The bond lengths and bending angles are kept constant (see Figure 3.18) and, as the rotation move, the chain index of the atom does not change.

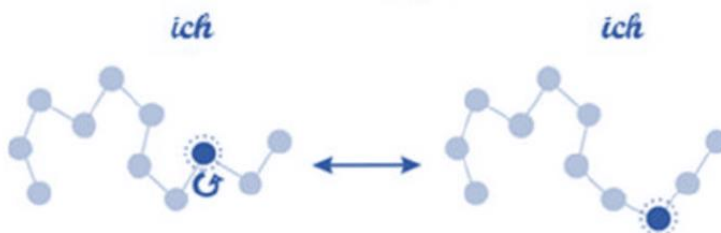


Figure 3.18: Internal Flip local move.

Unlike the previous moves, the intermolecular reptation move [13, 289] involves two randomly selected chains. Similarly to the reptation move, the move deletes one of the end monomers from one randomly selected chain (ich), and the monomer is now reconstructed at a random end of another random chain (jch), instead of the same chain as in the conventional reptation (see Figure 3.19). The chain lengths of both chains are modified (ich loses one monomer, while jch gains that monomer). Thus, because of this exchange, the move introduces dispersity in chain lengths. Obviously, the new chain lengths are required to be within the allowed limits (N_{min} , N_{max}) as dictated by the distribution of chain lengths. If this condition is not met, then the intermolecular reptation is rejected without passing to the (reconstruction) phase and the energetic calculations.



Figure 3.19: Intermolecular Reptation local move.

End-segment re-arrangement move (or previously CCB in Refs. [291, 292]) affects a group of successive monomers of a chain, being the most complex move between the local moves used in the *Simu-D* suite. The move selects randomly a chain and an end-segment of monomers to be deleted, whose number varies randomly from one to a maximum pre-set limit (n_{ccb}). The selected monomers are reconstructed, from the innermost monomer, one by one with a new bond geometry (bond length l , bending angle θ , and torsion angle ϕ).

Thus, the move produces a significant change in the structure of the chain (as can be seen in Figure 3.20), contributing strongly to the sampling of the phase space [290, 291]. However, its performance is severely affected by the maximum number of monomers to be cut (n_{ccb}) at high packing densities. The larger n_{ccb} is, the more computationally demanding the move and the lower the acceptance rate. Therefore, the maximum number of monomers to be cut (n_{ccb}) is determined by trial-and-error, looking for a balance between acceptance rate, computational time, and equilibration impact.

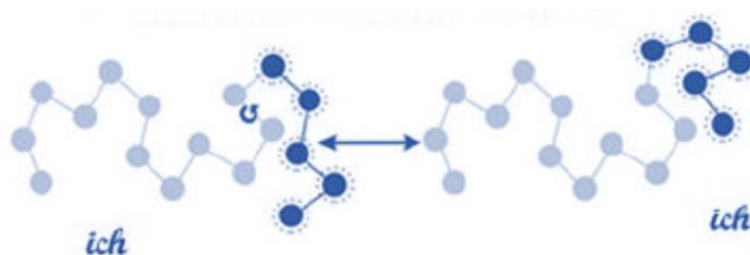


Figure 3.20: End-segment Re-arrangement local move (or CCB in Refs. [291, 292]).

3.3.2 Chain-Connectivity-Altering Moves

Because local moves are insufficient to equilibrate hard-sphere chain systems at high packing densities due to the limited displacements of monomers, chain-connectivity-altering moves are implemented in *Simu-D* to enhance long-range equilibrations at high packing densities. As explained in [13, 293], Chain-Connectivity-Altering Moves (CCAMs) delete and create new bonds between chains without modifying any atomic coordinates. Because these algorithms do not entail monomer displacements, their efficiency remains particularly high, even increasing, at high packing densities. As was mentioned before, the acceptance of local moves drops in systems under high concentrations, but the use of CCAMs allows major rearrangements of the chains. Thus, CCAMs produce global changes at the level of chains by changing the contours of the chains and the positions of their ends. This allows a wide sampling range for the local moves, reducing the “shuttling effect” where two successive transitions between microstates m and n , in a cyclic pattern $m \rightarrow n \rightarrow m$, produces practically a net result of zero in configurational change.

Chain-connectivity-altering moves only modify the arrangement of the chains without displacement of the monomers. Therefore, the non-bonded interactions are not modified after the application of the CCAMs. This means that there is no change in the non-bonded part of the energy. However, as new bonds are created and old ones are deleted, the bond geometry of the chains and, consequently, the corresponding bonded energy changes.

Moreover, CCAMs require that monomers of the affected chains lie close. So close that they can be connected by a bond whose length is within the predefined allowed bond length interval $[\sigma, \sigma + dl]$. Thus, these moves are not very efficient at low concentrations, especially when applied between different chains and for systems with very small bond gaps. However, their acceptance rate increases significantly with concentration, as they have more pairs of atoms that can initiate them. This is because as the packing density increases, atoms come closer and the contact network becomes richer. In fact, as demonstrated in [13], CCAMs as implemented here reach their peak performance in the vicinity of the Random Closed Packing (RCP).

The moves implemented in *Simu-D* are simplified versions of the End-Bridging (EB) [289, 290] and Double-Bridging (DB) [50, 288] algorithms developed by Theodorou *et al.* for the equilibration of poly(ethylene) melts. For the present work, the two CCAMs used are the simplified End-Bridging (sEB) and the simplified Intramolecular End-Bridging (sIEB) [2, 13, 25].

Simplified End-Bridging (sEB) move requires the participation of two chains: one “predator” chain ich , which gains monomers from the other “prey” chain jch , as can be seen in Figure 3.21. For the application of the move, it is required that the “predator” chain has one end

monomer in a bridgeable distance with an internal monomer of the “prey” chain. Depending on which bond is deleted, the move can proceed in two different ways. In addition, as for the intermolecular reptation move, at least one of the two possible results must produce chains whose new lengths fall within the specified polydispersity limits. If one of the requirements is not met, then the move is automatically rejected. For computational expedience, a list is kept with all neighbours that can initiate an sEB move. If this list is empty, the move is automatically rejected. If at least one pair exists, then one is randomly selected. In the case of the move being accepted, the resulting chains show completely different connectivity and bond geometry, as well as new bond lengths, bending, and torsion angles. In Figure 3.21, a schematic representation of the sEB move and the two possible execution patterns are shown. If both execution patterns fulfil the polydispersity constraints, one of them is selected randomly.

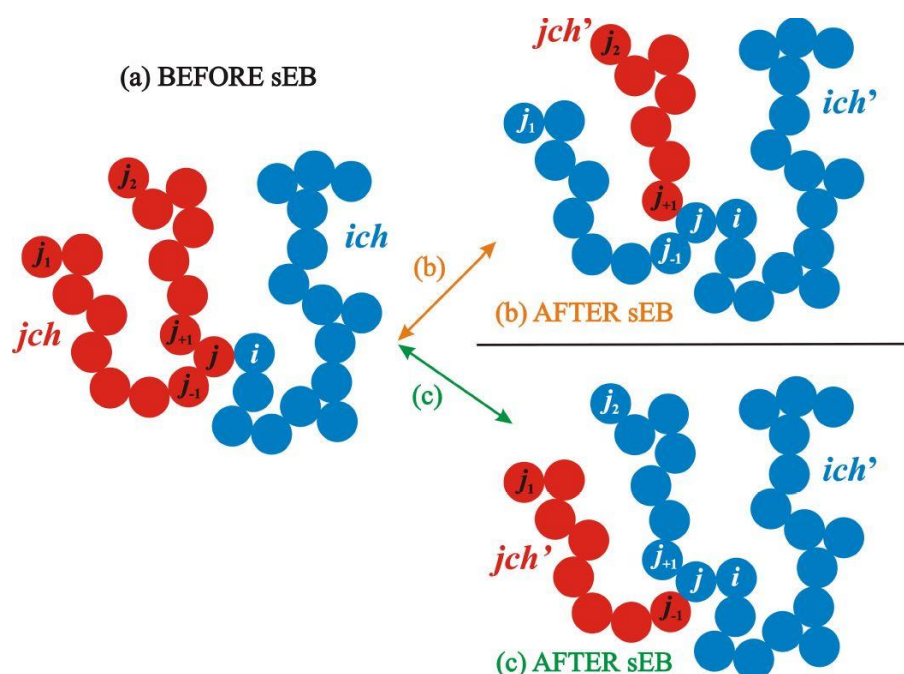


Figure 3.21: Simplified End-Bridging (sEB) move.

Simplified Intramolecular End-Bridging (sIEB) move works similarly to the sEB move, but it affects only one chain instead of two. The move checks if an end monomer i of a randomly selected chain is in contact (or within the allowed bridgeable distance) with one of the internal monomers j of the same chain. If the requirement is met, the execution of the chain creates a new bond between the i and j monomers and breaks the bond of the internal monomer j (as can be seen in Figure 3.22). The result of the move is that the contour path, bond lengths, bending and torsion angles of the chain are modified. As only a single chain is involved in the move, there is no change in length dispersity, as in the case of the sEB move.

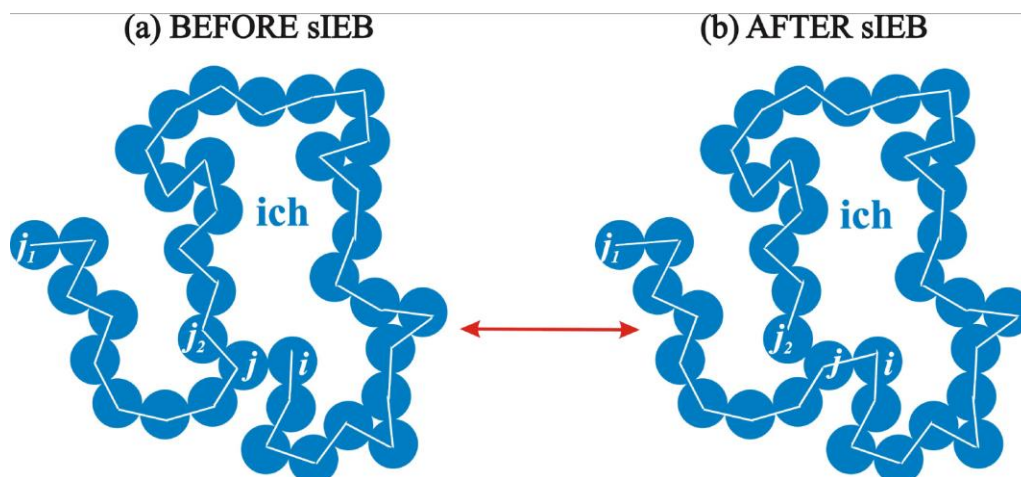


Figure 3.22: Simplified Intramolecular End-Bridging (sIEB) move.

3.3.3 Cluster-based Moves

Cluster-based moves are the most computationally demanding algorithms in the *Simu-D* suite. They are of paramount importance for square-well / shoulder simulations, where attraction leads to the formation of clusters, but which, in turn, may be isolated so that they must be displaced to allow further aggregation [31]. As a first step for every cluster move, an identification of all clusters of the system configuration is carried out. Cluster detection is conducted through an Euclidean distance criterion, regardless of the identity of each element (chain monomer or individual monomer). A monomer is considered to belong to a cluster if the distance between the monomer and any other monomer of the cluster is smaller than the inclusion distance, r_{clust} , which must be set slightly longer than the maximum bond gap ($\sigma + dl$) to avoid splitting a chain between different clusters. Thus, a monomer is first selected, and all monomers within the radius r_{clust} , are identified. This procedure is repeated until all monomers are assigned to a cluster and so all clusters are identified. In a second step, clusters are checked among themselves to identify possible aggregation to larger groups.

Once all clusters are identified through the Euclidean proximity criterion, a cluster is randomly selected to execute a move as a whole, i.e. as a single entity formed by the corresponding monomers. Two variants of cluster-based moves are implemented in *Simu-D*: Cluster Displacement and Cluster Rotation. The former move, Cluster Displacement, displaces the whole cluster by a random (limited) amplitude in a random direction. Cluster Rotation move proceeds to the rotation of the whole cluster by a random angle with respect to an axis that passes through its centre of mass. As the rest of the MC moves, the acceptance of the move is determined by the Metropolis criterion, immediately rejecting the move in the presence of overlaps. Figure 3.23 presents a schematic of the execution for the cluster-based moves.

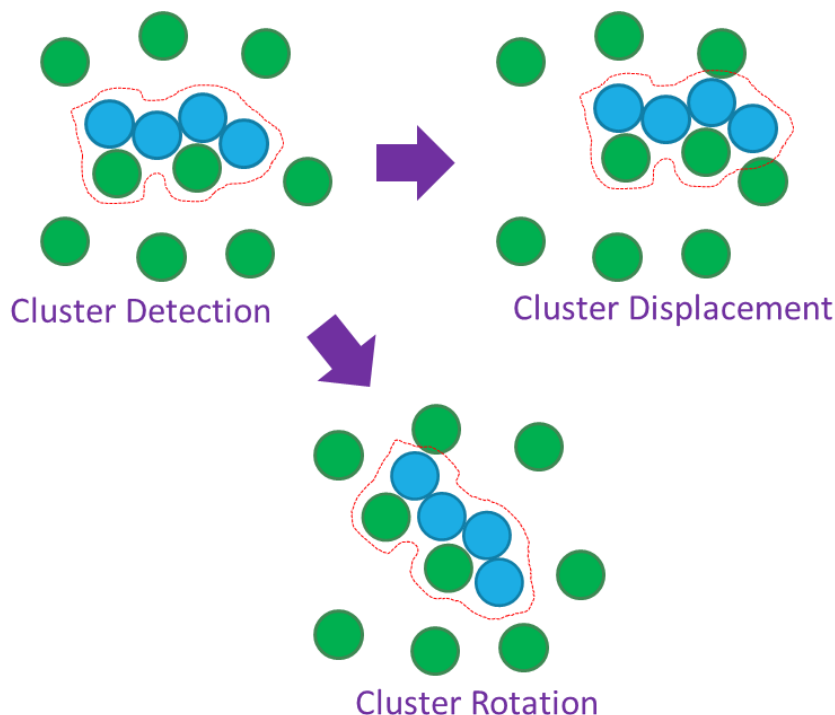


Figure 3.23: Schematic representation of Cluster Detection, Cluster Displacement, and Cluster Rotation for a mix of a chain (blue) and single (green) monomers. First, Cluster Detection is performed based only on the proximity criterion. The identified cluster is shown by the red contour line. Then, the cluster, as a unified group of monomers, may proceed to the displacement in a random direction and length (Cluster Displacement) or the rotation by a random angle with respect to the centre of mass (Cluster Rotation).

3.3.4 Identity Exchange Moves

Identity Exchange Moves (IdExMs) are a type of moves of paramount importance for the simulation of systems with mixtures/blends of elements of different identities, for example, mixtures of chains and individual monomers. These moves proceed by identifying any individual monomer that is within a bridgeable distance from a chain. The identity of the atom changes as it stops being an individual atom and becomes a new chain end (or its penultimate atoms depending on the variant of the move [2]). In parallel, on the other end of the chain (or on the same side, again depending on the variant of IdExM, see later), a monomer changes its identity and, from being part of the chain, it becomes an individual monomer. To keep the canonical (NVT) or isobaric-isothermal (NPT) ensemble, i.e. to keep the number of elements N_{ent} constant, the relative concentration of elements is kept constant. Because IdExMs are based on bridgeable elements, i.e. a pair of different elements is a distance within the maximum allowed bond length ($\sigma + dl$), thus, similarly to CCAMs, these moves do not entail a monomer displacement but rather the proper deletion and reconstruction of selected bonds. Consequently, no pairwise, non-bonded energetic change is produced, and so the acceptance of the move by the Metropolis criterion depends only on the bonded energy (change in bond length, bending, and torsion angles).

Figure 3.24 presents the three Identity Exchange moves, involving a single monomer and a chain or pair of chains, as implemented in the *Simu-D* suite [2]. IdEx1 move (top panel of Figure 3.24) is produced when a single monomer is at a bridgeable distance to one of the ends of the chain. The move connects the single monomer to the chain end through a bond, becoming the new chain end, while the last bond of the other chain end is deleted and the end monomer becomes a single monomer. IdEx2 move (middle panel of Figure 3.24) requires that the single monomer is within a bridgeable distance from the second monomer of the chain end (i.e. the second or penultimate monomer of the chain). In this case, the single monomer creates a bond with the bridgeable monomer, becoming the new chain end, while the corresponding chain end becomes a single monomer through bond deletion. Finally, the execution of IdEx3 (bottom panel of Figure 3.24) is similar to the IdEx1 move but involves two chains. The single monomer is connected at the bridgeable chain end of a chain; however, a single monomer is released by deletion of a terminal bond of a randomly selected chain, which is different from the chain that gains one monomer. Consequently, the IdEx3 move requires polydispersity in the system.

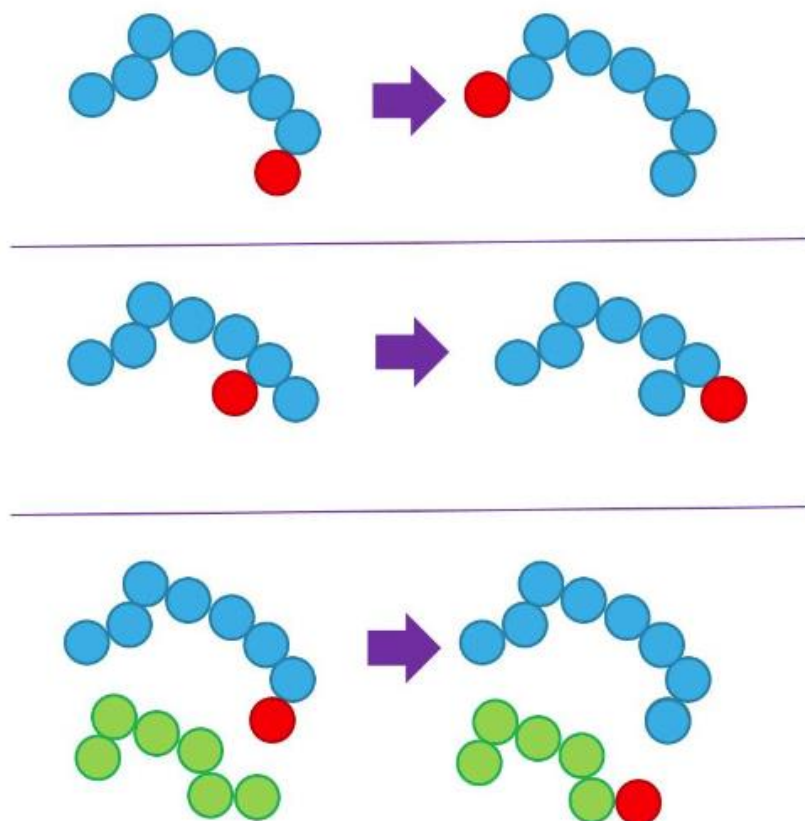


Figure 3.24: Identity Exchange Moves (IdExMs). In all cases, single monomers are coloured red and chain monomers, blue or green. From top to bottom: IdEx1 involves a chain and a single monomer at a bridgeable distance from a chain end, IdEx2 involves a chain and a single monomer at a bridgeable distance from the second monomer of the chain end, and IdEx3 involves a single monomer at a bridgeable distance from the end of a chain and another random chain.

3.3.5 Volume Fluctuation Moves

The volume fluctuation move modifies the volume of the simulation cell, and consequently, the coordinates of monomers and nanofillers without changing the connectivity and bond geometry of the chains. Thus, the volume is no longer constant and the MC simulations can be conducted on the isobaric-isothermal (NPT) ensembles [65, 294], where the number of atoms (N_{at}), the pressure (P), and the temperature (T) are constant. In addition, the move can be modified to continually shrink the simulation cell to generate denser configurations. This latter variant is called “shrinkage” and is especially relevant for reaching the high-concentration regime near the maximally random jammed (MRJ) state for athermal monomeric or polymeric systems, as explained in Section 3.2.2. For confined systems, cell compression is carried out by the MRoB algorithm, which has proved to be significantly faster than conventional volume shrinkage for systems at extreme confinement and/or very high concentrations [27].

The volume fluctuation move randomly changes the length dimensions of the simulation cell, $\mathbf{L} = (L_1, L_2, L_3)$, within a pre-defined limit ΔL_{max} according to Equation (3.27), and so modifying the volume from state m to state n . $\Delta \mathbf{L}$ is the change produced in the dimensions of the simulation cell, which is selected from the interval $[-\Delta L_{max}, +\Delta L_{max}]$. Selection is carried out using a randomly generated number ζ in the interval $[0,1)$. If the system is isotropic, the random number is the same for all dimensions, and so the change is the same in all dimensions. However, if the system exhibits anisotropy, the change is different for each dimension by generating a different random number ζ_k .

$$L_k^n = L_k^m + \Delta L_{max}(2\zeta_k - 1) = L_k^m + \Delta L_k \quad k = 1,2,3 \quad (3.27)$$

After the volume change, the coordinates of all elements inside the simulation cell are scaled according to the new volume. Therefore, chains, single monomers, and nanofillers are displaced by affine reconstruction inside the new simulation cell using a set of scaled coordinates, $\mathbf{s} = (\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_N)$. This set is calculated employing the original coordinates ($\mathbf{r}$) and dimensions ($\mathbf{L}$) according to Equation (3.28). Then, the new coordinates of the state n are determined following Equation (3.29). Chains keep their connectivity and bond geometry intact before and after the volume change, so the coordinates of the first monomer are only calculated following the equations, and the rest of the chain is rebuilt according to these coordinates, following the original bond geometry (bond length, bending, and torsion angles). Figure 3.25 shows a schematic representation of the volume fluctuation move in a 2D system.

$$\mathbf{s}_i = \mathbf{L}^{-1} \cdot \mathbf{r}_i \quad (3.28)$$

$$\mathbf{r}_i^n = \mathbf{r}_i^m + \Delta \mathbf{L} \cdot \mathbf{s}_i \quad (3.29)$$

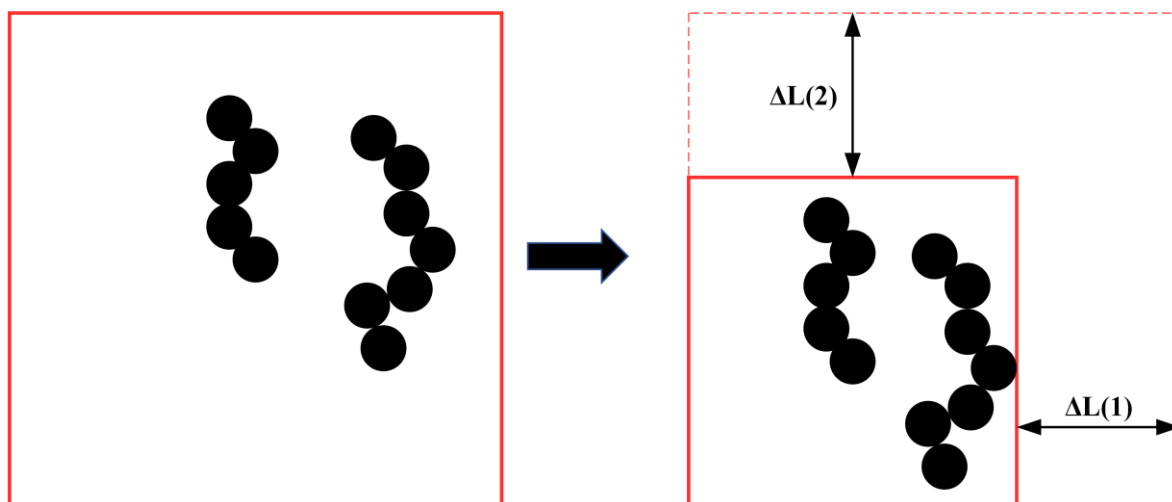


Figure 3.25: Volume fluctuation (compression) move.

Because the volume is no longer constant in the volume fluctuation move, the Metropolis criterion followed to evaluate the acceptance of the move corresponds to the isobaric-isothermal (NPT) ensemble. Thus, the transition probability P_{mn} from the state m to the state n corresponds to the expression of Equation (3.18), depending on the total energy difference ($\Delta\mathcal{V}_{nm}$) and the volume of the simulation cell in the states n and m . However, for the rest of the MC moves, the transition probability employed corresponds to the canonical (NVT) ensemble (Equation (3.14)) because the volume is not modified during the execution of these moves.

Due to the scaling of the coordinates, the total energy of the system in the new state changes with respect to the old one. The distances between all elements of the system are modified, and so are all pair-wise, non-bonded interactions. Thus, in order to calculate $\Delta\mathcal{V}_{nm}$ and, consequently, the transition probability P_{mn} , it is necessary to recalculate all these interactions in the new state n . However, the bonded energy remains constant in both states because the move does not affect the bond geometry of the chains.

After applying the Metropolis criterion, if the move is rejected, the dimensions of the simulation cell and the coordinates of the system are kept as in the state m . On the other hand, if the move is accepted, the dimensions of the simulation cell, the coordinates, and the total energy are updated to those corresponding to the new state n . Consequently, the volume change also produces a change in the packing density.

As can be understood by its description, the volume fluctuation move is a time-consuming and computationally demanding algorithm, as its attempt requires the calculation of all intermolecular and inter-species interactions. In general, the volume fluctuation move is more computationally expensive and time-consuming than the rest of the moves that displace monomer(s) or delete/add bonds (CCAMs). The volume fluctuation move, as it modifies the dimensions of the entire simulation, requires the recalculation of all pair-wise interactions

($\frac{1}{2}N_{at}(N_{at} - 1)$ calculations), while there are, at most, $2(N_{at} - 1)$ calculations of pair-wise interactions for the displacement of a monomer (the latter estimate without adopting tricks-of-the-trade like the separation of the main volume into subcells whose dimensions are dictated by the interaction range; see below).

For the shrinkage algorithm, the volume fluctuation move is modified to continually reduce the simulation cell until it reaches the desired packing density, as explained in Section 3.2.2. The algorithm shrinks the simulation cell periodically employing a constant ΔL without considering the energy and the criterion of acceptance for NPT ensembles. During a shrinkage simulation, the volume fluctuation move is accepted if there are no overlaps after the move in the new state n . The move is repeated until it reaches a target packing density with an accuracy of 10^{-7} . In this way, it is possible to generate dense configurations from dilute configurations for bulk and confined polymer systems in two or three dimensions, as well as for polymer nanocomposites.

3.3.6 Move strategy

For the best performance of the simulation, proper tuning of the strategy is carried out according to the characteristics of the simulated system, such as packing density, chain length, geometric constraints, confinement, the presence of blends, etc. Furthermore, different algorithms and strategies, such as a configurational bias (CB) pattern or the use of subcells, are included in *Simu-D* to improve the performance and efficiency of the Monte Carlo moves. Thus, key parameters of *Simu-D* are tuned for the simulation, such as the attempt probabilities of the MC moves and the number of trials for the CB pattern. These optimal values are decided by previous trial-and-error simulations for the kind of system to study.

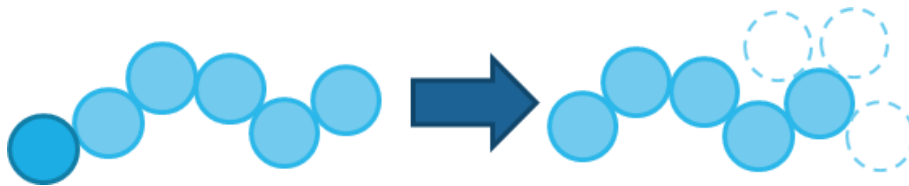
One of those key parameters to tune is the attempt probability for each MC move. The different Monte Carlo moves previously explained do not produce the same impact in the equilibration, nor require the same computational time for their execution, nor is the full set of moves required for the simulation of every system. Furthermore, too frequent attempts and acceptance of a specific move can produce a “shuttling” effect in which successive transitions cancel each other. Thus, the attempt probabilities for each MC move are tuned according to the simulation conditions to optimise the equilibration of the system. For this work, the percentages of attempt probabilities are collected in Table 3.2 for the different simulations executed. Because the systems are of pure hard-sphere chains, mainly at high densities, cluster-based moves and identity exchange (IdEx) moves are not employed (attempt probability equal to 0%).

Table 3.2: Percentage of attempt probabilities for each Monte Carlo move employed for shrinkage simulations, *NVT*-equilibrium simulations, and *NPT*-equilibrium simulations.

MC move	Attempt Probabilities (%)		
	Shrinkage Simulation	<i>NVT</i> -Equilibrium Simulation	<i>NPT</i> -Equilibrium Simulation
Reptation	10.0	10.0	10.0
Rotation	10.0	10.0	10.0
Flip	34.8	34.8	34.6
End-segment Re-arrangement	20.0	20.0	20.0
Intermolecular Reptation	25.0	25.0	25.0
Simplified End-Bridging (sEB)	0.1	0.1	0.1
Simplified Intramolecular End-Bridging (sIEB)	0.1	0.1	0.1
Volume Fluctuation	<i>*Every 10000 MC Steps</i>	0.0	0.2

Additionally, the concentration of the system is an important parameter that also affects the performance: the efficiency of local moves decreases as the packing density of the system increases. At high-volume fractions, the displacement of monomers is significantly inhibited because of the reduced available space, and so the probability of acceptance of a move is greatly reduced because of overlaps. Therefore, the equilibration efficiency of standard MC moves is poor at high packing density, as explained in [13].

The solution proposed to solve or, at least, mitigate the issue with the equilibration efficiency at increasing concentrations is the application of a Configurational Bias (CB) pattern [2, 13] for the chain moves. The Configurational Bias pattern consists of the generation of a number of trial configurations (n_{dis}) when an MC move is attempted, as can be seen in Figure 3.26 for the reptation move. Each possible configuration is constructed by modifying the newly formed torsion and/or bending angles. For every trial configuration $i = 1, 2, \dots, n_{dis}$, a probability weight $w(i)$ is assigned proportional to their energy according to $w(i) = \exp\left(\frac{-\mathcal{V}(i)}{k_B T}\right)$. A configuration i is selected among possible candidates based on its Boltzmann weight $w(i)$. In the case that all configurations lead to overlaps (infinity energy), the weight of every configuration is zero and the move is rejected.

**Figure 3.26:** Representation of the Configurational Bias (CB) pattern for a reptation move with $n_{dis} = 3$.

However, the introduction of more trials to accept the MC move in the forward transition (old $\rightarrow$ new) produces a bias in the system. This bias is removed by attempting the same number of trials in the reverse transition (new $\rightarrow$ old). So, $n_{dis} - 1$ configurations are attempted from the forward configuration (the initial state should be included in the set of the reverse trials) to guarantee microscopic reversibility. As in the case of the forward transition, the weight of each reverse configuration is determined as a function of its energy. Therefore, the acceptance criterion of a local move does not depend only on the energy difference, but also on the ratio of the weights of the forward and reverse transitions, which are the sum of the weights of each trial. The final acceptance probability P_{acc} of an MC move in a configuration bias pattern is given by:

$$P_{acc} = \min \left[1, \frac{w_{rev}}{w_{for}} \exp \left(-\frac{\Delta \mathcal{V}}{k_B T} \right) \right] \quad (3.30)$$

where w_{rev} and w_{for} are the weights of the reverse and forward transitions, respectively. Following the Metropolis criterion, a random number ζ is generated in the interval $[0,1)$ and compared with the probability P_{acc} . If $P_{acc} \geq \zeta$, the move is accepted, otherwise, it is rejected and the system returns to the state before the attempt.

In the case of CCAMs, since they do not entail a pairwise energy change, the configuration bias pattern is irrelevant. In parallel, the weights of the forward and reverse transitions are treated differently to respect microscopic reversibility. They are calculated by employing the total number of neighbour monomers (n_{CCAM}) that can initiate an sEB (or sIEB) move for the new and old chains. Therefore, the acceptance probability for CCAMs is determined by:

$$P_{acc} = \min \left[1, \frac{w_{rev}}{w_{for}} \exp \left(-\frac{\Delta \mathcal{V}}{k_B T} \right) \right] = \min \left[1, \frac{1/n_{CCAM(jend)}}{1/n_{CCAM(i)}} \exp \left(-\frac{\Delta \mathcal{V}}{k_B T} \right) \right] \quad (3.31)$$

The number of trials (n_{dis}) is carefully selected considering a balance between the computational time required per move and the improvement in the acceptance rate. Understandably, the CB pattern introduces more calculations with increasing n_{dis} , and so the simulation is more time-consuming. However, small values of n_{dis} present a low acceptance rate and, consequently, low performance at very dense and nearly jammed systems. In general, the number of trials n_{dis} increases with the increment of the concentration of the system. Its exact value is determined by trial and error on the system under study.

For the present work, the number of trials (n_{dis}) is collected in Table 3.3 as a function of the packing density (φ) and the surface coverage (φ_{sup}) for systems in three and two dimensions, respectively. Values for 3D follow the presented ones in Table 1 of Ref. [13], which

were determined through trial and error for bulk systems of hard-sphere chains. For 2D, the values have been modified according to the surface coverage to apply to a wide range of superficial densities.

Table 3.3: Number of trial positions (n_{dis}) per attempted Monte Carlo move as a function of concentration for 2D and 3D systems.

n_{dis}	Packing Density (φ)	Surface Coverage (φ_{sup})
1	< 0.10	-
5	$0.10 - 0.40$	< 0.50
10	$0.40 - 0.45$	$0.50 - 0.60$
20	$0.45 - 0.50$	$0.60 - 0.70$
40	$0.50 - 0.56$	$0.70 - 0.80$
50	$0.56 - 0.60$	> 0.80
70	$0.60 - 0.63$	-
100	> 0.63	-

Another strategy to improve the performance of *Simu-D* consists of the division of the simulation cell into sub-cells to increase the efficiency of the MC moves. The calculation of energy is the most time-consuming process in the simulations, and it is performed at every attempted transition (move). This calculation is unnecessary when the energy is calculated for a pair of atoms that lie far apart, especially if the potential model (HS, SW/SS, or LJ) has a short range. Thus, to take advantage of the short-range nature of the applied models, we split the main simulation cell into identical sub-cells with a size approximately equal to the non-bonded interaction range, for example, the monomer diameter σ for HS potential or the interaction range σ_2 for SW/SS potential. In this way, the pair-wise interactions are only calculated between the reference monomer sites that belong to the same or the adjacent sub-cells (for example, a total of 27 in 3D and a total of 9 in 2D), reducing the number of calculations per MC step. Besides, the larger the simulation cell, the greater the benefit of using the sub-cells for the calculation of non-bonded interactions. In the case of confinement, the number of adjacent sub-cells is reduced if the sub-cell is in contact with a wall. Thus, the presence of confinement accordingly reduces the number of energy calculations, but, on the other hand, the presence of walls requires further calculations of the monomer-wall interactions.

Furthermore, *Simu-D* incorporates a strategy of dual sub-cells: smaller regular ones that correspond to the collision diameter of the monomers (σ), and larger sub-cells whose size depends on the interaction range of the potential model, such as σ_2 for SW/SS potential. Thus, the mesh of size σ is first applied to check that the monomer displacement does not lead to overlaps, while, if the first check is successful, the larger mesh of σ_2 is used to perform the energy calculation of the trial configurations. In this manner, we avoid investing computational

time to calculate the energy for configurations that lead to physically unrealistic overlaps. The application of this dual sub-cell strategy is especially recommended as it improves the performance of simulations on systems with long interaction ranges ($\sigma_2 > 1.3$) at high concentrations. For systems employing the HS potential, both sub-cells practically coincide.

3.4 Post-Simulation Analysis

In the post-processing step, diverse analyses are performed to extract relevant physical information from the raw binary data of the trajectory files. Because Monte Carlo simulations do not provide dynamical information about the system due to their stochastic nature, the post-processing step is focused on the analysis of the local and global structure, self-organisation, topology, and phase behaviour.

The simulation trajectory contains information about the system, such as coordinates, chain connectivity, simulation cell size, total energy, and statistics. System configurations (“frames”) are periodically stored on the trajectory. Thus, simulation trajectories consist of huge files of hundreds to thousands of system configurations. Through homemade codes, total energy, local structure, molecular length distribution, chain sizes, etc. are extracted from the trajectories. Computer-generated visualisations of the system configurations are also an important tool for gaining a better understanding of the systems analysed. Visual inspection is performed using VMD software from the University of Illinois [295].

As stated in the Introduction, particular interest is placed on the structure, entropy-driven self-organisation, phase behaviour, and crystallisation of random packings of semi-flexible, hard-sphere polymers. For this, the development and application of descriptors are required to identify and quantify the order of the system at the local and global levels. The local order, at the level of the monomers, is gauged by the Characteristic Crystallographic Element (CCE) norm descriptor [3, 4], which identifies the disorder-order transition and quantifies the degree of crystallinity of the systems. The CCE norm is integrated into the descriptor part of the MC-based *Simu-D* suite [2]. The global order, at the level of the chains, is related to the orientational, Long-Range Order (LRO) of the chains [226], which is observed in rod-like chains (isotropic-to-nematic transition). Thus, the isotropic-to-nematic transition is identified and chain orientational order is quantified through the orientational (nematic) order parameter, q [5].

3.4.1 Characteristic Crystallographic Element (CCE) Norm

The study of phase behaviour and crystallisation requires a procedure to identify and quantify the local structure of a simulated system. The simplest approach is the visual

observation through computer-generated images of the system. However, this inaccurate approach lacks the capacity to quantify the degree of order and is prone to observer bias.

Integrated into the descriptor part of *Simu-D* [2], the Characteristic Crystallographic Element (CCE) Norm is a metric that can identify the crystalline morphology (and its absence) at the local level and accurately gauge the degree of crystallinity (local order) of an atomic or particulate system in two or three dimensions. The CCE norm descriptor is explained in more detail in Refs. [3, 4].

The crystal detection of the CCE norm is based on the concept that there exists a univocal correspondence between a given crystal and its unique set of symmetry operations (elements of its point group) [296-299]. These geometric operations correspond to inversions, rotations, mirror planes, or roto-inversions. Therefore, the CCE norm descriptor quantifies the crystallinity of a system by comparing the “real” (more precisely the “computer-generated”) local environment around each site of the system with a set of “ideal” reference X -type crystals and their respective point groups. Although in theory it is required to include all the elements of the point group of a reference crystal to determine the similarity around a given atom, in practice, a properly selected subset of symmetry elements is sufficient to discriminate between two competing crystal types, as demonstrated in previous work [300].

The current version of the CCE norm descriptor can identify similarity with respect to the following 3D crystals: Hexagonal Close-Packed (HCP), Face-Centred Cubic (FCC), Hexagonal (HEX), and Body-Centred Cubic (BCC). For 2D systems, it can identify: Triangular (TRI), Square (SQU), and Honeycomb (HON). Moreover, Fivefold (FIV) and Pentagonal (PEN) local symmetries can also be identified in three and two dimensions, respectively. These local symmetries cannot grow and fill the space periodically, as befits crystals. Sites that cannot be assigned to any of the previous reference environments are labelled as amorphous (AMO) or, more precisely, as “unidentified”.

In an atomic or particulate system, for every site i defined by its position vector $\mathbf{r}_i$, the first step of the CCE norm is to identify the nearest neighbours j ($j \in [1, N(i)]$) and the number of nearest neighbours $N(i)$ through Voronoi tessellation, employing the voro++ software [301] for 3D and the qhull software [302] for 2D. This number of nearest neighbours is compared to the coordination number of each reference crystal $N_{coord}(X)$, introducing a penalty function $\varepsilon_i^{X,0}$ if $N(i) < N_{coord}(X)$. Then, the environment of the site i , i.e. the closest $N_{coord}(X)$ neighbours j and their coordinates $\mathbf{r}_j$ (with respect to the given site), is compared for each X reference crystal employing the appropriate number of geometric symmetry elements $N_{el}(X)$ and the corresponding actions for each element $N_{act}(k, X)$. Thus, the “real” local environment of the given site i is compared against the “ideal” coordinates $\mathbf{R}_j^X$ of the reference crystal and

the transformation matrix $\mathbf{S}_{k,m}^X$ related with each k symmetry action that defines the point group. Finally, the CCE norm can generally be defined as follows:

$$\varepsilon_i^X = \varepsilon_i^{X,0} + \min \left[\frac{1}{\sigma \sqrt{N_{coord}(X) \sum_{k=1}^{N_{el}(X)} N_{act}(k,X)}} \sqrt{\sum_{k=1}^{N_{el}(X)} \sum_{m=1}^{N_{act}(k,X)} \sum_{j=1}^{N_{coord}(X)} (\mathbf{r}_j - \mathbf{S}_{k,m}^X \mathbf{R}_j^X)^2} \right] \quad (3.32)$$

Therefore, for each given site i , the calculation of the CCE norm with respect to each X reference crystal provides a value ε_i^X , which corresponds to the global minimum of the norms calculated over all possible orientations of all symmetry elements. By construction, the closer the X -CCE norm is to zero, the greater the similarity of the local environment to the respective X reference crystal. Furthermore, the CCE norm is highly discriminating, so the value of the CCE norm of a site cannot be simultaneously very low for two different reference crystals. Site i is identified as an X -type crystal when the calculated CCE norm is lower than a critical threshold, $\varepsilon_i^X < \varepsilon^{thres}$. This critical threshold adopts an empirical value of 0.245, which was determined in past studies for packings of non-overlapping spheres [3, 4, 20] in the bulk [19-22, 198, 199] and under confinement [6, 29, 30].

The process described above is repeated over all sites of the system for each X reference crystal. Once the CCE norm is calculated for each site and reference crystal, a probability distribution function of norms, $P(\varepsilon^X)$, is determined for each system configuration (frame) of the simulation trajectory. Integrating the probability distribution function below the empirical threshold, an order parameter for each X reference crystal, S^X ($S^X \in [0,1]$), can be calculated for a system configuration as:

$$S^X = \int_0^{\varepsilon^{thres}} P(\varepsilon^X) d\varepsilon^X \quad (3.33)$$

Additionally, a degree of order, degree of crystallinity or total crystallinity (τ_c) can be calculated as the sum of the order parameters of all the reference crystals for bulk, 3D systems τ_c^{3D} (Equation (3.34)) and 2D systems τ_c^{2D} (Equation (3.35)).

$$\tau_c^{3D} = \sum_{k=1}^4 \int_0^{\varepsilon^{thres}} P(\varepsilon^X) d\varepsilon^X = \sum_{k=1}^4 S^k = S^{HCP} + S^{FCC} + S^{BCC} + S^{HEX} \quad (3.34)$$

$$\tau_c^{2D} = \sum_{k=1}^3 \int_0^{\varepsilon^{thres}} P(\varepsilon^X) d\varepsilon^X = \sum_{k=1}^3 S^k = S^{TRI} + S^{SQU} + S^{HON} \quad (3.35)$$

3.4.2 Global (Long-Range) Orientational Order

The orientational, Long-Range Order (LRO) of the chains [226] is an important aspect to quantify to study the global order of a system that can present isotropic or nematic phases, especially when we simulate semi-flexible chains. In nematic order, the chains exhibit a long-range orientation with their long axis aligned along a preferential direction, the nematic director $\mathbf{n}$. The isotropic-to-nematic transition is influenced by parameters such as packing density [231, 232] and chain size ratio [228-230].

Chain orientational order is determined through averages of a second-order invariant [303]. The orientation of each molecule is defined by the unit vector $\mathbf{u}$ along the long axis of the molecule. To determine the long axis of each chain, the inertia tensor $\mathbf{I}$, a second-order tensor, is calculated using the coordinate vector of the centre of mass ($\mathbf{x}_{cm}$) of the chain and the coordinate vectors of each monomer ($\mathbf{x}_i$) in the chain according to Equation (3.36), where $N(j)$ is the number of monomers of the chain, m_i is the mass of the monomer (considered for this work as the unit), and δ is the identity tensor. The long axis of each chain corresponds to the eigenvector $\mathbf{v}_3$ of the lowest eigenvalue of the inertia tensor $\mathbf{I}$. The unit vector $\mathbf{u}$ is calculated by normalizing the eigenvector $\mathbf{v}_3$.

$$\mathbf{I} = \sum_{i=1}^{N(j)} m_i \left(\left\| \frac{\mathbf{x}_i - \mathbf{x}_{cm}}{\sigma} \right\|^2 \delta - \mathbf{x}_i \mathbf{x}_i \right) \quad (3.36)$$

$$\mathbf{u} = \frac{\mathbf{v}_3}{\|\mathbf{v}_3\|} \quad (3.37)$$

However, the vector $\mathbf{u}$ cannot be used as an order parameter since the average of the vector $\mathbf{u}_i$ over all molecules vanishes due to the centre of symmetry of molecules. Thus, the second-order tensor $\mathbf{Q}$ is defined as an average of all dyadic products of the molecular orientations according to:

$$\mathbf{Q} = \frac{1}{N_{ch}} \sum_{i=1}^{N_{ch}} \mathbf{u}_i \mathbf{u}_i - 1/3 \delta \quad (3.38)$$

The $\mathbf{Q}$ tensor counts with two properties that allow for a reduction of the number of independent terms from 9 to 5:

- 1) The $\mathbf{Q}$ tensor is symmetric ($Q_{ij} = Q_{ji}$) by definition.
- 2) The $\mathbf{Q}$ tensor is traceless, i.e. the sum of the diagonal elements is zero.

$$tr(\mathbf{Q}) = Q_{1,1} + Q_{2,2} + Q_{3,3} = 0 \quad (3.39)$$

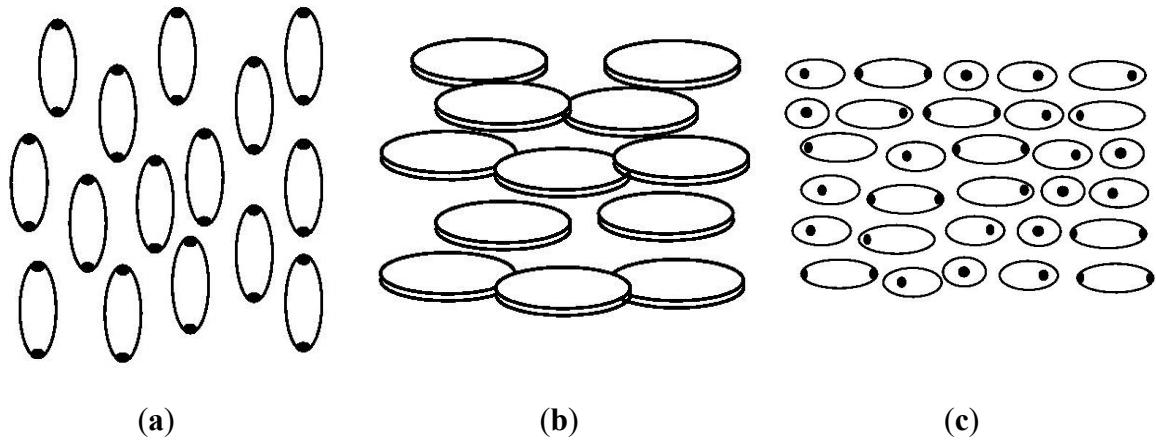


Figure 3.27: Schematic arrangements in globally ordered mesophases: (prolate) nematic mesophases, where all molecules aligned along the z -axis, with (a) prolate (PRO) and (b) oblate (OBL) mesogens and (c) oblate nematic mesophase, where molecular axes are uniformly distributed in the xy plane. Images adapted from “Fig. 4 in Ref. [303]” by Denis Andrienko licensed under [CC BY 4.0](https://creativecommons.org/licenses/by/4.0/).

The $\mathbf{Q}$ tensor can be calculated for the different ideal phases (isotropic phase; prolate mesogen, nematic mesophase; and oblate mesogen, nematic mesophase; for their schemes, see Figure 3.27). For the isotropic phase, here denoted as “ISO”, molecules can present any random orientation with equal probability, so no orientation is preferred. Thus, all components of the resulting matrix $\mathbf{Q}^{ISO}$ are zero.

$$\mathbf{Q}^{ISO} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (3.40)$$

In the perfectly aligned prolate mesogen, the long axis of every molecule is aligned along a preferred orientation (nematic director $\mathbf{n}$) leading to the nematic mesophase. In a coordinate system in which the preferred orientation of the system is along the x -axis, the matrix representation of $\mathbf{Q}$ in its own reference frame of eigenvectors for the perfect prolate mesogen, nematic mesophase, denoted here as “PRO”, takes the form:

$$\mathbf{Q}^{PRO} = \begin{pmatrix} 2/3 & 0 & 0 \\ 0 & -1/3 & 0 \\ 0 & 0 & -1/3 \end{pmatrix} \quad (3.41)$$

In the oblate mesogen, nematic mesophase, it is the short axis of the molecules that tends to align with the nematic director $\mathbf{n}$. In the same coordinate system, the matrix representation of $\mathbf{Q}$ for the oblate mesogen, nematic mesophase, here denoted as “OBL”, and oblate nematic mesophase takes the form:

$$\mathbf{Q}^{OBL} = \begin{pmatrix} -1/3 & 0 & 0 \\ 0 & 1/6 & 0 \\ 0 & 0 & 1/6 \end{pmatrix} \quad (3.42)$$

Because the $\mathbf{Q}$ tensor calculated for MC frames will, in general, not present a preferred orientation that corresponds to one of the three coordinate axes, making the physical interpretation of the mesophase difficult, the symmetric $\mathbf{Q}$ tensor is diagonalized to determine its normalized eigenvalues as unit vectors of a new Cartesian coordinate system where $\mathbf{Q}'$ is diagonal and its diagonal elements are its eigenvalues (λ_1 , λ_2 , and λ_3), ordered by decreasing absolute value (as expressed in Equation (3.43)). The eigenvector of the largest absolute eigenvalue λ_1 , in the case of a uniaxial nematic mesophase (here denoted as “NEM”), would correspond to the preferred orientation of the system or nematic director $\mathbf{n}$. That way, the diagonal $\mathbf{Q}'$ tensor allows to identify the similarities of the system with the ideal cases explained above.

A scalar-order parameter q is obtained by comparing the diagonal $\mathbf{Q}'$ tensor with the corresponding $\mathbf{Q}^{PRO}$ tensor of a perfect prolate mesogen, nematic mesophase. This scalar q represents the degree of alignment between the chains. In an isotropic system, where $\mathbf{Q}$ is the zero tensor, $q \rightarrow 0$. For a perfectly aligned prolate mesogen, nematic mesophase system, $q = 1$, while $q = -1/2$ for the ideal oblate mesogen, nematic mesophase or oblate nematic mesophase. Thus, the orientational long-range order (LRO) parameter takes values in the range $-1/2 \leq q \leq 1$.

$$\mathbf{Q}' = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} = q \begin{pmatrix} 2/3 & 0 & 0 \\ 0 & -1/3 & 0 \\ 0 & 0 & -1/3 \end{pmatrix} \quad |\lambda_1| > |\lambda_2| \geq |\lambda_3| \quad (3.43)$$

In this way, the global LRO is quantified in three dimensions (3D) by the scalar orientational order parameter q and the nematic director $\mathbf{n}$. Calculating the global LRO in two dimensions (2D) requires considering the reduction in the dimensionality of the system. Thus, the second-order tensor is instead calculated as a 2×2 matrix in the form [256]:

$$\mathbf{Q}_{2D} = \frac{1}{N_{ch}} \sum_{i=1}^{N_{ch}} \mathbf{u}_i \mathbf{u}_i - 1/2 \boldsymbol{\delta} \quad (3.44)$$

Consequently, considering the properties of the second-order tensor explained above, the second-order tensor for a system of molecules perfectly aligned in one direction (for example, direction x), i.e. leading to a perfectly nematic mesophase, corresponds to:

$$\mathbf{Q}_{2D}^{PRO} = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \quad (3.45)$$

In the same way as for three-dimensional systems, the second-order tensor $\mathbf{Q}_{2D}$ is determined and subsequently diagonalised ($\mathbf{Q}'_{2D}$). The resulting eigenvector corresponding to the largest eigenvalue defines the nematic director $\mathbf{n}$ and the eigenvalues ($|\lambda_1| > |\lambda_2|$) are compared with the expected ones for the ideal nematic case (Equation (3.45)) to calculate the nematic order parameter q .

$$\mathbf{Q}'_{2D} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & -\lambda_1 \end{pmatrix} = q \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \quad (3.46)$$

Chapter 4: RESULTS AND DISCUSSION

The objective of the present doctoral thesis is to study the structure and behaviour of semi-flexible polymers, modulated through a bending angle potential, in both two (2D) and three (3D) dimensions and how these structures compare against the ones exhibited by fully flexible (freely-jointed) polymers and their monomeric analogues. Specifically, we investigate the influence of the packing density (φ) and the equilibrium bending angle (θ_0) on the structure of random packings and the phase behaviour, self-organisation, and the short- and long-range order of semi-flexible athermal systems after long enough simulations, expanding past studies by the LSM on freely-jointed hard-sphere chains [14-21]. For that, extensive Monte Carlo (MC) simulations are executed employing the *Simu-D* suite [2] and following the hierarchical methodology explained in Chapter 3. Relevant physical results are extracted from the resulting trajectories in the post-processing step and advanced analyses are performed to identify and quantify the local and global order.

Initial semi-flexible polymer systems are created in three dimensions under dilute conditions inside a cubic cell under periodic boundary conditions (PBCs). These systems are composed of linear chains of tangent hard spheres of uniform diameter (σ). Chain lengths range widely from 6 to 1500 monomers per chain for systems of different sizes with average chain lengths $N_{av} = 12, 24, 100, 500$, or 1000 monomers per chain. All systems follow a uniform chain length distribution with the half-width set at $\Delta = 0.5$ in all cases. For example, for the system of $N_{av} = 12$, this means that chain lengths fluctuate uniformly in the interval $N \in [6, 18]$. The sizes of the different generated systems are collected in Table 3.1. Chain stiffness is effectively controlled by a bending angle potential (Equation (3.20)) that depends on a bending constant (k_θ) and an equilibrium bending angle (θ_0). The bending constant for all semi-flexible systems corresponds to $k_\theta/k_B T = 9 \text{ rad}^{-2}$ (or for simplicity $k_\theta = 9$) and the studied equilibrium bending angles are $\theta_0 = 0, 60, 90, 108$, and 120° . Figure 4.1 hosts snapshots of computer-generated configurations of short semi-flexible polymer systems for the different equilibrium bending angles simulated at dilute conditions ($\varphi = 0.10$).

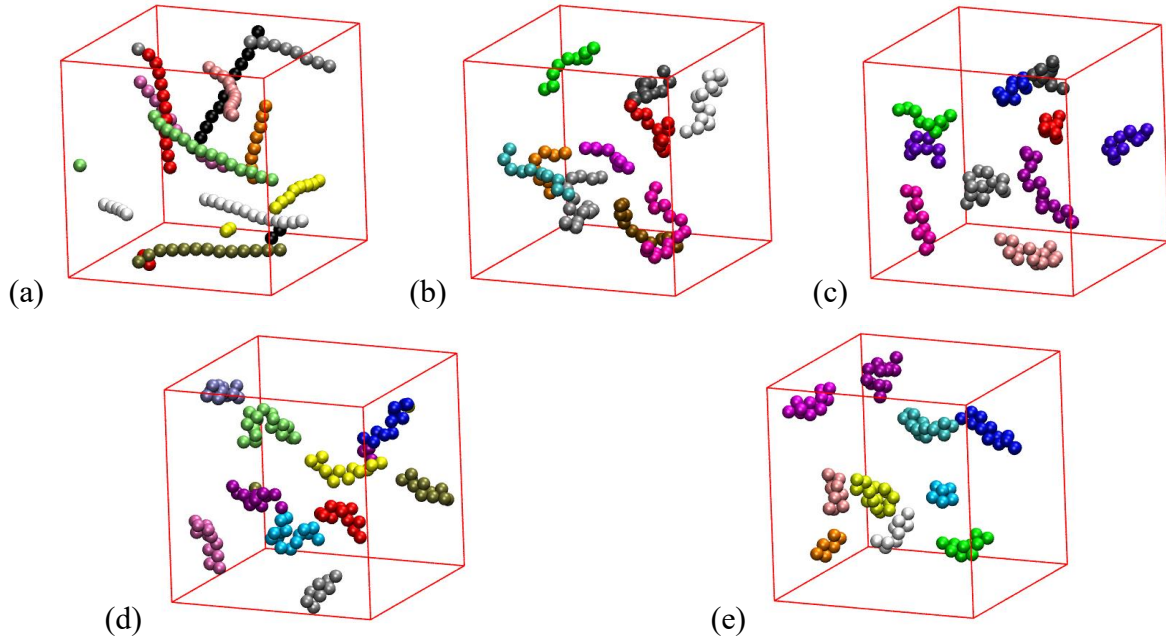


Figure 4.1: Snapshots of systems of semi-flexible, hard-sphere chains ($N_{ch} = 100$, $N_{av} = 12$) at a packing density $\varphi = 0.10$ with a bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0^\circ$ (a), 60° (b), 90° (c), 108° (d), and 120° (e). Only 10 chains are shown for clarity. Monomers are coloured according to their parent chain, and the coordinates of their centres are subjected to periodic boundary conditions. Images created with VMD visualisation software [295].

For the three-dimensional systems, the dilute initial configurations were isotropically compressed employing the shrinkage algorithm of *Simu-D*, which uses a modified volume fluctuation move, to generate polymeric systems at higher packing densities until the Random Close-Packed (RCP) limit is reached, which as will be demonstrated in the continuation depends on the equilibrium bending angle. Thus, random structures of semi-flexible polymers are analysed in the four different scaling regimes, as these are determined for freely-jointed chains [15-17]. On the other hand, for the system in two dimensions, thin polymeric films with thickness equal to the monomer diameter were created through the confinement of dilute 3D systems in one dimension and a unilateral adsorption procedure until the formation of a single-layer film. Later, thin-film systems are compressed until the RCP limit with the shrinkage algorithm, as the 3D semi-flexible systems. Again, for monolayers and the corresponding quasi-2D systems, the RCP limit depends strongly on the stiffness of the chain.

All systems generated in two and three dimensions are equilibrated in MC simulations employing the Hard Sphere (HS) model under constant volume and temperature in the canonical (NVT) ensemble. The length of the simulations ranged from 8×10^{10} to 8×10^{11} MC steps, depending on the system and, especially, the packing density employed. The results obtained from the MC simulations are analysed in the post-processing step and are presented in this chapter. First, the local and global order in dense packings of short chains is studied in three dimensions. Next, the influence of chain stiffness on the structure of random packings is analysed, exploring a wide variety of chain lengths and packing densities under the four

different scaling regimes, as determined for freely-jointed chains. Finally, we analyse the packing ability of polymers in two dimensions (thin films) as well as their short- and long-range orders for fully flexible and semi-flexible chains.

4.1 Global and Local Order

In this section, emphasis is placed on the phase behaviour of polymer chains under the effect of chain stiffness. Therefore, motivated by previous studies on the crystallisation of fully flexible chains of hard spheres [15, 18-25, 29, 30], the global and local order of semi-flexible chains of tangent hard spheres is analysed as a function of the equilibrium bending angle (θ_0) and packing density (φ). This is achieved by processing the MC trajectories of length that range from 2×10^{11} to 8×10^{11} MC steps, of mainly dense packings ($\varphi > 0.50$) of short chains ($N_{av} = 12$). The global order, at the level of chains, is quantified through the orientational (nematic), Long-Range Order (LRO) parameter (q) [5, 303]. The local order, at the level of monomers, is gauged through the Characteristic Crystallographic Element (CCE) norm descriptor [3, 4]. Compiling the results of the simulated systems, phase diagrams are presented to reflect the combined effect of packing density and equilibrium bending angle on the local and global orders of the semi-flexible polymers. The results of this section have been partially published in: Martínez-Fernández, D.; Herranz, M.; Foteinopoulou, K.; Karayiannis, N.C.; Laso, M. *Local and Global Order in Dense Packings of Semi-Flexible Polymers of Hard Spheres*. *Polymers*, 2023, 15 (3), 551. <https://doi.org/10.3390/polym15030551> (article available in [5]).

As a previous step, a preliminary visual inspection of the initial and final system configurations of the MC simulations is performed. Computer-generated snapshots at the end of the simulation are shown in Figure 4.2 for the studied semi-flexible hard-sphere systems of short chains at $\varphi = 0.60$. Through these preliminary visualisations with monomers colour-coded according to the parent chain, self-organisation at the level of monomers (local structure) is observable when some of the semi-flexible systems reach high packing densities, similar to the trends observed for freely-jointed (fully flexible) chains [15, 19-21].

In the case of rod-like chains ($\theta_0 = 0^\circ$), the visual inspection of the initial configurations from Figure 4.3 suggests a transition from an isotropic ($\varphi = 0.10$ and 0.20) to a nematic phase ($\varphi = 0.30$ and 0.50) with increasing packing density i.e., the rod-like chains align collectively along the common nematic director. According to the configurations observed, this transition occurs at a packing density lower than for solidification, which qualitatively agrees with past independent works on similar systems [226, 231, 232].

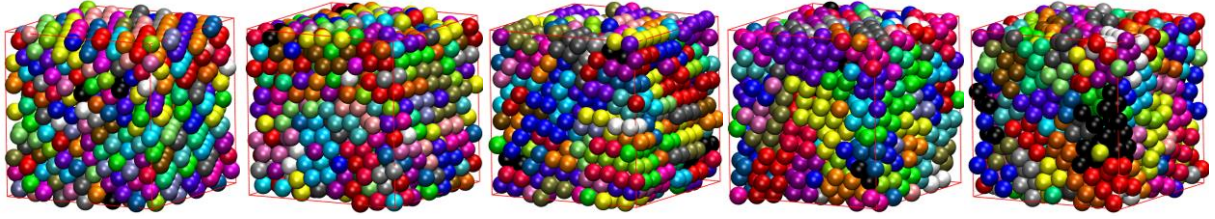


Figure 4.2: Snapshots of the final configurations from MC simulations on 100-chain systems of semi-flexible, hard-sphere chains of average chain length $N_{av} = 12$ at $\varphi = 0.60$ with $k_\theta = 9$ and equilibrium bending angles (from left to right) $\theta_0 = 0, 60, 90, 108$, and 120° . Monomers are coloured according to the parent chain. The coordinates of monomers are subjected to periodic boundary conditions in all dimensions. Images created with VMD visualisation software [295].

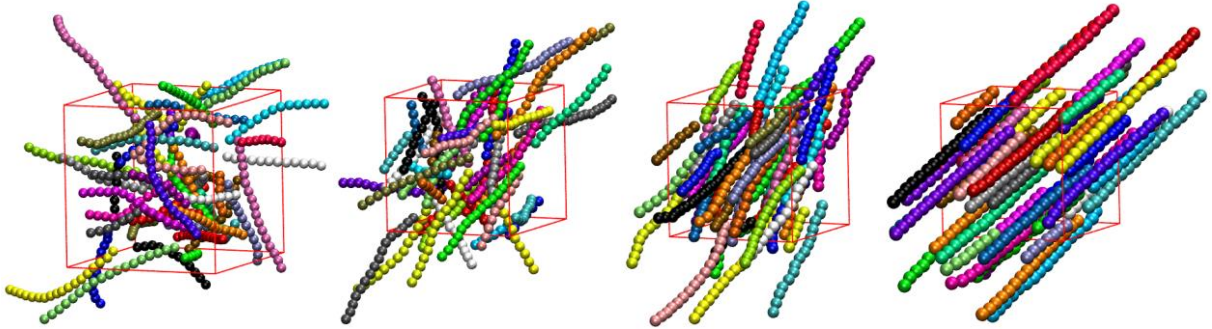


Figure 4.3: Visual representations of the initial configurations for the 100-chains, $N_{av} = 12$, $k_\theta = 9$, $\theta_0 = 0^\circ$ system showing at increasing packing densities, $\varphi = 0.10, 0.20, 0.30$, and 0.60 (from left to right). Monomers are coloured according to the parent chain, and their coordinates are fully unwrapped in space. For clarity, only 50 chains (half of the total population) are shown. Images created with VMD visualisation software [295].

4.1.1 Global Order: Long-range orientation

Following the preliminary visual inspection of the initial configurations of the studied semi-flexible polymer systems, the global order is analysed through the second-order tensor ($\mathbf{Q}$) and the scalar (nematic) long-range order (LRO) parameter (q), as explained in Section 3.4.2. Thus, the orientational ordering (isotropic/nematic) at the level of the chains is identified and quantified. The dependence of the nematic order parameter (q) on the packing density (φ) is presented in Figure 4.4 for all semi-flexible systems of $N_{av} = 12$ under study ($\theta_0 = 0, 60, 90, 108$, and 120°), averaged over all frames of the equilibrated part of the simulation trajectory. In line with Figure 4.3, an increase in packing density is associated with an increase in the degree of alignment or LRO parameter (q) for the rod-like chains. Thus, rod-like chains of average chain length $N_{av} = 12$ show a well-defined isotropic-nematic transition in the interval $0.15 \leq \varphi \leq 0.20$, closely resembling the prediction of Onsager's theory and the findings of similar past simulation studies [226-232]. Due to the unentangled initial configurations of the systems observed in Figure 4.3, rod-like systems become progressively more stable in their respective phases with the increase of the LRO. At higher volume fractions, the rod-like chains form a prolate mesogen, nematic mesophase (PRO). Finally, a perfect PRO phase ($q \rightarrow 1$) is established at packing densities approximately equal to $\varphi = 0.45$. The transition from the isotropic to the nematic phase, ISO $\rightarrow$ PRO (i.e., nematic mesophase with

prolate mesogen) for rod-like athermal chains occurs at significantly lower packing densities ($\varphi^{nem}(N_{av} = 12) \approx 0.20$) than the freezing ($\varphi_{monomers}^F \approx 0.495$) and melting ($\varphi_{monomers}^M \approx 0.545$) points of monomeric hard spheres and the melting transition of fully flexible chains ($\varphi_{chains}^F \approx 0.57$).

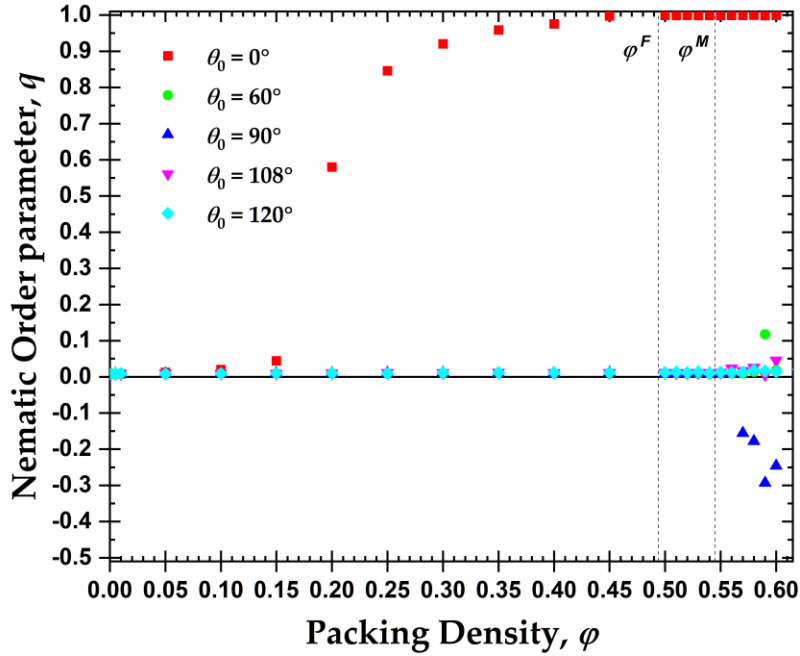


Figure 4.4: Evolution of the LRO (nematic) parameter (q) as a function of the packing density (φ) for 100-chain, $N_{av} = 12$ systems at different equilibrium bending angles (θ_0). The freezing ($\varphi_{monomers}^F \approx 0.495$) and melting ($\varphi_{monomers}^M \approx 0.545$) points of monomeric hard spheres are also shown as dashed vertical lines for comparison.

A comparison of the isotropic-to-nematic transition for the different rod-like systems is shown in Figure 4.5 by means of the evolution of the LRO parameter (q) as a function of the packing density (φ) for rod-like systems of different average chain lengths (N_{av}). As for chains of $N_{av} = 12$, all rod-like systems transit to an orientational nematic order at packing densities lower than the solidification point for hard-sphere polymers and monomers, reaching high values of LRO, $q \rightarrow 1$, independently of the chain length. This isotropic-to-nematic transition shifts to lower concentrations with the increase of the chain length (N) of the rod-like polymers. Additionally, increasing the chain length speeds up the transition process until it stabilises for systems with an average chain length of $N_{av} = 500$ and 1000. Thus, the perfect PRO phase is formed at lower packing densities with longer rod-like chains, from packing densities at $\varphi = 0.10$ for rod-like chains of $N_{av} = 500$ and 1000 to $\varphi = 0.45$ for $N_{av} = 12$. This dependence of chain length agrees with the phase diagrams for spherocylinders developed by Bolhuis and Frenkel, who established that the isotropic-to-nematic transition moves to lower densities with increasing shape anisotropy L/D of mesogens [227]. Khokhlov and Semenov also determined this behaviour for polymers as a function of the size ratio of the chains [228-230].

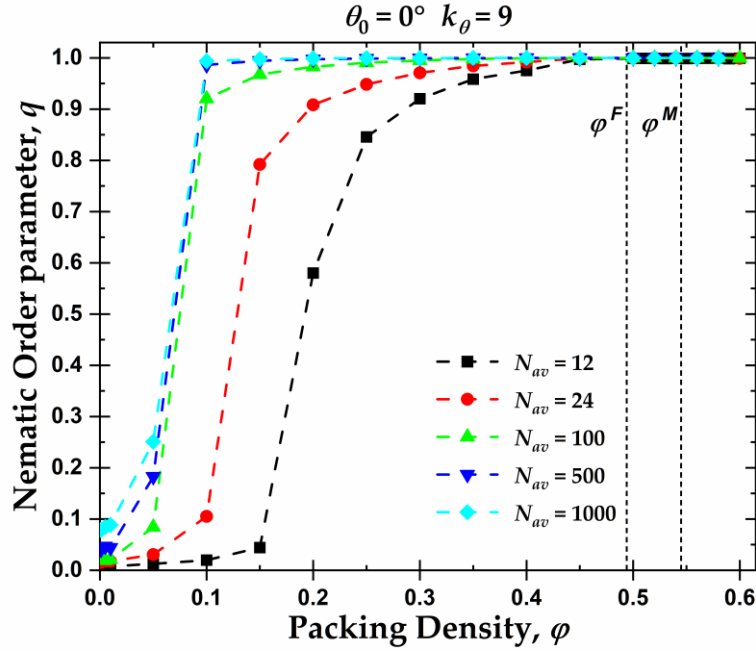


Figure 4.5: Evolution of the LRO (nematic) parameter (q) as a function of the packing density (ϕ) for systems of rod-like chains ($\theta_0 = 0^\circ$, $k_\theta = 9$) with different average chain length (N_{av}). The freezing ($\phi_{monomers}^F \approx 0.495$) and melting ($\phi_{monomers}^M \approx 0.545$) points of monomeric hard spheres are also shown as dashed vertical lines for comparison. Dashed lines between scatter points are a visual aid.

In addition to the expected isotropic-to-nematic (ISO $\rightarrow$ PRO) transition exhibited by rod-like chains, a nematic mesophase with oblate mesogen (OBL, $q < 0$) is also observed in Figure 4.4 for semi-flexible chains with $\theta_0 = 90^\circ$. In contrast to the orientational LRO of rod-like chains, the isotropic-to-oblate (ISO $\rightarrow$ OBL) transition takes place at $\phi^{obl} \approx 0.57$, which is higher than the melting point of hard spheres but is very close to the established range for fully flexible chains of hard spheres.

For the remaining values of the equilibrium bending angles, each chain system remains in the isotropic phase (ISO, $q \rightarrow 0$) over the whole concentration range as long as the $N_{av} = 12$ realization is concerned. Although a small peak is produced at very high packing densities for chains primarily of $\theta_0 = 60^\circ$, corresponding to the values of the LRO parameter of around $q \approx 0.15$, this can be associated with chains taking some preferred directions for the establishment of the FCC and HCP crystallites (see below in Local Order: Crystallisation). These crystallites enforce specific bending angles that are compatible with these crystals. If such bending angles are not available through intra-chain arrangements, then the only other option is inter-chain ones, thus inducing partial alignment among the chains at a local level.

Further insights into the orientational order for semi-flexible chains with $\theta_0 = 90^\circ$ can be gleaned from the evolution of the exponential running average of the LRO parameter (q) as a function of the MC steps (Figure 4.6) for the packing densities where a certain degree of nematic order was observed in Figure 4.4. After a sufficiently long simulation time, a tendency is observed for the formation of an oblate mesogen, nematic mesophase, whose LRO increases

with the volume fraction, as shown by q approaching the ideal value $-1/2$ for the OBL phase. Comparing this evolution with the crystallisation at the level of monomers (see below in Local Order: Crystallisation in Figure 4.12), the ISO $\rightarrow$ OBL transition for $\theta_0 = 90^\circ$ practically coincides with crystallisation i.e., self-organisation at the local and global levels appear synchronized.

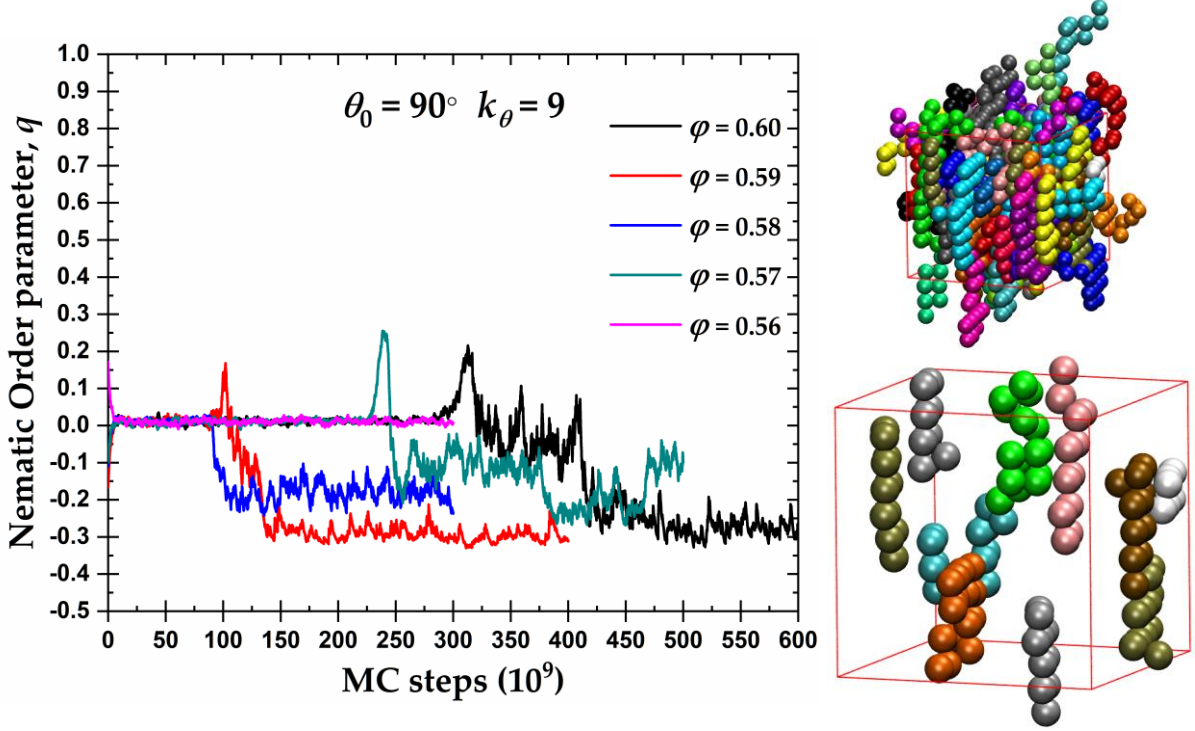


Figure 4.6: (Left) Exponential moving average of the LRO parameter (q) as a function of MC steps for the 100-chain, $N_{av} = 12$ system with bending constant $k_\theta = 9$ and equilibrium bending angle $\theta_0 = 90^\circ$ at different packing densities (φ). (Right) Snapshots of the system at $\varphi = 0.59$ showing all 100 chains (top) and 10 randomly selected chains (bottom). Coordinates of the monomers are fully unwrapped in space, and monomers are coloured according to the parent chain. Images created with VMD visualisation software [295].

The right panels of Figure 4.6 show semi-flexible chains with $\theta_0 = 90^\circ$ at $\varphi = 0.59$ at the end of the MC simulation, once the system has reached the OBL state. The top snapshot presents the unwrapped semi-flexible chains of the complete system. The bottom snapshot contains only 10 randomly selected chains from the same system for clarity. Right-angle semi-flexible chains tend to form flat layers, occasionally interrupted by approximately right-angle jumps between planes, which is geometrically consistent with the constraint of $\theta_0 = 90^\circ$. These flat chain configurations (oblate mesogens) generally have a common behaviour that further explains the OBL phase in Figure 4.4 and the left panel of Figure 4.6.

4.1.2 Local Order: Crystallisation

The local structure is gauged by means of the CCE norm descriptor [3, 4] (see Section 3.4.1 for explanation). For consistency with previous studies of the LSM on flexible chains of hard spheres, a threshold of $\varepsilon^{thres} = 0.245$ is employed to label a site as X -type,

where X is the reference crystal or local symmetry. For the analysis of semi-flexible chains in three dimensions, X corresponds to hexagonal close-packed (HCP), face-centred cubic (FCC), and fivefold (FIV), given that no appreciable population of body-centred cubic (BCC) or simple hexagonal (HEX) sites is detected in any of the simulated systems. The results from semi-flexible systems are also compared with those of fully flexible (freely-jointed) chains of tangent hard spheres simulated and analysed through the *Simu-D* software under the same conditions of packing density and average chain length [18-21, 25].

Figure 4.7 presents the CCE-based order parameters for HCP (S^{HCP}), FCC (S^{FCC}), and FIV (S^{FIV}), along with the degree of crystallinity (τ_c) as a function of the MC steps for all the semi-flexible systems at a packing density $\varphi = 0.59$, including the fully flexible one as reference. This packing density is higher than the packing density for the melting transition of the freely-jointed hard-sphere chains [19-21, 23]. An inspection of all the panels shows clearly that the mechanism of the phase transition, here in the form of crystallisation, is very similar among them, including the freely-jointed chains, and rather independent of the equilibrium bending angle. The initial packings are amorphous (AMO) as the fraction of sites with non-ordered local structure is vastly dominant: the percentage of close-packed sites does not exceed 5% and, in most cases, the FIV population is commensurate or even exceeds the combined HCP+FCC one. This initial state of the AMO athermal chain packings is consistent with previous works on dense monomeric and polymer assemblies [21, 30, 198-200]. Out of all the systems, the rod-like one is characterised by the lowest population of FIV sites, as FIV appears to be incompatible with the perfect nematic ordering exhibited by the chains at this range of volume fractions.

Once crystallites of the HCP and FCC characters start growing, the fraction of the FIV-like sites gradually decreases, at almost identical rates, until it practically disappears. The structural competition, observed here for all semi-flexible chain systems, between the FIV local symmetry and crystallisation in the form of the HCP and FCC sites is in perfect match with identical observations in simulations of the fully flexible chain [19-23, 29, 30] and monomeric HS systems [198, 199], including bead-spring under quenching [204, 304]. Once the population of FIV sites practically disappears, a trend manifestly valid for all of the simulated packings, the relative fractions of the HCP and FCC crystals undergo a sharp variation, which is followed by the establishment of the final, stable ordered structures of the crystalline (CRY) character. For semi-flexible systems at $\varphi = 0.59$, the average degree of crystallinity in the final CRY phase approximately ranges between 0.60 and 0.85, with the lowest and highest values corresponding to the semi-flexible chains with $\theta_0 = 60^\circ$ and rod-like chains, respectively.

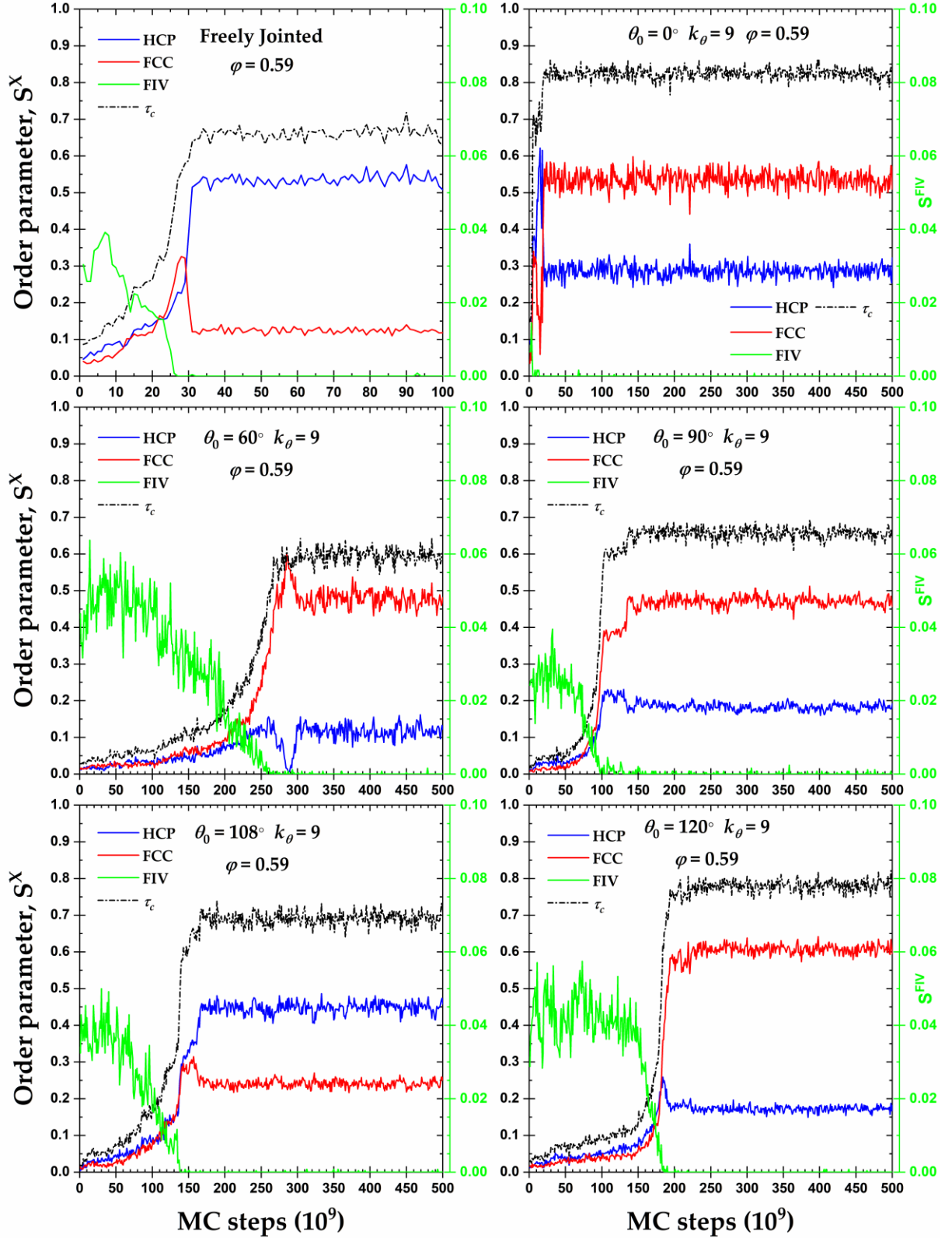


Figure 4.7: Crystal nucleation and growth, as quantified by the evolution of the HCP, S^{HCP} , and FCC, S^{FCC} , order parameters (**left y-axis**), and the fraction of fivefold-like sites, S^{FIV} (**right y-axis**), as a function of MC steps for 100-chain, $N_{av} = 12$ systems of freely-jointed chains and semi-flexible chains with bending constant $k_\theta = 9$ and equilibrium bending angle $\theta_0 = 0, 60, 90, 108$, and 120° at a packing density $\varphi = 0.59$.

As seen in the graphs of Figure 4.7, all the formed crystals at $\varphi = 0.59$ contain appreciable fractions of the HCP and FCC sites, and no perfection is registered. Therefore, one expects that the morphologies correspond to fivefold-free but defect-ridden random hexagonal close-packed (rHCP) crystals. Figure 4.8 shows the snapshots at the beginning and the end of the corresponding MC simulations for all the systems presented in Figure 4.7. All initial configurations show amorphous structures (small yellow spheres) with a remarkable population of FIV-like sites (green spheres). At the end of the MC simulations, the crystalline phase of every system shows a stable configuration of mixed HCP/FCC structures, being defect-ridden and fivefold-free. In their majority, the semi-flexible chain packings form rHCP structures of alternating layers of unique FCC and HCP character with a single stacking direction, as in the freely-jointed chains (a). Additionally, the semi-flexible systems can also form crystal structures with multiple, random stacking directions, as observed for the system with $\theta_0 = 90^\circ$ (d).

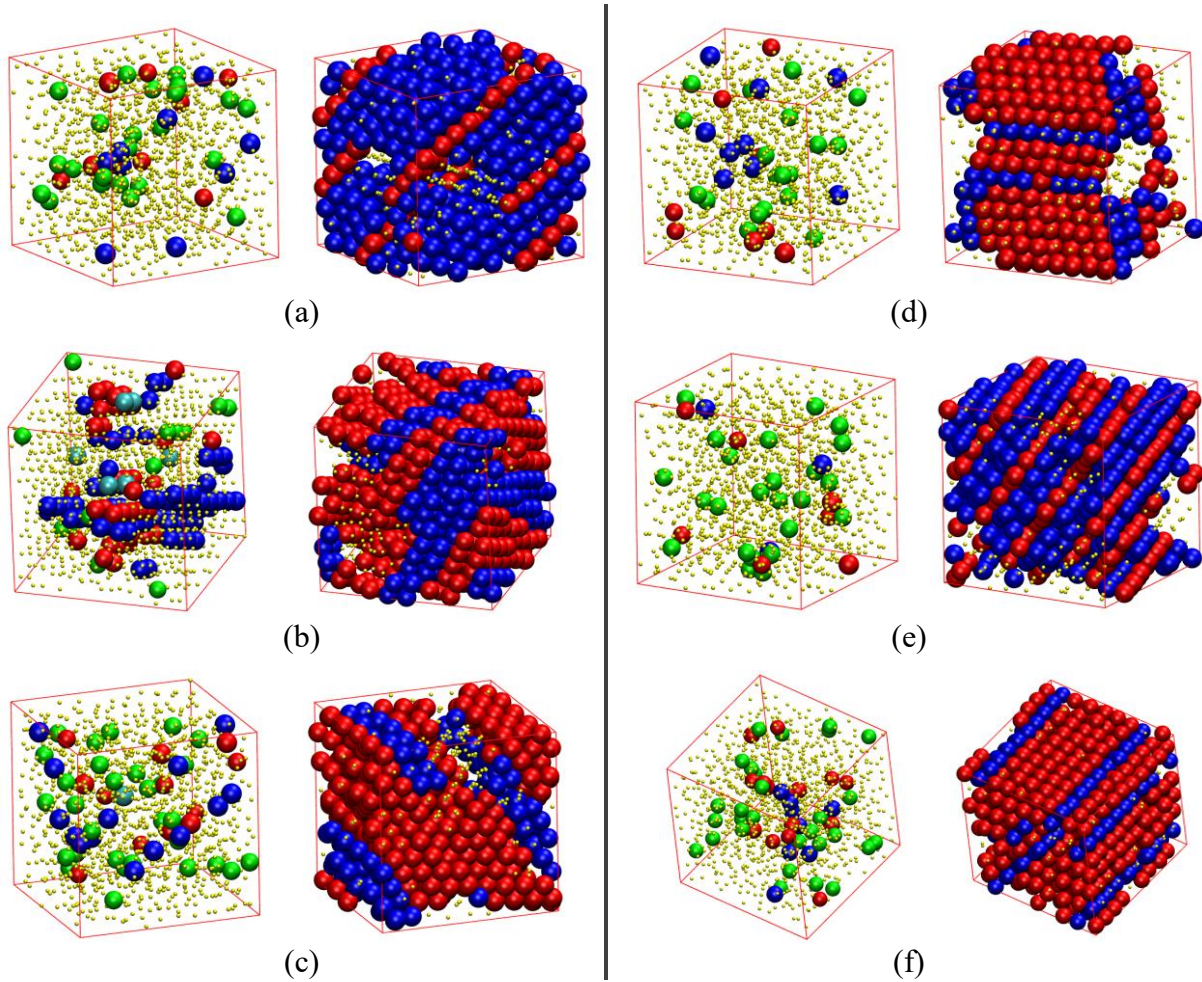


Figure 4.8: Computer-generated representations of the initial (**left**) and final (**right**) configurations of the MC simulations for the 100-chain, $N_{av} = 12$ systems at $\varphi = 0.59$ of freely-jointed chains (a) and semi-flexible chains ($k_\theta = 9$) with equilibrium bending angle $\theta_0 = 0^\circ$ (b), 60° (c), 90° (d), 108° (e), and 120° (f). Monomers are colour-coded according to the CCE norm. Blue, red, cyan, purple, and green correspond to HCP-, FCC-, BCC-, HEX-, and FIV-like sites, respectively. Amorphous (AMO) sites are coloured yellow and are shown with reduced dimensions for visual clarity. Images created with VMD visualisation software [295].

Although almost all the semi-flexible systems crystallise into rHCP crystals of mixed HCP/FCC layers, two important exceptions are identified for the rod-like chains at $\varphi = 0.58$ and $\varphi = 0.60$. Figure 4.9 ($\varphi = 0.58$) and Figure 4.10 ($\varphi = 0.60$) present the CCE-based local order parameters (S^X) and the total crystallinity (τ_c) as a function of the MC steps, together with the CCE-based snapshots for the final configurations. Both systems show very similar trends: after a very short initial period, characterised by the rapid increase in the HCP and FCC sites and the parallel reduction of the FIV population, the growth rates start to differ, and one type grows in favour of the other. At $\varphi = 0.58$, the resulting morphology is an almost perfect FCC crystal ($\tau_c = 0.83$, $S^{FCC} = 0.83$), while the opposite occurs at $\varphi = 0.60$, where a (less) perfect HCP crystal emanates ($\tau_c = 0.77$, $S^{HCP} = 0.74$). In the case of the HCP crystal at $\varphi = 0.60$, the resulting structure is not as stable as that of the FCC crystal, alternating between the almost perfect HCP crystal ($S^{FCC} \rightarrow 0$) and an HCP crystal with a small population of FCC-like sites ($S^{FCC} \approx 0.1$). For the latter case, when FCC “impurities” appear in the HCP crystal, these are produced on the border of the crystal with a regime of defects in the form of amorphous or “unidentified” (AMO) sites. Figure 4.11 shows a computer-generated CCE-based visualisation of the crystal nucleation and growth for the rod-like chains at $\varphi = 0.58$ and $\varphi = 0.60$, as explained in Figure 4.9 and Figure 4.10.

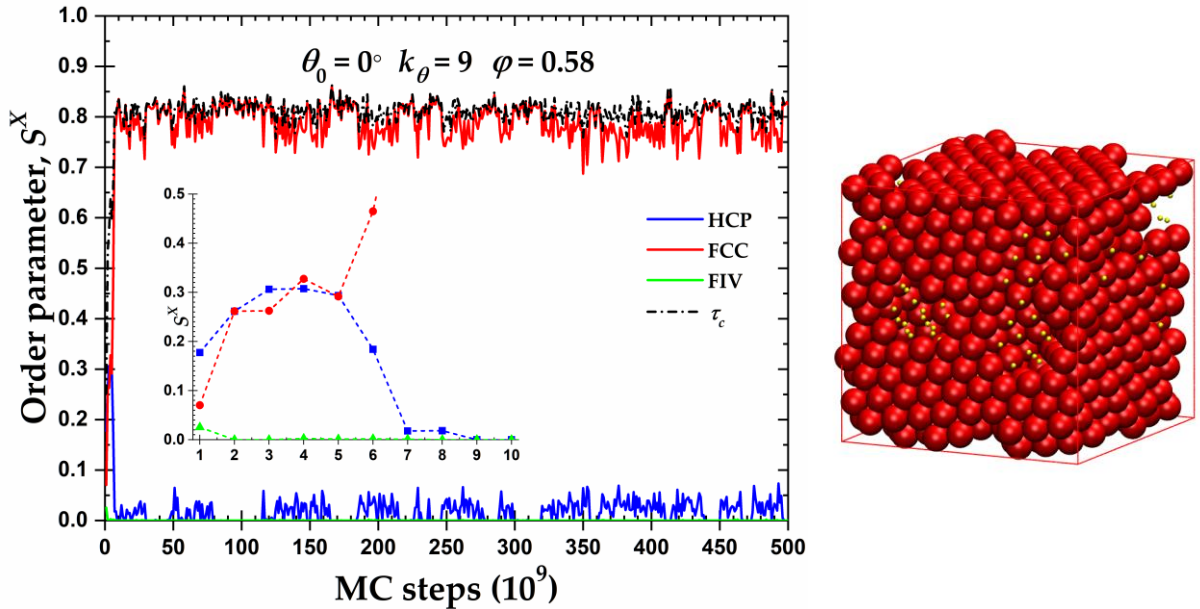


Figure 4.9: (Left) CCE norm order parameter (S^X) as a function of MC steps for the 100-chain, $N_{av} = 12$ system of semi-flexible chains with bending constant $k_\theta = 9$ and equilibrium bending angle $\theta_0 = 0^\circ$ at packing density $\varphi = 0.58$. Inset corresponds to the early part of the MC trajectory (10×10^9 MC steps). Dashed black line corresponds to the degree of crystallinity (τ_c). (Right) Snapshot of the final configuration of the same system. Monomers are colour-coded according to the CCE norm. Blue, red, and green correspond to HCP-, FCC-, and FIV-like sites, respectively. Amorphous (AMO) sites are coloured yellow and are shown with reduced dimensions for visual clarity. Images created with VMD visualisation software [295].

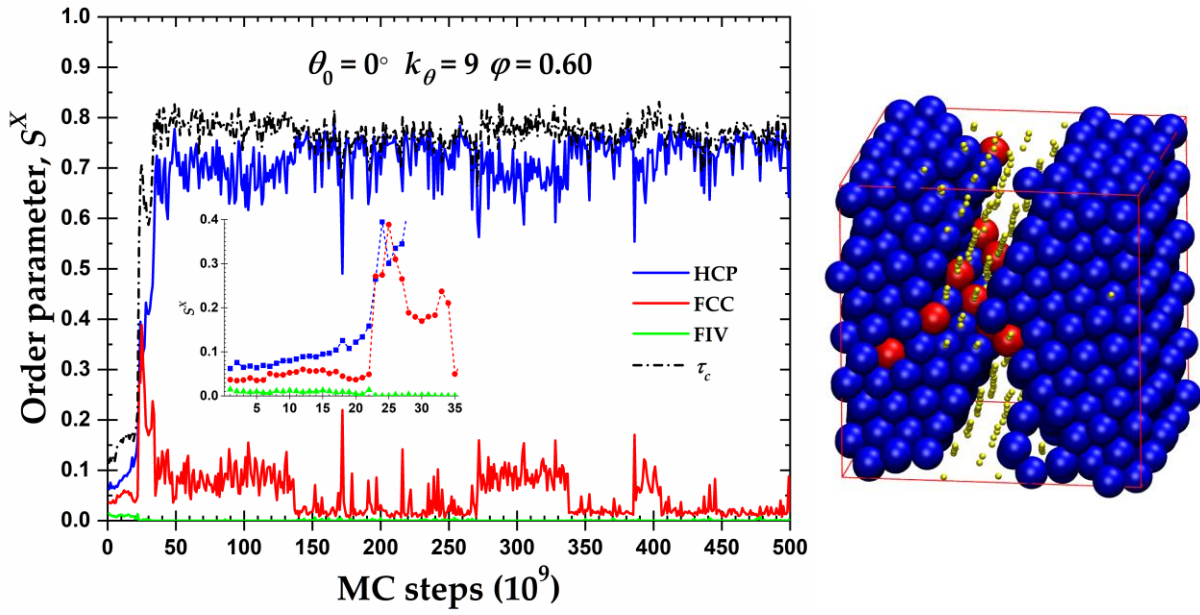


Figure 4.10: Same as Figure 4.9 for the semi-flexible system chain at $\varphi = 0.60$. Inset corresponds to the early part of the MC trajectory (35×10^9 MC steps).

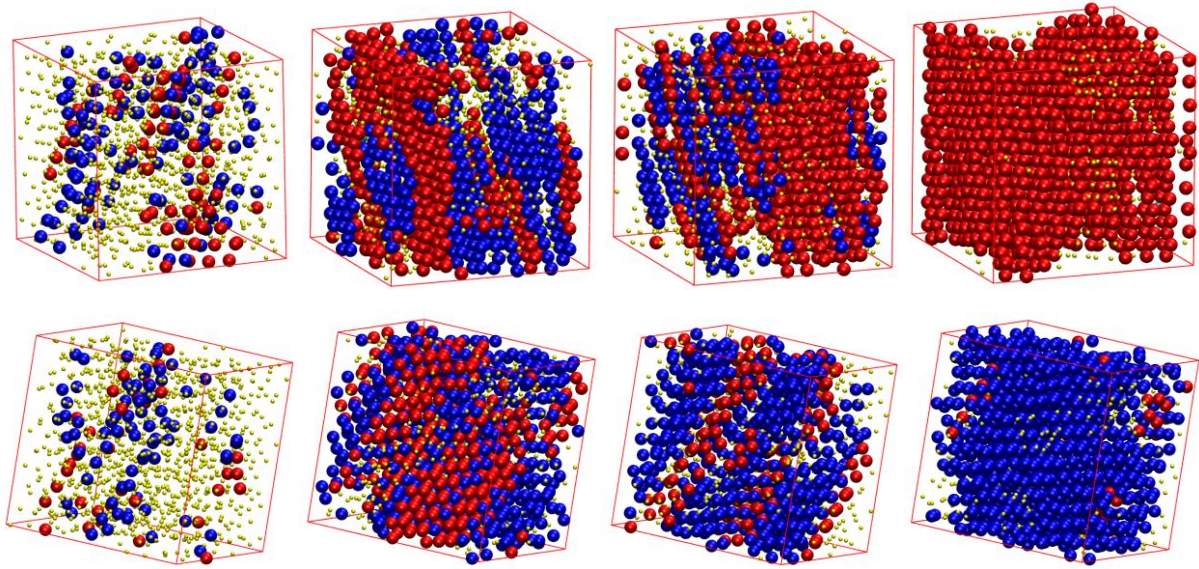


Figure 4.11: Computer-generated representations of the crystal growth for the 100-chain, $N_{av} = 12$ semi-flexible systems with bending constant $k_\theta = 9$ and equilibrium angle $\theta_0 = 0^\circ$ at a packing density of $\varphi = 0.58$ (**top**) after 1, 25, 60, and 100×10^8 MC steps (from left to right, respectively) and $\varphi = 0.60$ (**bottom**) after 1, 240, 300, and 350×10^8 MC steps (from left to right, respectively). Monomers are colour-coded according to the CCE norm. Blue, red, and green correspond to HCP-, FCC-, and FIV-like sites, respectively. Amorphous (AMO) sites are coloured yellow. For visual clarity, monomers are shown with reduced dimensions. Images created with VMD visualisation software [295].

Although perfection in the form of an FCC crystal has been reported very recently from extremely long simulations on freely-jointed chains of hard spheres [23], it is the first time that an almost perfect HCP crystal, made of hard-sphere chains in extended rod-like conformations, is observed. The ease with which the crystal perfection is observed could be related to the nematic ordering exhibited by the rod-like chains.

The total degree of crystallinity (τ_c) for all semi-flexible systems of average chain length $N_{av} = 12$, along with the ones of fully flexible (freely-jointed) analogues is shown in Figure 4.12 as the evolution of the degree of crystallinity as a function of MC steps at different packing densities (φ) more specifically, at all simulated packing densities in the vicinity of the melting point for chains of tangent hard spheres, $\varphi_{chains}^M (> 0.56)$ [19, 20, 22], or higher. In comparison to the corresponding graph for freely-jointed polymers, the rod-like chains present semi-crystalline and crystalline phases due to the effect of the nematic ordering at packing densities significantly lower than the melting point of freely-jointed chains, but also of monomeric hard spheres. On the other hand, for semi-flexible chains with $\theta_0 = 60^\circ$, crystallisation is produced at a higher volume fraction than all of the other systems, as at $\varphi = 0.57$ no crystal nucleation and growth is observed in the corresponding graph, even after a generally sufficient long simulation time (6×10^{11} MC steps).

Based on the results of Figure 4.12 and using the value of total crystallinity in the final, stable part of the MC simulation, a one-dimensional phase diagram of local order is further extracted and compiled in Figure 4.13 as a function of the packing density and the equilibrium bending angle. As stated numerous times, the local order of the phase diagram is quantified by the degree of crystallinity. It is worth remembering here that the melting point for monomeric hard spheres is $\varphi_{monomers}^M = 0.545$, while freely-jointed chains of tangent hard spheres crystallize at higher volume fractions, $\varphi_{chains}^M (> 0.56)$. Some important conclusions can be drawn from the diagram. First, as seen in Figure 4.12 and as the most important simulation finding, all semi-flexible chain packings eventually crystallise, independently of the equilibrium bending angle. Second, the equilibrium bending angle affects profoundly the onset of the phase transition of the systems. For example, the rod-like chains present semi-crystalline and crystalline phases at packing densities significantly lower than the melting point for freely-jointed chains, even lower than the melting point for monomeric hard spheres, due to the effect of the nematic (global) ordering that precedes the local order (as will be demonstrated in the continuation). Finally, based on the above, the melting transition shows the trend: $\varphi_{chains}^M(0^\circ) < \varphi_{monomers}^M = 0.545 < \varphi_{chains}^M(120^\circ) < \varphi_{chains}^M(108^\circ) < \varphi_{chains}^M(90^\circ) = \varphi_{chains}^M(FJ) < \varphi_{chains}^M(60^\circ)$.

In general, with the sole exception of rod-like chains, the presence of constraints related to bond geometry in the form of bonds or bending angles increases the melting transition with respect to the monomeric analogues. Nevertheless, it is quite surprising that the systems with obtuse bending angles ($\theta_0 = 120$ and 108°) crystallise earlier, and the right angle ($\theta_0 = 90^\circ$) crystallise at a very similar packing density as the fully flexible chains, which are completely free of bending constraints. Obtuse angles are favoured at high packing densities, as they minimise the local volume compared to acute ones. However, one should consider the fact that only specific geometric arrangements of polymer chains are compatible with the connectivity

of neighbouring sites of ideal FCC and HCP crystals. For example, FCC and HCP share bending angles of 0, 60, 90, and 120°, while angles of 33.5 and 70.5° exist exclusively in the HCP crystal [23]. The lack of bending angles compatible with these crystals would require the adjacent sites to be occupied by monomers belonging to other chains, imposing specific arrangements at the intermolecular level.

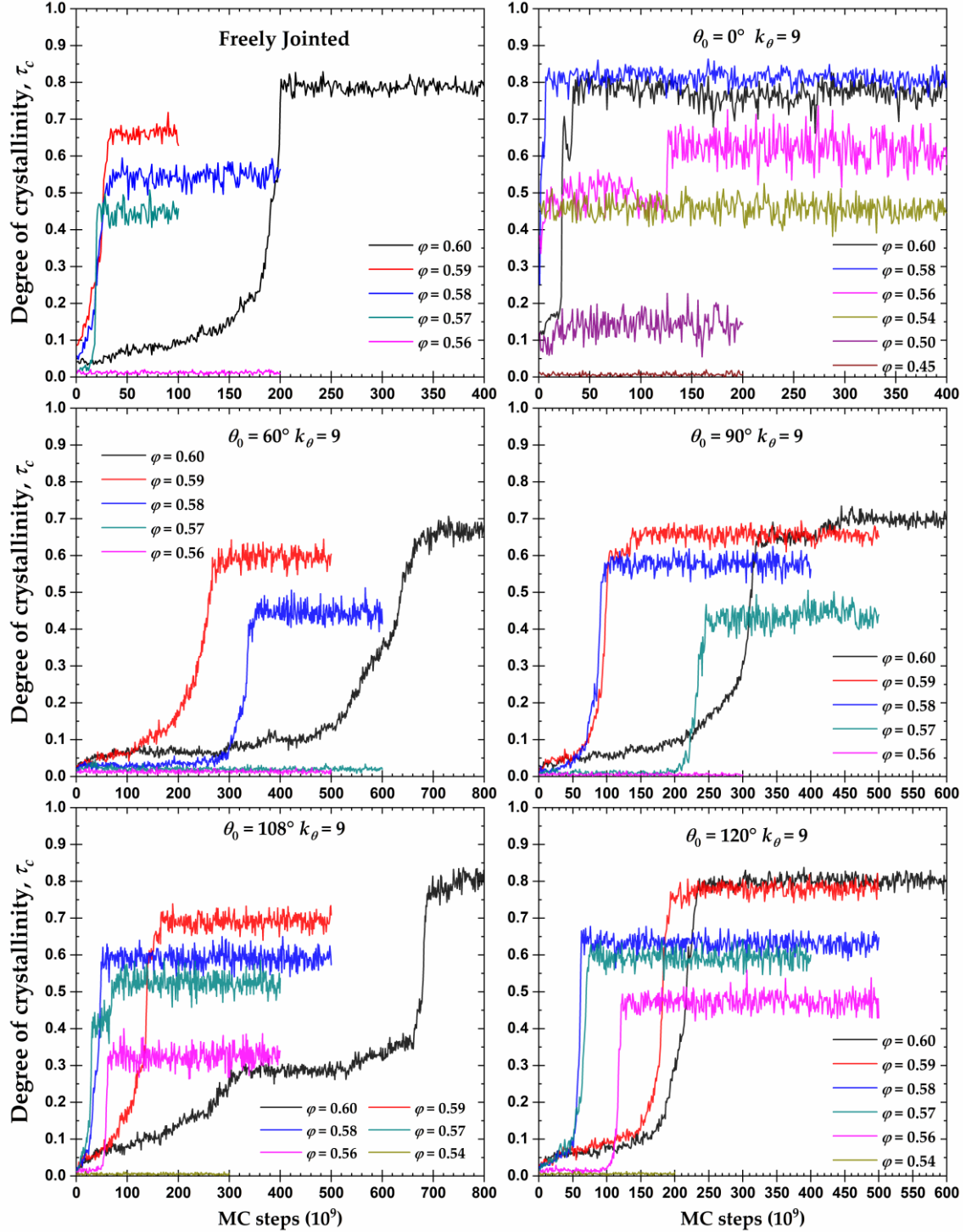


Figure 4.12: Degree of crystallinity (τ_c) as a function of MC steps at different packing densities (ϕ) for 100-chain, $N_{av} = 12$ systems of freely-jointed chains and semi-flexible chains with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° .

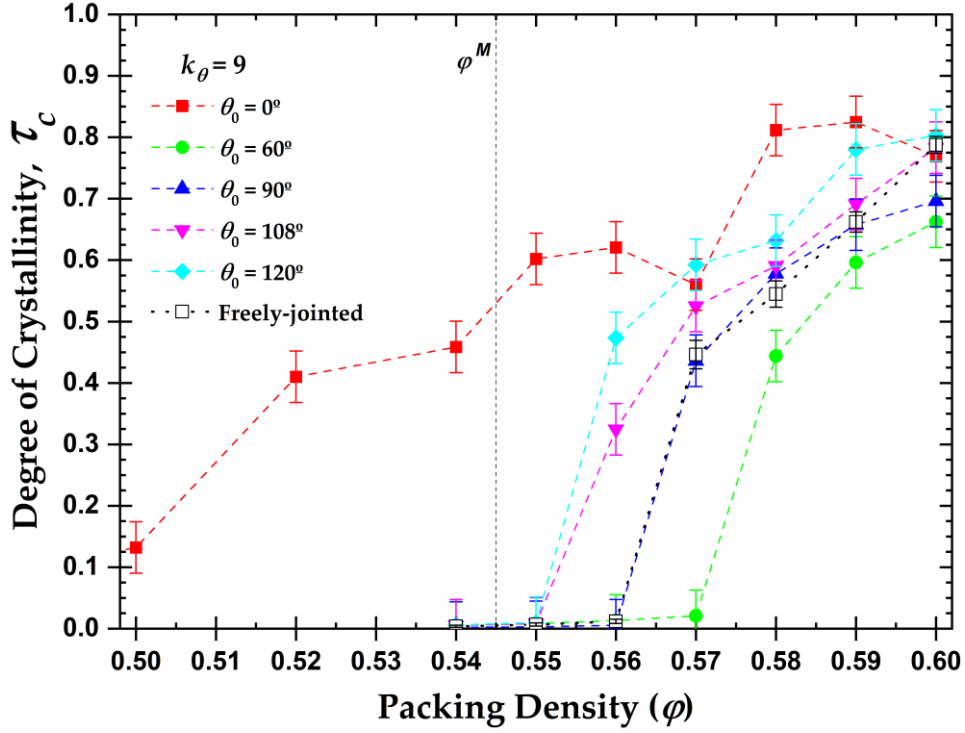


Figure 4.13: Degree of crystallinity (τ_c) as a function of packing density (ϕ) and equilibrium bending angle (θ_0) for 100-chain, $N_{av} = 12$ system of semi-flexible chains with bending constant $k_\theta = 9$ (filled symbols) and freely-jointed chains (open square). Dashed lines connecting points are used as visual aid. Vertical dashed line corresponds to the melting transition ($\phi_{monomers}^M \approx 0.545$) for monomeric hard spheres.

The phase behaviour at the local (CCE-based crystallinity, τ_c) and global (orientational LRO parameter, q) levels as a function of the density for rod-like and right-angle chains are presented in Figure 4.14. As was explained above and based on the data in Figure 4.4, the rod-like chains present an isotropic-to-nematic transition for short chains of average chain length $N_{av} = 12$ at $\phi^{nem} \approx 0.20$, a packing density significantly lower than the freezing point for monomeric hard spheres ($\phi_{monomers}^F = 0.494$), in accordance with the trends presented in Refs. [231, 232]. At packing densities close to the freezing point, these rod-like systems reach a practically perfect PRO phase. According to Shakirov and Paul [206], the rod-like chains self-arrange into a 2D hexagonal crystal structure in the plane perpendicular to the nematic director at a packing density $\phi = 0.47$, driven by 2D translational entropy. Thus, those 2D hexagonal crystal structures evolve into a 3D semi-crystalline phase of rHCP structures with the increase in concentration in the range between the freezing and melting point for monomeric hard spheres. After the melting point for monomeric hard spheres is reached, the nematic systems start to crystallise in the HCP, FCC, or mixed HCP/FCC structures, maintaining the nematic order. Thus, rod-like systems pack at high densities into Nematic Close Packed (NCP) structures, as was observed by independent researchers through MD simulations [203, 204].

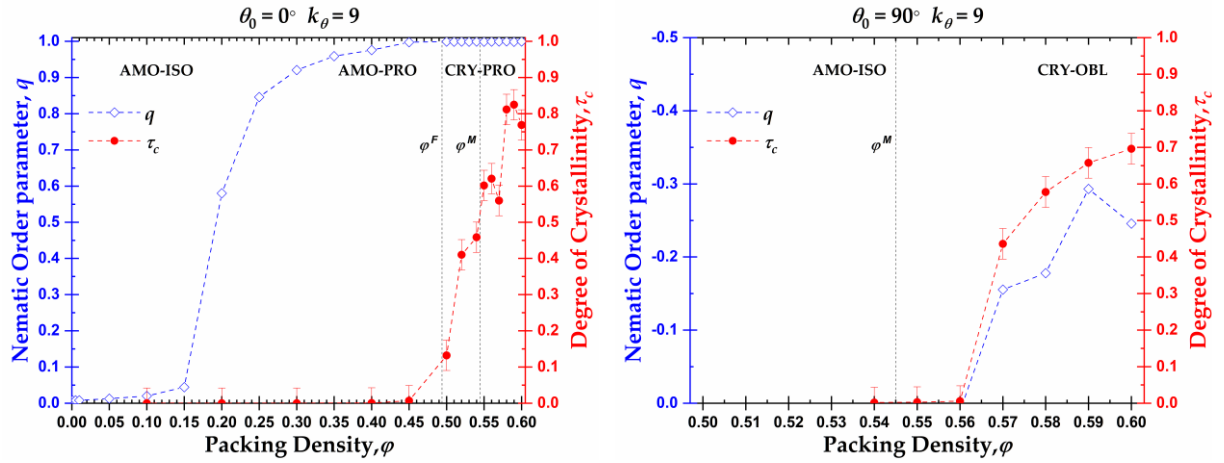


Figure 4.14: Orientational order parameter, q (left y-axis, blue colour), and crystallinity, τ_c (right y-axis, red colour), as a function of the packing density, ϕ , for 100-chain, $N_{av} = 12$ system of semi-flexible chains with bending constant $k_\theta = 9$ and equilibrium bending angle $\theta_0 = 0^\circ$ (left) and $\theta_0 = 90^\circ$ (right). Dashed lines connecting points are used as visual aid. The freezing ($\phi_{monomers}^F \approx 0.495$) and melting ($\phi_{monomers}^M \approx 0.545$) points of monomeric hard spheres are also shown as dashed vertical lines for comparison.

Therefore, based on the local and global phase behaviour, the one-dimensional diagram as a function of the packing density (Figure 4.14) can be divided into distinct regions, marked by XX-YY, where the first index XX corresponds to the local structure (XX = AMO or CRY) and the second index YY to the global structure (YY = ISO, PRO, or OBL). Consequently, for the rod-like chains studied in this section ($N_{av} = 12$, $k_\theta = 9$, $\theta_0 = 0^\circ$), the following approximate three domains of phase behaviour (left panel of Figure 4.14) are observed: (i) AMO-ISO ($\phi \leq 0.15$), where the system is amorphous at the local level and isotropic at the global; (ii) AMO-PRO ($0.20 \leq \phi \leq 0.45$), where the packing is amorphous locally and nematic with prolate mesogens globally; (iii) CRY-PRO ($0.50 \leq \phi$), where the system shows crystallinity in the form of HCP and FCC close-packed morphologies of varied degrees of perfection and perfect nematic ordering of prolate mesogens at the global orientational level. When comparing the local and global trends, a delay is evident as the local order is established at packing densities significantly higher than the ones for the ISO $\rightarrow$ PRO transition. This delay, as seen in Figure 4.5, will be affected by the length of the rod-like chains.

In the case of the right-angle chains ($\theta_0 = 90^\circ$), the phase behaviour is quite different compared to rod-like chains, as seen in the right panel of Figure 4.14. First, we should note that the small decrease in the orientational LRO can be attributed to higher statistical uncertainty, as the higher the packing density and the closer to jamming, the more difficult the sampling, even when such advanced MC algorithms are employed. Consequently, significantly longer simulations are required, and the statistical uncertainty is higher. The right-angle systems crystallise once they reach packing densities higher than the melting point for monomeric hard spheres ($\phi_{monomers}^M = 0.545$). Then, the ISO $\rightarrow$ OBL transition occurs simultaneously with the crystal nucleation and growth. The formation of rHCP structures requires a semi-nematic OBL

phase for the right-angle systems, as the right-angle chain exists but is not dominant in the FCC and HCP crystals. Accordingly, for their creation, specific inter-chain alignments are required. As a result, local and global orders are established simultaneously and no delay is observed. Therefore, the phase diagram for right-angle chains consists of only two regimes: (i) AMO-ISO ($\varphi \leq 0.56$), where the system is amorphous at the local level and isotropic at the global; and (ii) CRY-OBL ($\varphi > 0.15$), where the system shows rHCP morphologies and a nematic order of oblate mesogens.

4.1.3 Local Chain Structure: Amorphous vs Crystal

In previous studies of LSM, the entropic origins of the spontaneous crystallisation of athermal dense packings of freely-jointed polymers were revealed as a self-arrangement of monomers adopting specific conformations in order to the local environment of monomers becomes more symmetric, isotropic and spherical in the crystal phase. Thus, monomers can explore more efficiently the accessible volume in their close vicinity, increasing the translational entropy. Consequently, during the disorder (amorphous) to order (crystal) transition, losses in conformational and orientational entropy, due to the conformational and structural alteration of the systems, are compensated by a significantly larger increase in translational entropy. This total increase in entropy drives the transition of athermal, fully flexible polymer packings to random hexagonal close-packed (rHCP) morphologies [18, 20, 21, 23] in the majority of constant-volume simulations. However, if simulation time is significantly extended, transitions between polymorphs can be observed eventually leading to the formation of a defect-free FCC crystal [23, 24]. With a process of crystallisation similar to that of fully flexible polymers, chain conformations and sphere arrangements for semi-flexible polymeric systems are studied in disordered and ordered states, realising a comparison to the athermal polymer systems of freely-jointed chains of tangent hard spheres studied in Refs. [18, 20, 21]. This comparison focuses especially on the characteristic conformations that emerge after the phase transition.

It was shown above that semi-flexible chains of tangent hard spheres transit from an initial amorphous phase to a crystalline phase with generally rHCP morphology after long enough simulations, similar to fully flexible systems. Neighbour sites that conform ideal FCC and HCP structures adopt specific bending angles of $\theta = 0, 60, 90$, and 120° , while conformations of $\theta = 33.5$ and 70.5° are only present in HCP structures. Figure 4.15 presents the probability distributions of bending angles in the amorphous (AMO) and crystalline (CRY) phases for the semi-flexible polymeric systems studied with different equilibrium bending angles ($\theta_0 = 0, 60, 90, 108$, and 120°) at a packing density of $\varphi = 0.59$. After the crystallisation, all systems present an appreciable change in the bending angle distributions with peaks compatible with rHCP structures. Semi-flexible polymer systems with $\theta_0 = 0$ and 120°

present narrow distributions with very sharp peaks in the amorphous phase, while these peaks are broader in the crystalline phase. In return, there is a small increase in the probability density for bending angles close to the equilibrium bending angle, especially for $\theta_0 = 120^\circ$. This behaviour increases the flexibility of the chains to allow for the self-arrangement of the monomers and the formation of the HCP and FCC local environments. On the other hand, the wide distribution curves for the systems with $\theta_0 = 60$ and 90° change to show sharper peaks centred around the equilibrium bending angle. In addition, these curves present tails for larger bending angles, which result in more compact systems. For the system with $\theta_0 = 108^\circ$, the distribution curve is initially distorted with respect to its equilibrium bending angle because the local packing of the system is enforced by the high volume fraction. After crystallisation, two characteristic peaks grow for 90° and 120° , the closest bending angles (to $\theta_0 = 108^\circ$) that are compatible with the HCP and FCC structures. The emergence of these peaks in the crystal phase should be because these bending angles are within reach given ($\pm 20^\circ$) for the employed bending constant.

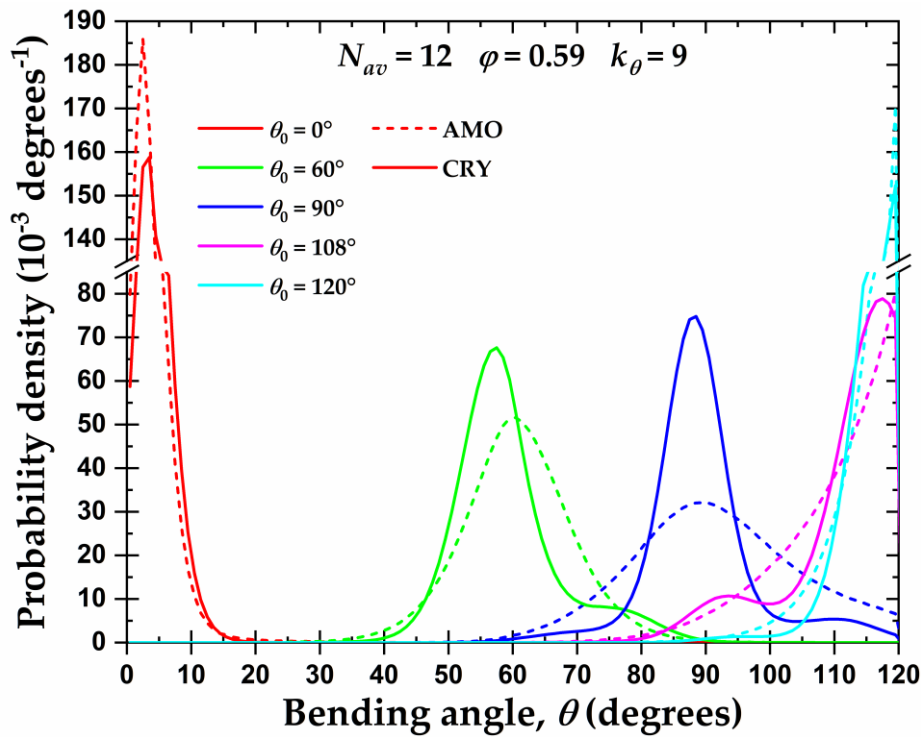


Figure 4.15: Distribution of bending angle (θ) in the initial disordered (amorphous, AMO) and final ordered (crystalline, CRY) phases for 100-chain, $N_{av} = 12$ semi-flexible systems with bending constant $k_\theta = 9$ and different equilibrium bending angles (θ_0) at a packing density of $\varphi = 0.59$.

In Figure 4.16, the probability distribution of torsion angles is shown for semi-flexible polymers with different equilibrium bending angles at different high packing densities. Clearly, characteristic torsional conformations are adopted as the systems crystallise. Torsion angle distributions for the different semi-flexible systems present very sharp peaks, whose maxima (and minima) increase (and decrease) with the packing density, after the disorder-order

transition, following a behaviour very similar to that of fully flexible chains [20]. These characteristic peaks correspond to torsional conformations of 0, 70.5, 109.5, 124, and 120°, which are expected to appear in the HCP and FCC structures. The case of rod-like systems ($\theta_0 = 0^\circ$) is an exception: differences in the distribution between the amorphous and the crystal phase are almost negligible for the whole density range, except at the highest packing density shown here. In this case, the peak of the co-planar, all-trans maximum is more intense in the ordered state compared to the disordered one. Both the equilibrium bending angle, which leads to the formation of straight trimers, and the establishment of the global nematic order promote this specific conformation and, consequently, the chain stiffness of these polymers as straight chains.

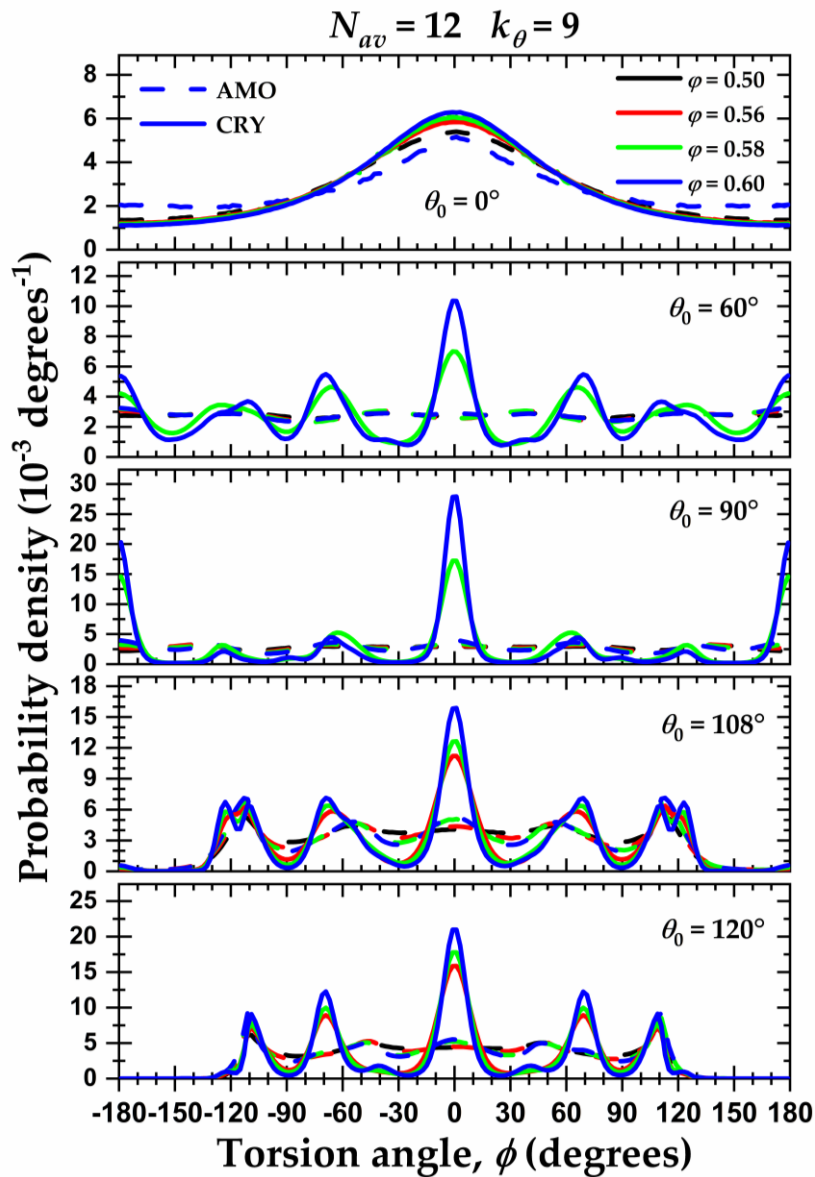


Figure 4.16: Distributions of torsion angle (ϕ) in the initial disordered (amorphous, AMO) and final ordered (crystalline, CRY) phases for 100-chain, $N_{av} = 12$ semi-flexible systems with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° (from top to bottom, respectively) at different packing densities (ϕ). Dashed lines correspond to amorphous phase. Solid lines, crystalline phase.

The change in the torsion angle distribution for the $\theta_0 = 90^\circ$ systems during the disorder-order transition is remarkable. After crystallisation, right-angle chains adopt very specific torsional conformations with very sharp peaks at 0° and $\pm 180^\circ$ and wide, almost flat regions of zero probability. This preference for trans ($\phi = 0^\circ$) and cis ($\phi = \pm 180^\circ$), co-planar conformations, together with very small maxima at $\pm 90^\circ$, in the crystalline phase is correlated with the tendency of the right-angle chains to form oblate mesogens, as observed in Figure 4.6.

Another remarkable behaviour during the phase transition is observed for polymer systems with $\theta_0 = 108^\circ$ and 120° . In the amorphous phase, these systems have a preference for gauche- and gauche+ states ($\phi = \pm 120^\circ$) compared to other local conformations, especially extended ones (explained more extensively in Section 4.2.1). Both conformations lead to a reduction of the chain size due to the collapse of the local geometry. However, after crystallisation, the systems adopt trans-local conformations, which lead to fully extended chains and an increase in chain size. Therefore, at constant volume, the crystallisation of semi-flexible systems with $\theta_0 = 108^\circ$ and 120° leads to an increase in chain size, while inter-chain packing occupies the rest of the required sites of the local environment to conform the HCP and FCC structures.

The radial (i.e. orientationally averaged) arrangement of the systems during the phase transition is presented in Figure 4.17, which shows the intramolecular, $w_{intra}(r)$, and intermolecular, $g_{inter}(r)$, pair radial distributions at a packing density of $\varphi = 0.60$ for different equilibrium bending angles. As expected, the intramolecular pair radial density, $w_{intra}(r)$, is determined by the equilibrium bending angle. After crystallisation, peaks for all semi-flexible systems become sharper, while their positions remain unaffected by the transition. For the systems with $\theta_0 = 108^\circ$ and 120° , a new maximum peak appears in the previous minimum at approximately $r = \sqrt{2}$ after the transition, leading to coiled conformations. These systems present an intramolecular behaviour which is very similar to one of the freely-jointed chains, except for the absence of the strong peak at $r = 2$ [18, 20]. The system that shows the greatest variation in $w_{intra}(r)$ between the amorphous and crystalline phases corresponds to $\theta_0 = 90^\circ$, where the sharp maxima and minima are due to specific preferred polymer conformations adopted in the crystalline phase that give rise to oblate mesogens. In contrast to $w_{intra}(r)$, the intermolecular distribution function, $g_{inter}(r)$, shows similar trends for all semi-flexible systems studied, presenting only slight differences in the intensity of the peaks. These curves are similar to those observed in the crystallization of freely-jointed athermal polymers [18, 20]. The specific intramolecular arrangements of each equilibrium bending angle, especially for the extended semi-flexible polymers such as $\theta_0 = 0^\circ$, 60° , and 90° , cannot provide all the neighbours required in the local environment of the crystal structures by themselves. Thus, the appearance of characteristic peaks and minima in the crystalline phase for all semi-flexible systems attests that monomers of other chains, through inter-chain interactions, cover the

positions required to complete the local environment corresponding to the HCP and FCC structures.

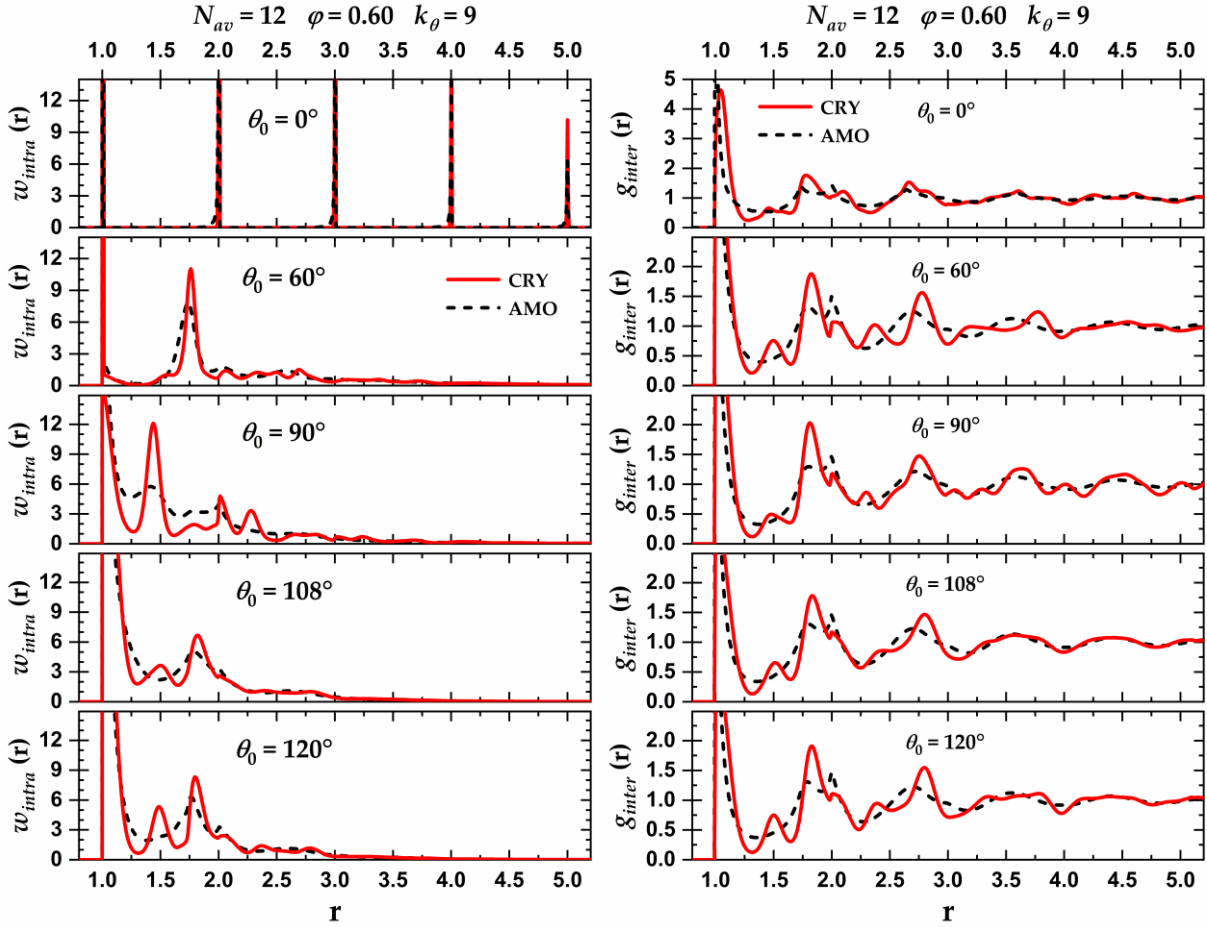


Figure 4.17: (Left) Intramolecular pair radial density function, $w_{intra}(r)$, and (Right) intermolecular pair radial distribution function, $g_{inter}(r)$, as functions of radial distance, r , in the initial disordered (amorphous, AMO) and final ordered (crystalline, CRY) phases for 100-chain, $N_{av} = 12$ semi-flexible systems with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° (from top to bottom, respectively) at a packing density of $\varphi = 0.60$. Dashed black lines correspond to amorphous phase. Solid red lines correspond to crystalline phase.

Figure 4.18 presents the total pair radial distribution functions, $g_{total}(r)$, in the initial amorphous and final crystalline phases for the different equilibrium bending angles at a packing density of $\varphi = 0.60$. The total sphere arrangement in the crystalline phase is very similar for all semi-flexible systems with different equilibrium bending angles, as well as fully flexible polymers [18, 20]. The formed HCP and FCC structures, while resulting from different intra- and inter-molecular arrangements between the different bending angles, are structurally very similar, if not identical, especially if the systems reach similar degrees of ordering (crystallinities). Therefore, the arrangement of the monomers for semi-flexible polymers during the disorder-order transition can be considered universal and independent of the equilibrium bending angle, finally giving rise to crystals of random hexagonal close-packed (rHCP) structure, as stated previously in Figure 4.7 and Figure 4.8.

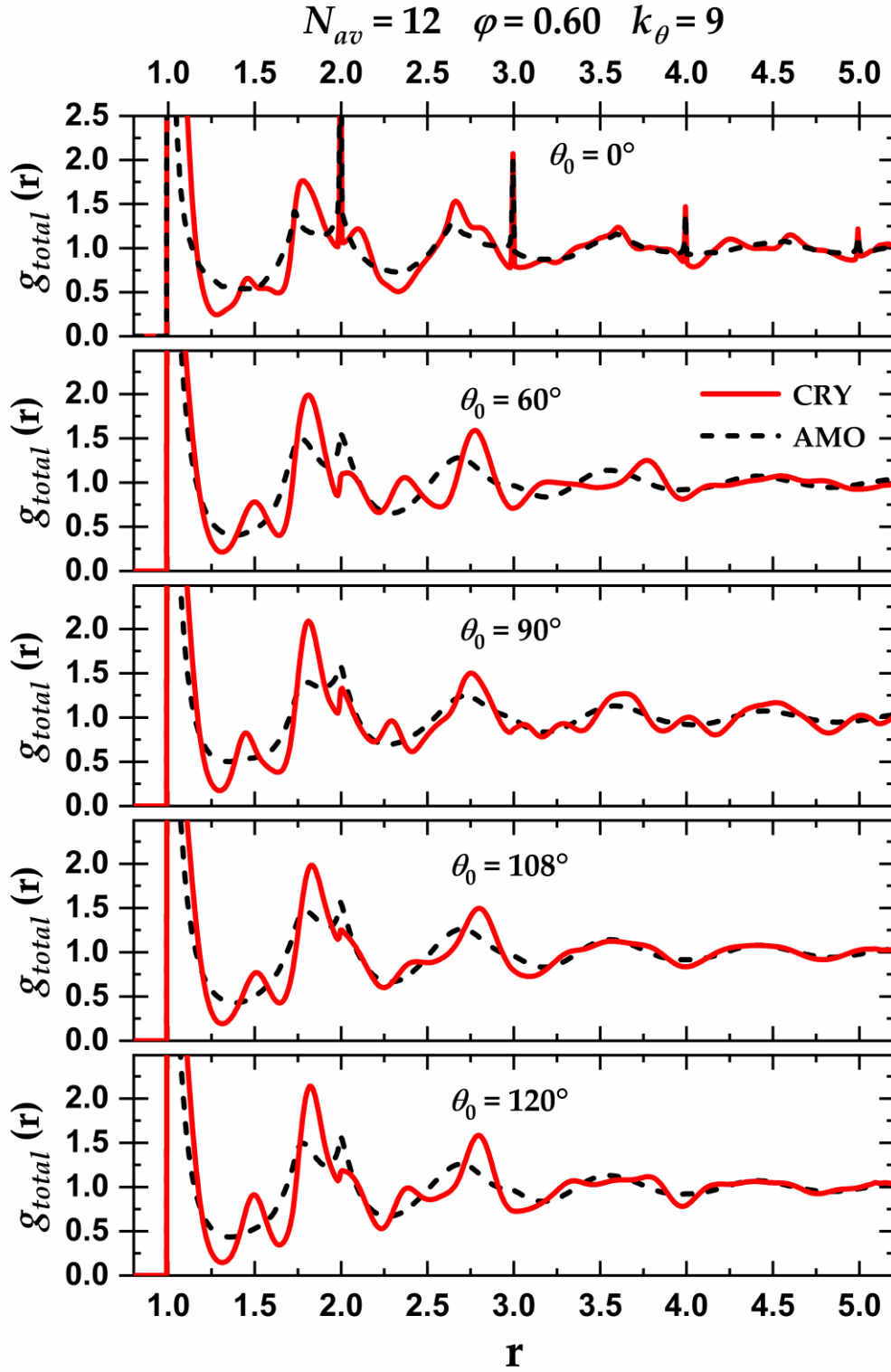


Figure 4.18: Total pair radial distribution function, $g_{total}(r)$, as a function of radial distance, r , in the initial disordered (amorphous, AMO) and final ordered (crystalline, CRY) phases for 100-chain, $N_{av} = 12$ semi-flexible systems with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° (from top to bottom, respectively) at a packing density of $\varphi = 0.60$. Dashed black lines correspond to amorphous phase. Solid red lines, crystalline phase.

4.2 Structure of Random Packings

Past studies of LSM analysed the structure of random packings of freely-jointed (FJ) chains of tangent hard spheres in the entire range of volume fractions up to the maximally random jammed (MRJ) state ($\phi_{chains}^{MRJ} \approx 0.639 \pm 0.004$) [14-16, 18, 33], as explained in more detail in Section 2.2. From these studies, a power-law dependence of the global size of fully flexible hard-sphere chains on the packing density ($C_N \sim \phi^n$) was extracted, displaying four unique scaling behaviours with increasing packing density and marking the corresponding regimes as: dilute, semi-dilute, marginal and concentrated [16, 33], in agreement with theoretical expectations [34, 45, 147, 148]. In the dilute state, chains are isolated and thus do not interact; in the semi-dilute regime, they begin to “feel” each other, which leads to a systematic decrease in size; in the marginal regime, chains collapse as monomers are locally arranged in such patterns so as to minimise the local volume; and finally, in the concentrated regime, no further reduction in size is achievable.

In the present section, we extend these studies to analyse the influence of chain stiffness on the structure and chain conformations of random packings of semi-flexible polymers in three dimensions, exploring the whole volume fraction range, from very dilute configurations to the Random Close-Packed (RCP) limit. We should note here that the RCP limit is, in turn, a function of the employed equilibrium bending angle. Specifically, the combined effect of packing density (ϕ), equilibrium bending angle (θ_0), and chain length (N) is studied on chain conformations, local structure and chain size for semi-flexible polymers with a bending constant $k_\theta/k_B T = 9 \text{ rad}^{-2}$. Random amorphous phases of equilibrated MC simulation trajectories are analysed from systems with a variety of different chain lengths ($N_{av} = 12, 24, 100, 500, \text{ and } 1000$) and at different packing densities, especially exploring the four distinct scaling regimes (dilute, semi-dilute, marginal, and concentrated) as established for freely-jointed chains [33].

Employing the shrinkage protocol of *Simu-D* [2], semi-flexible systems are isotropically compressed from very dilute conditions until the RCP limit is reached. Table 4.1 summarises the maximum achieved packing densities (ϕ^{RCP}) for the different semi-flexible polymer systems and each equilibrium bending angle studied, $\theta_0 = 0, 60, 90, 108, \text{ and } 120^\circ$. We recall that the RCP limit obtained is strongly influenced by the generation protocol. Here, the RCP state is determined practically as the state when no further compression is available after a prolonged simulation time, i.e. the acceptance rate of the compression tends to zero even for infinitely low amplitudes. As Hoy stated in Ref. [218] for freely-rotating chains, the RCP limit of semi-flexible systems is affected by the equilibrium bending angle and the average chain length. Therefore, the maximum achieved packing density increases with the equilibrium

bending angle, generally reaching maximum values with $\theta_0 = 90^\circ$, and decreases with average chain length.

Table 4.1: Maximum packing densities (φ^{RCP}) reached through the shrinkage algorithm of semi-flexible polymeric systems with different average chain lengths (N_{av}) and equilibrium bending angles (θ_0).

φ^{RCP}	N_{av}				
	12	24	100	500	1000
$\theta_0 = 0^\circ$	0.609	0.600	0.600	0.599	0.584
$\theta_0 = 60^\circ$	0.630	0.634	0.610	0.590	0.595
$\theta_0 = 90^\circ$	0.633	0.644	0.620	0.613	0.607
$\theta_0 = 108^\circ$	0.642	0.641	0.619	0.594	0.593
$\theta_0 = 120^\circ$	0.630	0.635	0.600	0.566	0.557

4.2.1 Bending and torsion angle distributions

Local chain conformations constitute an important aspect of the conformational analysis for random packings of polymers. Both bending and torsion angles can dictate the local arrangement but also determine the global size of the chains. For freely-jointed chains of tangent hard spheres, at dilute concentrations, both bending and torsion angles are dominated solely by intra-molecular constraints imposed by the coordinates of the local neighbours. As the packing density increases, chains start to interact with each other, and they collapse, especially in the marginal regime, adopting more compact and coiled conformations. Consequently, bending and torsion angles are forced to adopt characteristic conformations that allow the most efficient local packing [15, 18]. For the present work on semi-flexible polymers, we should recall here that the bending angles are controlled by a corresponding potential, so the chain conformations will be primarily influenced by the chain stiffness of the systems and, to a lesser degree, by the volume fraction.

In Figure 4.19, probability distributions of bending angle are presented for a semi-flexible system of average chain length $N_{av} = 100$ with each equilibrium bending angle studied ($\theta_0 = 0, 60, 90, 108$, and 120°) and at different packing densities, corresponding to the four scaling regimes for freely-jointed chains. As expected, at dilute ($\varphi = 0.001$) and semi-dilute ($\varphi = 0.20$) concentrations, the bending angle distributions are solely determined by the corresponding intra-molecular constraints of the isolated chains, and so the distributions are centred on the equilibrium bending angle (θ_0) and are not affected by the effect of packing density (φ). As packing density increases in the marginal ($\varphi = 0.50$) and concentrated ($\varphi = 0.60$) regimes, the systems with equilibrium bending angles, which are compatible with a better packing ($\theta = 0, 60$, and 120°) as observed in freely-jointed chains, show an increase of the peaks, especially for 0 and 120° . On the other hand, the bending angle distributions for systems with equilibrium bending angles of $\theta_0 = 90$ and 108° are “distorted” to search for

bending angles that promote better local packing, favouring compact configurations. Thus, the distribution peak for systems with $\theta_0 = 108^\circ$ is shifted towards bending angles of $\theta = 120^\circ$ with increasing packing density. At the concentrated regime, the distribution peak corresponds to 120° . For the case of right-angle chains, although the maximum peak is kept centred around the bending angle of 90° , the intensity decreases, the curve broadens and becomes less symmetric. In fact, at $\varphi = 0.60$, the distribution curve for right-angle chains presents a second, smaller peak on the bending angle of 120° .

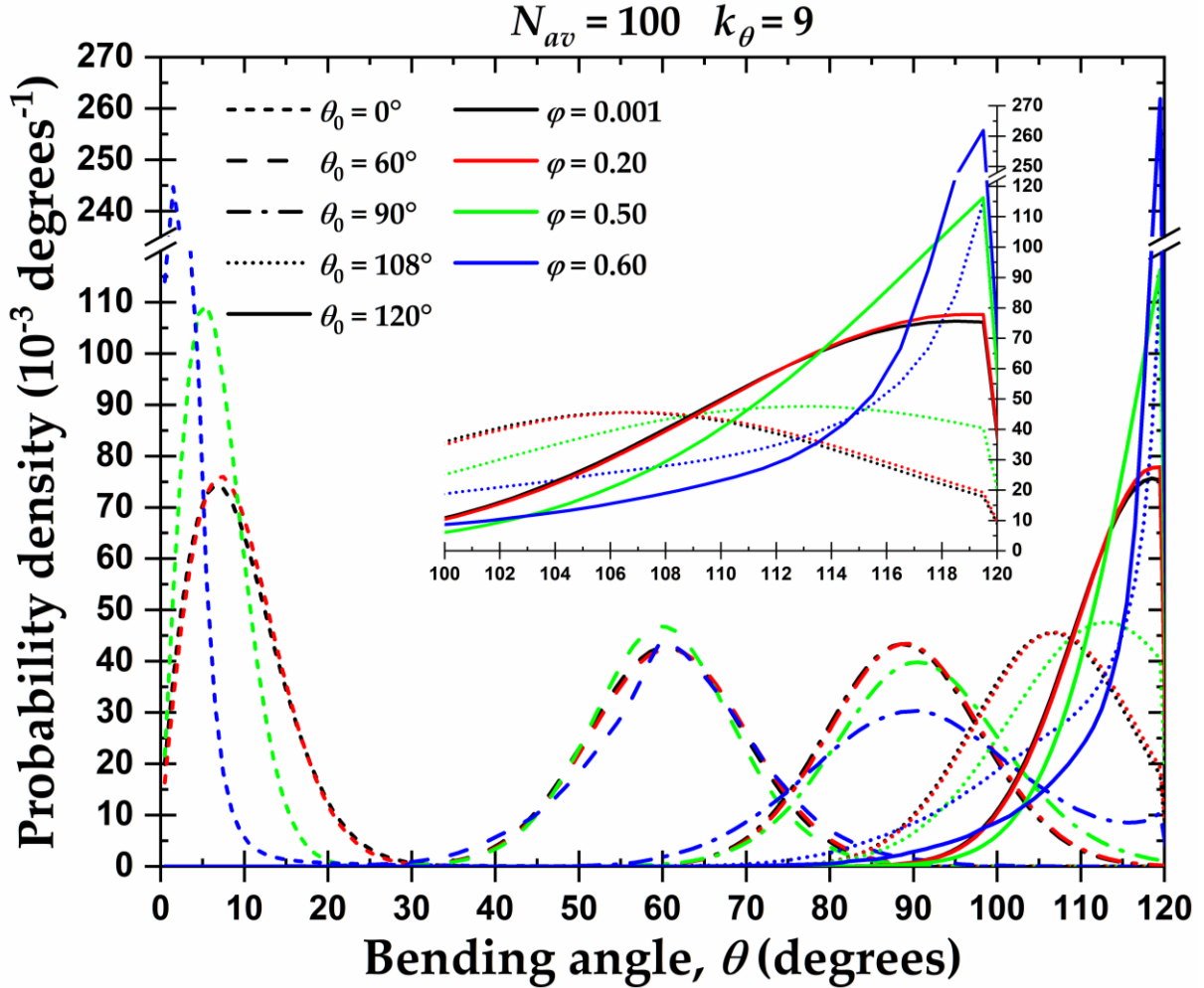


Figure 4.19: Distribution of bending angle (θ) as a function of packing density (φ) for 48-chain, $N_{av} = 100$ semi-flexible systems with bending constant $k_\theta = 9$ and different equilibrium bending angles (θ_0). The inset shows part of the distribution corresponding to the most coiled bending angles, $\theta \geq 100^\circ$.

Figure 4.20 presents the bending angle distributions for each equilibrium bending angle studied as a function of the average chain length (N_{av}) at dense packing densities of $\varphi = 0.50$ and $\varphi = 0.58$. The average chain length does not have a notable effect on the probability distribution curves of the bending angle, regardless of the equilibrium bending angle, as observed at $\varphi = 0.50$. At concentrated packing densities, the differences in the curves increase slightly, except for right-angle chains where chain length continues to have no impact on the bending angle distribution.

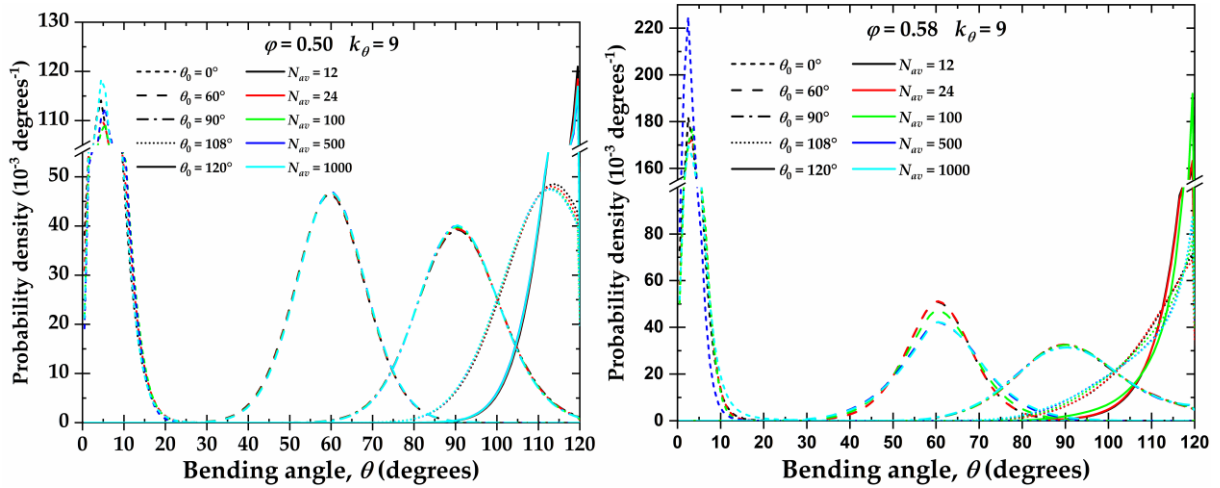


Figure 4.20: Distribution of bending angle (θ) as a function of average chain length (N_{av}) for semi-flexible chain systems with bending constant $k_\theta = 9$ and different equilibrium bending angles (θ_0) at packing densities of $\varphi = 0.50$ (left) and $\varphi = 0.58$ (right).

In an analogous pattern, Figure 4.21 presents the probability distributions of the torsion angle for a semi-flexible system of average chain length $N_{av} = 100$ with each equilibrium bending angle studied and at different packing densities, corresponding to the four scaling regimes for freely-jointed chains. In the case of freely-jointed chains, the chain collapse with the concentration leads to the appearance of peaks in the torsion angle distribution at 0° , 54.7° , 70.5° , 109.5° , and 180° , allowing the formation of a locally, dense structure [15, 18]. For semi-flexible polymers, torsion angle distributions only present small changes between dilute and semi-dilute regimes for every equilibrium bending angle, showing a slight preference for trans ($\phi = 0^\circ$) conformations, which lead to extended chains. As packing density increases, the distribution curves for semi-flexible polymers generally show the appearance of characteristic minima and maxima, as was observed for freely-jointed chains [15, 18]. The simplest case corresponds to rod-like chains ($\theta = 0^\circ$), which shows a unique peak at 0° with the increase of packing density. This clear preference for all-trans, coplanar conformations agrees with the formation of the nematic phase, as explained in Section 4.1.1, leading to extended chains. In the opposite case, semi-flexible polymers with $\theta = 60^\circ$ present uniform distributions in torsion angle conformations, growing very small peaks in the marginal regime. The noise observed in the distribution can be attributed to inefficient sampling, which is indicative of the close proximity to the MRJ state, which can be further verified by the data in Table 4.1. For $\theta = 90^\circ$, a preference for cis ($\phi = \pm 180^\circ$) conformations is observed in the torsion angle distribution of concentrated packing density, being higher than the observed ones for freely-jointed chains and other semi-flexible polymers. Finally, a remarkable behaviour is observed for semi-flexible systems with $\theta > 90^\circ$. These semi-flexible systems favour the gauche- and gauche+ states ($\phi = \pm 120^\circ$) compared to other local conformations, notably sharpening these peaks with the packing density. In addition, higher torsion angles are not present because they lead to

unrealistic chain conformations that are incompatible with the corresponding equilibrium bending angles. Thus, the gauche conformations of these semi-flexible systems make it possible to fold into the locally densest possible conformation, followed by a reduction of chain size.

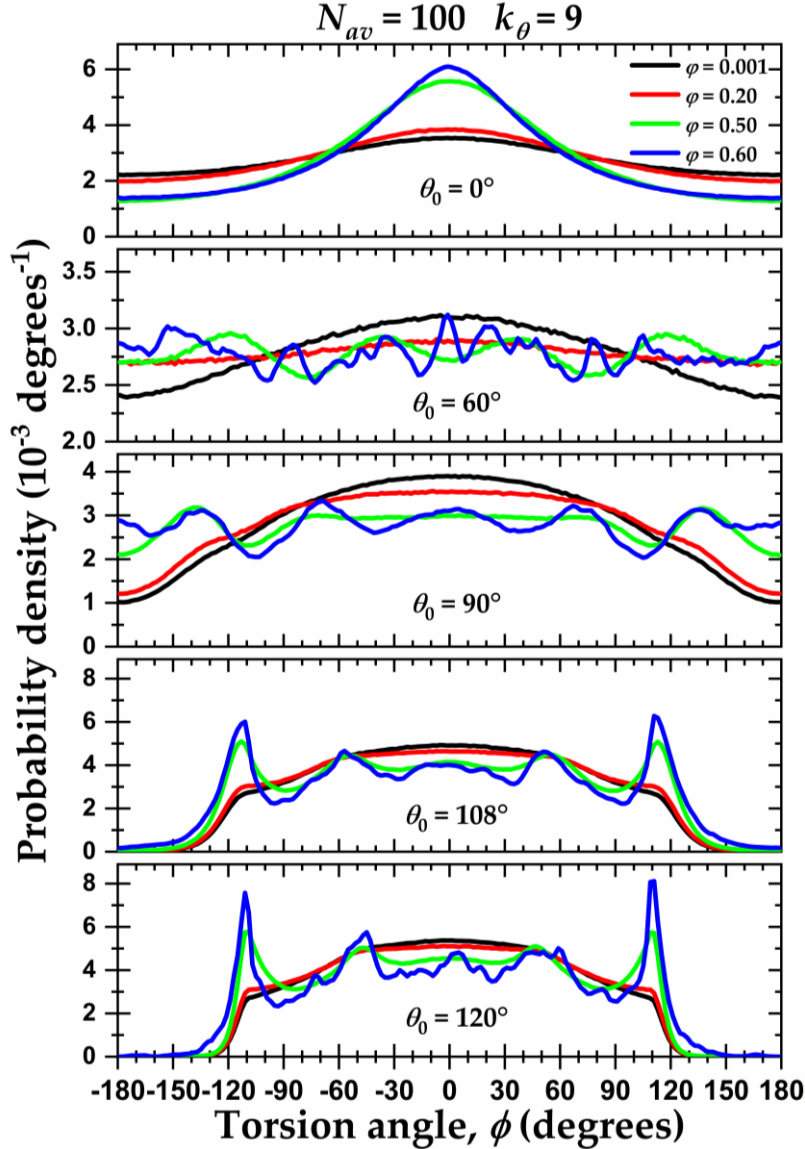


Figure 4.21: Distribution of torsion angle ϕ as a function of packing density ϕ (corresponding to four scaling regimes) for 48-chain, $N_{av} = 100$ semi-flexible systems with bending constant $k_{\theta} = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° (from top to bottom, respectively).

The distribution curves of the torsion angle as a function of average chain length (N_{av}) are presented in Figure 4.22 for each equilibrium bending angle studied at the dense packing densities of $\phi = 0.50$ and $\phi = 0.58$. Again, as for the bending angle distributions, the average chain length does not show an appreciable effect, especially at $\phi = 0.50$, on the torsion angle conformations, regardless of the equilibrium bending angle. At denser concentrations, the curves present slightly sharper minima and maxima with systems of shorter chain length, especially for $\theta_0 = 60^\circ$. This behaviour could be since these shorter systems have reached more stable phases within the same MC steps, starting the crystal nucleation and growth.

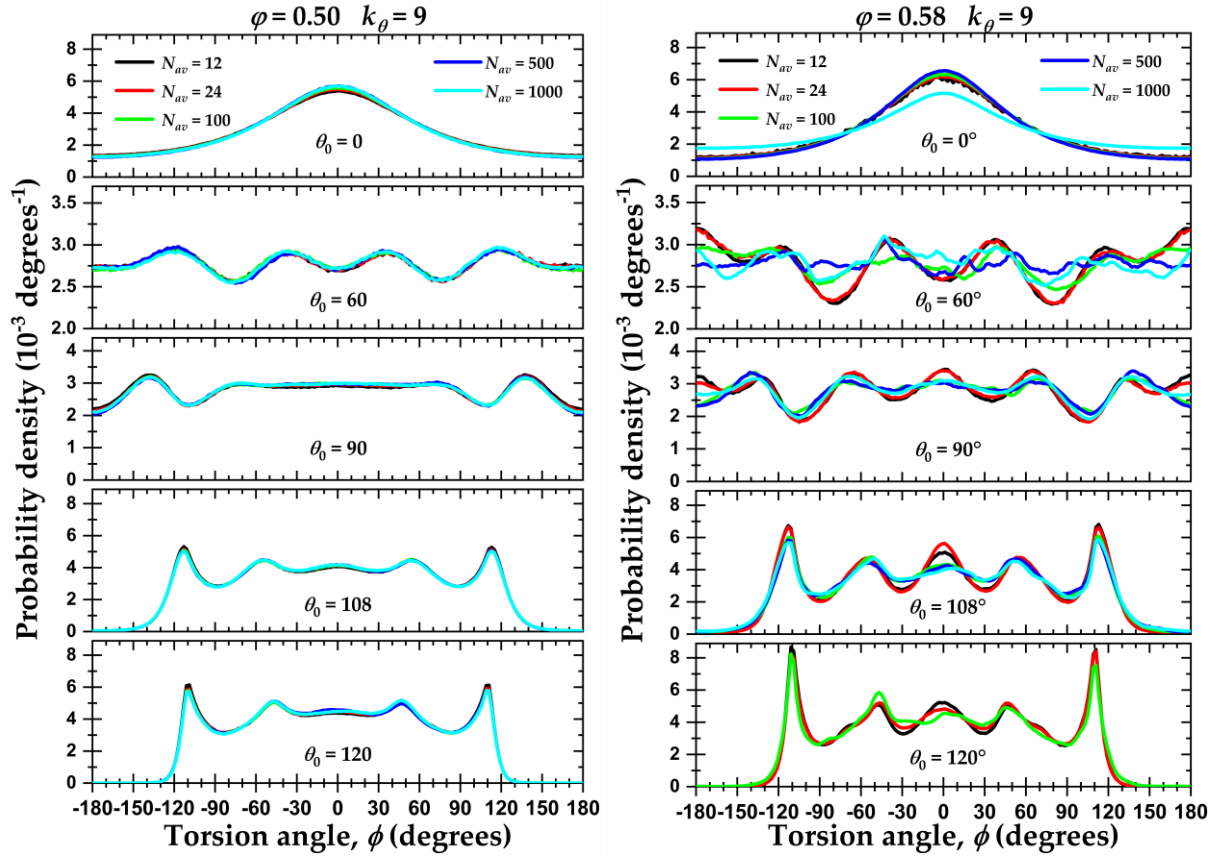


Figure 4.22: Distribution of torsion angle (ϕ) as a function of average chain length (N_{av}) for semi-flexible chain systems with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° (from top to bottom, respectively) at packing densities of $\varphi = 0.50$ (left) and $\varphi = 0.58$ (right).

4.2.2 Radial distribution function

A refined descriptor of local structure is the pair radial distribution function, $g(r)$. For any atomic or particulate system, it can provide complete information on the radial distribution of pairs of particles or atoms. In the past, LSM has studied the evolution of the pair radial distribution with the volume fraction in athermal freely-jointed polymer packings. As the packing density increases, both intramolecular and intermolecular pair radial distributions develop sharper maxima and minima at characteristic values, which correspond to the non-overlapping condition, tangency in bonds, the positioning of the second nearest neighbour, etc. Furthermore, fully flexible polymer packing of tangent hard spheres near the MRJ state shows a curve remarkably similar to the one of monomeric packings, the latter being free of any constraints related to chain connectivity [14, 15, 18].

For the case of semi-flexible polymeric packings in three dimensions, Figure 4.23 shows the intramolecular pair radial density function, $w_{intra}(r)$, and intermolecular pair radial distribution function, $g_{inter}(r)$, for systems of average chain length $N_{av} = 100$ with each equilibrium bending angle studied ($\theta_0 = 0, 60, 90, 108$, and 120°) at increasing packing densities (φ), representing the four scaling regimes observed in freely-jointed chains [16, 33].

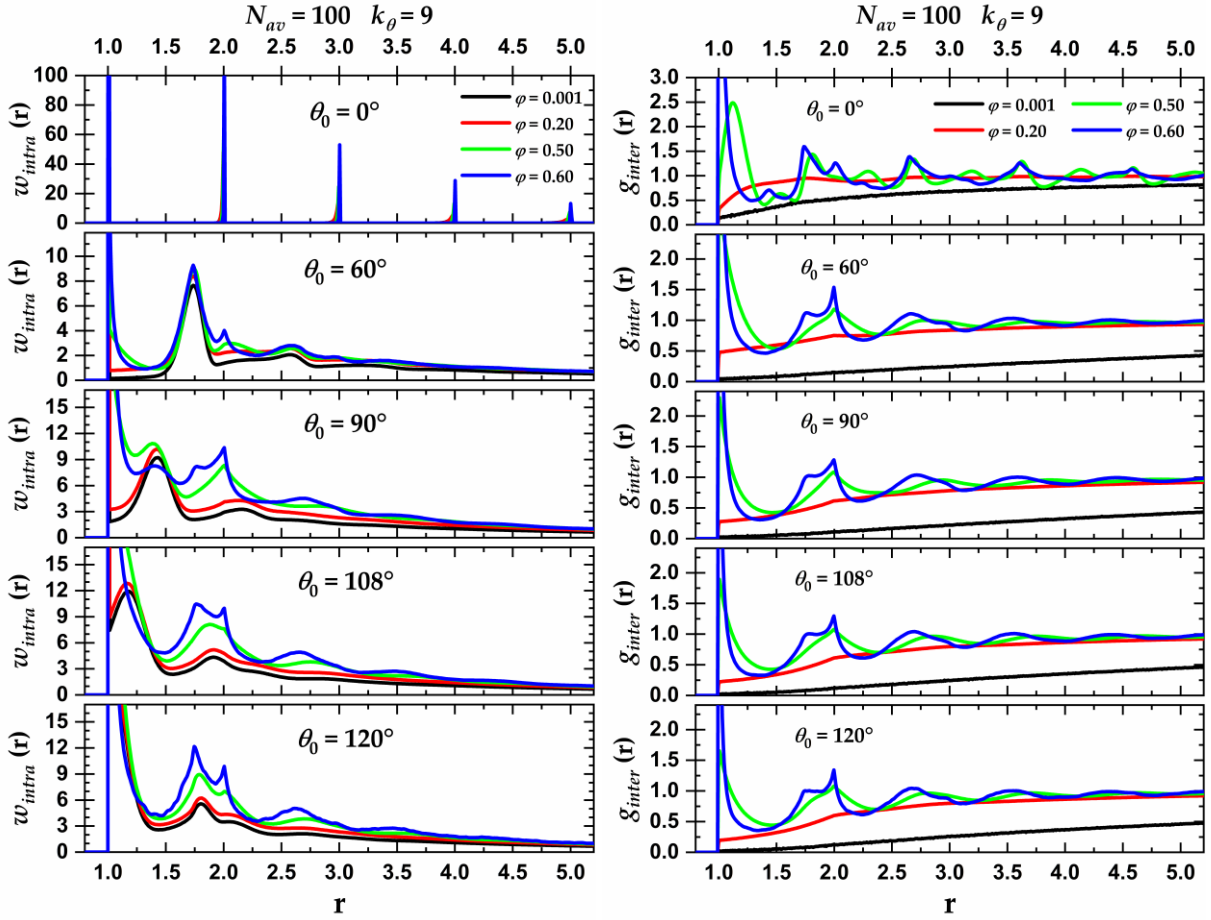


Figure 4.23: (Left) Intramolecular pair radial density function, $w_{intra}(r)$, and (Right) intermolecular pair radial distribution function, $g_{inter}(r)$, as functions of radial distance, r , at different packing densities, φ , for 48-chain, $N_{av} = 100$ semi-flexible systems with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° (from top to bottom, respectively).

At dilute and semi-dilute concentrations, the intramolecular pair radial density, $w_{intra}(r)$, for semi-flexible polymers shows characteristic peaks determined by the corresponding equilibrium bending angle, i.e. $r = 1, 2, 3, \dots$ for $\theta_0 = 0^\circ$, $r = \sqrt{3}$ for $\theta_0 = 60^\circ$, $r = \sqrt{2}$ for $\theta_0 = 90^\circ$, $r = 1.18$ for $\theta_0 = 108^\circ$, and $r = 1$ and $\sqrt{3}$ for $\theta_0 = 120^\circ$. As the packing density increases, sharper peaks emerge that promote better local packing. Thus, $w_{intra}(r)$ curves of systems with equilibrium bending angle compatible with dense local packings ($\theta_0 = 60$ and 120°) only sharpen their original peaks at dilute conditions. On the other hand, systems such as $\theta_0 = 90$ and 108° give rise to new peaks at characteristic values of r related to local compact packing, i.e. chain conformations with bending angles of $\theta = 120^\circ$, while the peaks corresponding to their equilibrium bending angles broaden as volume fraction increases. In the case of $\theta_0 = 108^\circ$, the peak at $r = 1.18$ is merged with the one at $r = 1$ (tangency) when the marginal regime is reached. Then, the intramolecular pair radial density function becomes progressively similar to the corresponding curve for the system with $\theta_0 = 120^\circ$. This behaviour

for $\theta_0 = 90$ and 108° agrees with the emergence of chain conformations with $\theta = 120^\circ$ at dense packing densities, as seen above in Figure 4.19.

The intermolecular pair radial distribution functions, $g_{inter}(r)$, from Figure 4.23 present very similar curves for every equilibrium bending angle, regardless of the packing density. Furthermore, these curves also coincide with the intermolecular pair radial distribution function observed in freely-jointed chains of tangent hard spheres, as seen in Fig. 3 in Ref. [15]. Thus, the inter-chain arrangement of monomers is independent of the chain stiffness of the system. The sole exception to this behaviour is observed in the rod-like systems ($\theta_0 = 0^\circ$). Due to the formation of the ordered nematic phase as explained in Section 4.1, the $g_{inter}(r)$ curves for rod-like polymers at dense concentrations present characteristic peaks at values of r that correspond to ordered structures [18, 20, 21], such as self-arrangement in a 2D hexagonal ordered structure in the perpendicular plane to the nematic director [206].

Figure 4.24 presents the total pair radial distribution function, $g_{total}(r)$, for the same semi-flexible polymeric systems in Figure 4.23 as a function of packing density (φ). Comparing the distribution curves to the ones in Figure 4.23, the total pair radial distribution functions for every equilibrium bending angle are mainly governed by intramolecular arrangements, $w_{intra}(r)$, at low concentrations, as expected due to the isolation of chains at dilute and semi-dilute packing densities. Consequently, the characteristic peaks at dilute and semi-dilute conditions are determined by the equilibrium bending angle. On the other hand, as the packing density increases, the polymer chains encounter each other, and then the inter-chain arrangements, $g_{inter}(r)$, start to govern the total radial distribution. Thus, $g_{total}(r)$ curves for every equilibrium bending angle gradually become similar between themselves, especially at concentrated packing densities, with the sole exception of rod-like polymers ($\theta_0 = 0^\circ$) as explained above.

The effect of the average chain length, N_{av} , on the intramolecular pair radial density function, $w_{intra}(r)$, and intermolecular pair radial distribution function, $g_{inter}(r)$, is analysed in Figure 4.25 and Figure 4.26 at dense packing densities of $\varphi = 0.50$ and $\varphi = 0.58$, respectively. Both $w_{intra}(r)$ and $g_{inter}(r)$ present the same curves for each equilibrium bending angle (θ_0) and packing density (φ) regardless of the average chain length (N_{av}). The only difference is observed in $w_{intra}(r)$, where the increase of the average chain length provides parallel curves with higher pair radial density values. This is expected as the longer the chain, the higher the probability of finding a monomer from the same chain, especially with coiler configurations.

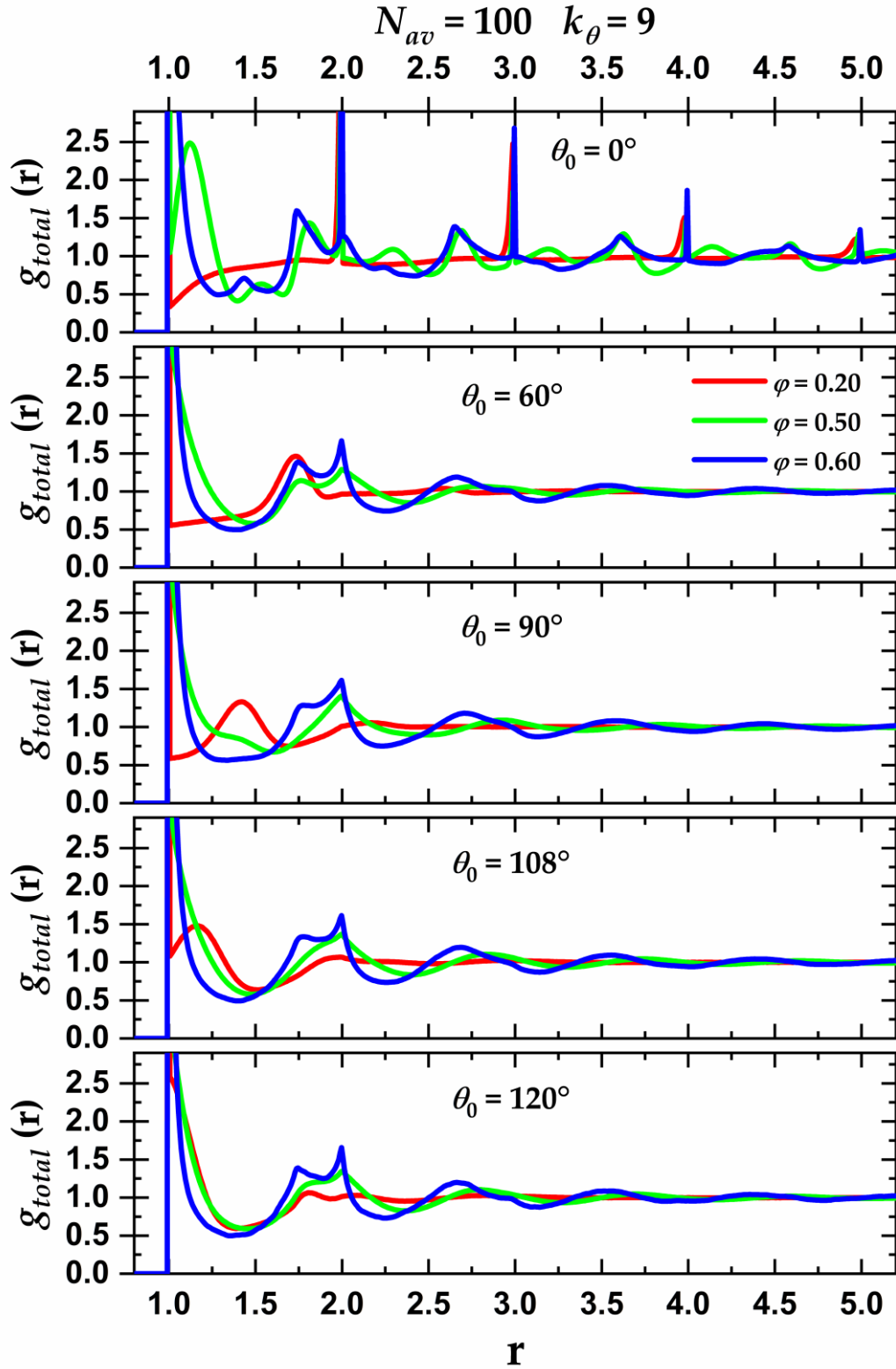


Figure 4.24: Total pair radial distribution function, $g_{total}(r)$, as a function of radial distance, r , at different packing densities, ϕ , (corresponding to four scaling regimes) for 48-chain, $N_{av} = 100$ semi-flexible systems with bending constant $k_{\theta} = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° (from top to bottom, respectively).

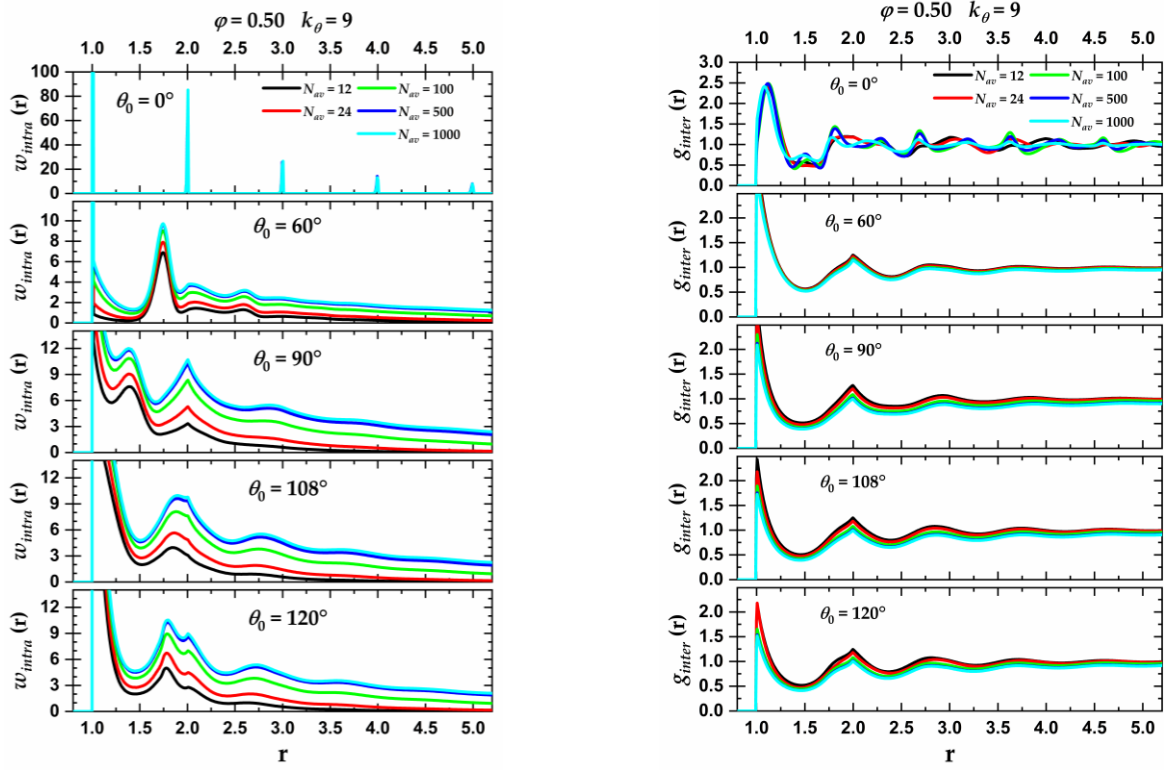


Figure 4.25: (Left) Intramolecular pair radial density function, $w_{intra}(r)$, and (Right) intermolecular pair radial distribution function, $g_{inter}(r)$, as functions of radial distance, r , for semi-flexible systems of different average chain lengths, N_{av} , with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° (from top to bottom, respectively) at a packing density of $\varphi = 0.50$.

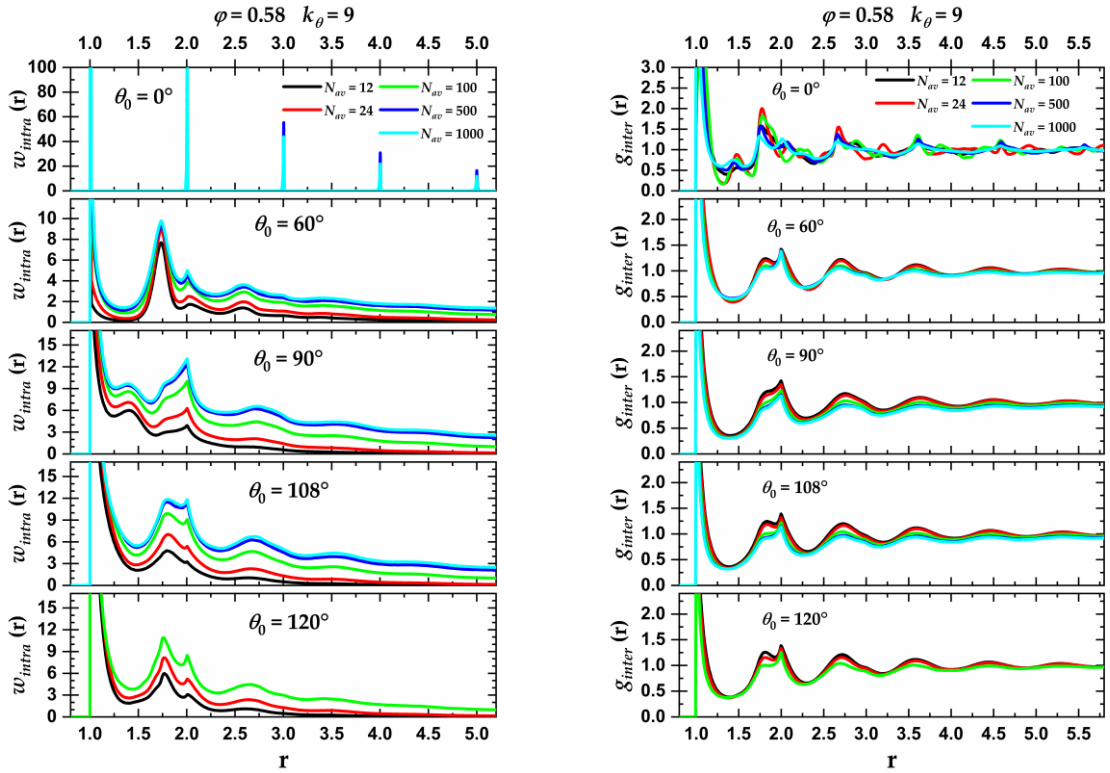


Figure 4.26: Same as Figure 4.25 at a packing density of $\varphi = 0.58$.

The same behaviour is shown in Figure 4.27 for the total pair radial distribution function, $g_{total}(r)$, as a function of the average chain length (N_{av}) at the packing densities of $\varphi = 0.50$ and $\varphi = 0.58$. The $g_{total}(r)$ curves are independent of the average chain length for each equilibrium bending angle and packing density. The only differences between curves of different N_{av} are observed for the rod-like systems. These differences are due to the emergence of different degrees of ordered inter-chain arrangements, as observed in the intermolecular pair radial distribution functions, $g_{inter}(r)$, in Figure 4.25 and Figure 4.26.

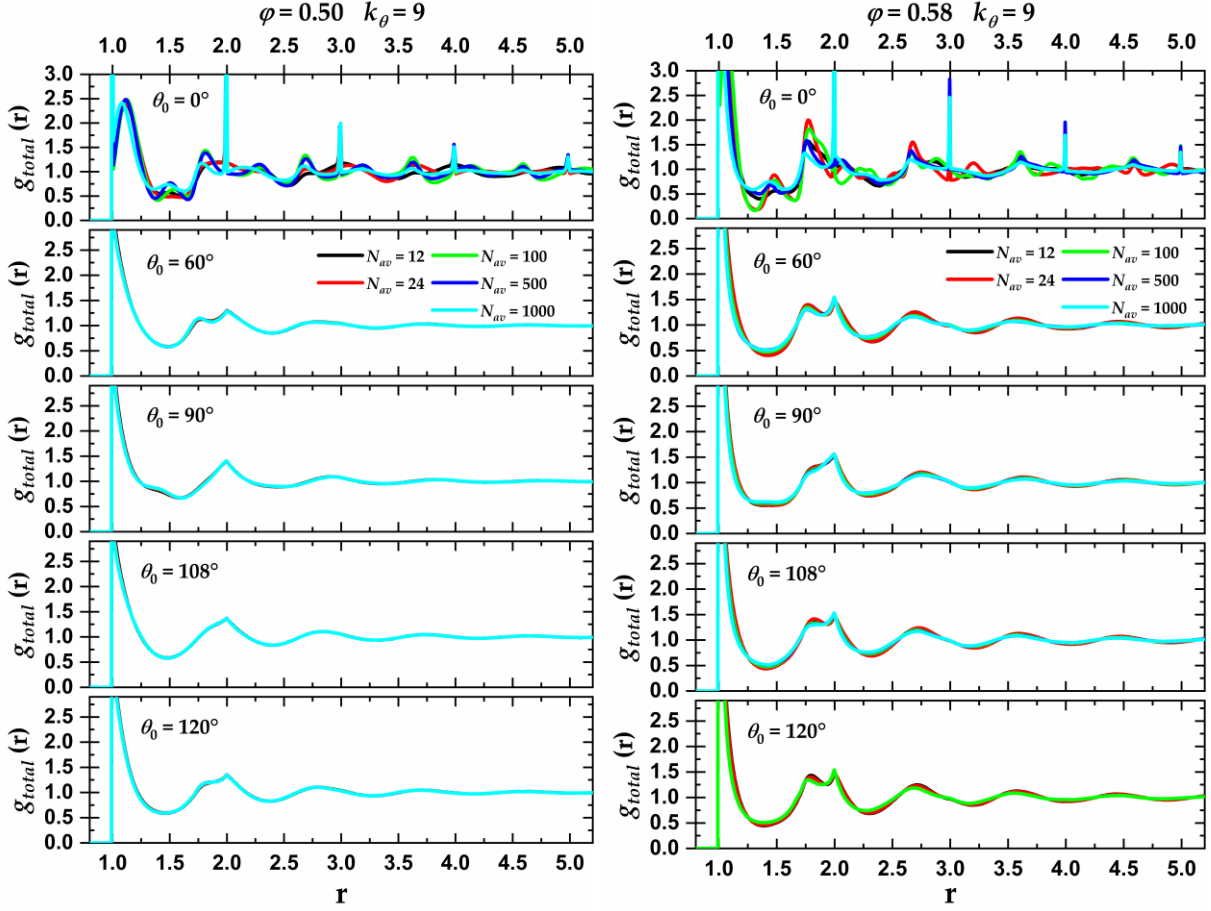


Figure 4.27: Total pair radial distribution function, $g_{total}(r)$, as a function of radial distance, r , for semi-flexible systems of different average chain lengths, N_{av} , with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0, 60, 90, 108$, and 120° (from top to bottom) at packing densities of $\varphi = 0.50$ (left) and $\varphi = 0.58$ (right).

4.2.3 Chain size

The rearrangements of the local conformations, which are produced as the packing density increases, have a clear influence on the global size of the chains, especially in high concentrations. Chain size is generally quantified through the end-to-end vector ($\mathbf{R}$), its magnitude (R), and the radius of gyration (R_g). For a linear chain of N monomers, both measures are calculated from the position vectors ($\mathbf{r}_i$) of all monomers along the chain backbone

($i \in [1, N]$). The end-to-end vector, $\mathbf{R}$ (and its magnitude), is the simplest and most direct measure of chain size and corresponds to the vector that joins the two ends of the chain.

$$\mathbf{R} = \sum_{i=1}^N \mathbf{r}_i = \mathbf{r}_N - \mathbf{r}_1 \quad (4.1)$$

However, the end-to-end vector is not a valid variable for more complex chain architectures, such as long/short-chain branched, cyclic or star polymers. On the other hand, the radius of gyration measures the chain size of the polymer as an extension relative to the centre of mass ($\mathbf{r}_{cm}$) for the chain. For a polymer with all monomers having equal unit mass, the square radius of gyration (R_g^2) is defined for a chain of N monomers as:

$$R_g^2 = \frac{1}{2N^2} \sum_{i \neq j} (\mathbf{r}_i - \mathbf{r}_j)^2 \quad (4.2)$$

According to the worm-like chain (WLC) model [217], the mean square end-to-end distance, $\langle R^2 \rangle$, and the mean square radius of gyration, $\langle R_g^2 \rangle$, can be described through the persistence length, l_p , and the contour length, $R_{max} = (N - 1)l$ where l is the bond length. Brackets $\langle \rangle$ denote ensemble average over all chains. For freely-jointed chains in the limit of long chains ($R_{max} \gg l_p, N \rightarrow \infty$), the relation between $\langle R^2 \rangle$ and $\langle R_g^2 \rangle$ is $\langle R^2 \rangle = 6\langle R_g^2 \rangle$. In contrast, if a very rigid polymer (hard rod) is considered, the corresponding relation becomes $\langle R^2 \rangle = 12\langle R_g^2 \rangle$. Furthermore, the radius of gyration can be estimated as $\langle R_g^2 \rangle \propto N^{2\nu}$ where ν is the Flory exponent, as proposed by Flory through a mean-field approach based on the concept of excluded volume interaction and chain coiling. The Flory exponent depends on the solvent of the polymeric system [42].

In the present work, the chain size of semi-flexible polymeric systems in three dimensions is quantified through the characteristic ratio (C_N), which is defined as:

$$C_N = \frac{\langle R^2 \rangle}{(N - 1)l^2} \quad (4.3)$$

The characteristic ratio is a measure of the chain size that also depends on the chain length, N , but will reach an asymptotic value (C_∞) for large values of N . C_∞ is called the Flory's characteristic ratio and can be considered a measure of the stiffness in a given ideal chain model: $\langle R^2 \rangle = C_\infty(N - 1)l^2$. For ideal freely-jointed chains, the characteristic ratio takes the value of $C_N = 1$, while $C_N > 1$ for non-ideal chains with angular correlations. For freely-rotating chains, the Flory's characteristic ratio can be expressed as $C_\infty = (1 + \cos \theta)/(1 - \cos \theta)$.

The logarithmic evolution of the characteristic ratio (C_N) as a function of packing density (φ) is displayed in Figure 4.28 for semi-flexible polymers of chain length $N = 100$ with

each equilibrium bending angle studied here ($\theta_0 = 0, 60, 90, 108$, and 120°). Chain size for every equilibrium bending angle, except for the systems of $\theta_0 = 0$ and 60° , shows an approximately similar evolution as the packing density increases to the four scaling regimes, similar to that determined for freely-jointed chains of tangent hard spheres. Additionally, Figure 4.29 presents the evolution of the characteristic ratio (C_N) as a function of the packing density (φ) and the chain length (N) for semi-flexible systems with $\theta_0 = 0^\circ$ (a), $\theta_0 = 60^\circ$ (b), and $\theta_0 = 120^\circ$ (c). The corresponding behaviour of chain size for each equilibrium bending angle is independent of the chain length, although the statistic variation remarkably increases with higher chain lengths ($N \geq 500$).

As expected, rod-like polymer systems ($\theta_0 = 0^\circ$) keep a constant chain size at dilute conditions until the packing density for the isotropic-to-nematic transition is reached. Then, stiffness and chain size increase with packing density, reaching the state of maximum extension, i.e. end-to-end distance is equal to contour length, when the nematic phase is established (see Section 4.1.1). At lower densities, the chains can slightly coil and thus deviate from the ideal rod configuration because of the more dilute local environment, increasing this effect the longer the chain. The jump in the characteristic ratio reflects the adoption of a straight configuration by the chains as the observed perfect nematic ordering requires inter-chain alignment along the whole polymer contours. Therefore, the intensity of this jump increases with the chain length, as seen in panel (a) of Figure 4.29.

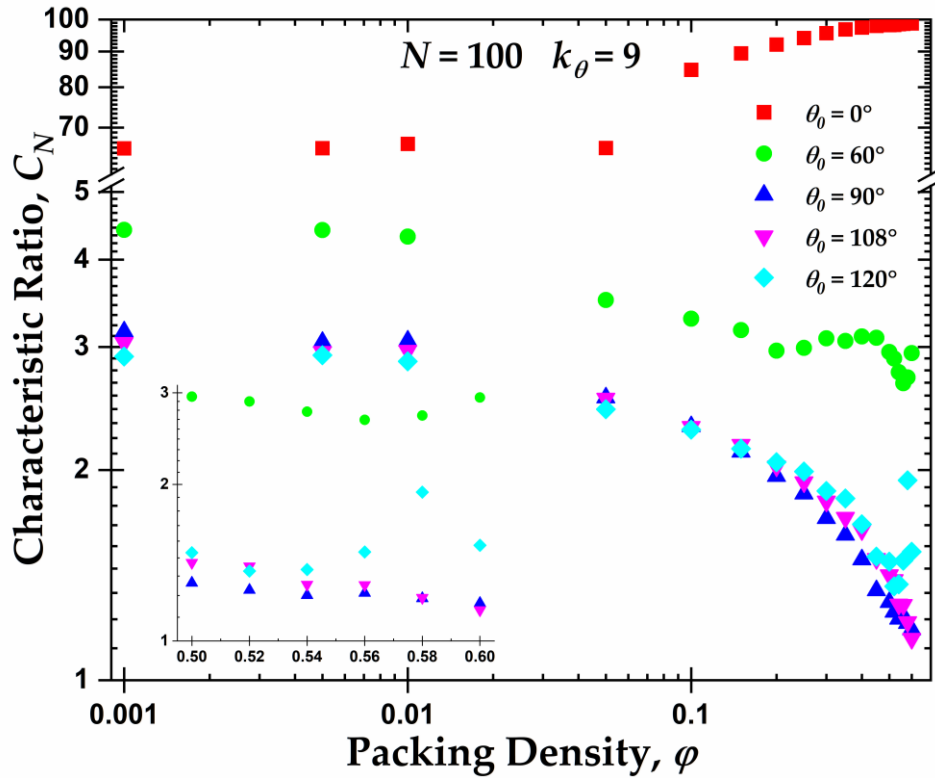


Figure 4.28: Characteristic ratio (C_N) as a function of packing density (φ) for semi-flexible polymers of chain length $N = 100$ with bending constant $k_\theta = 9$ and different equilibrium bending angles (θ_0). Inset: Zoom of the characteristic ratio into the marginal and concentrated regimes for freely-jointed chains [16, 33, 34].

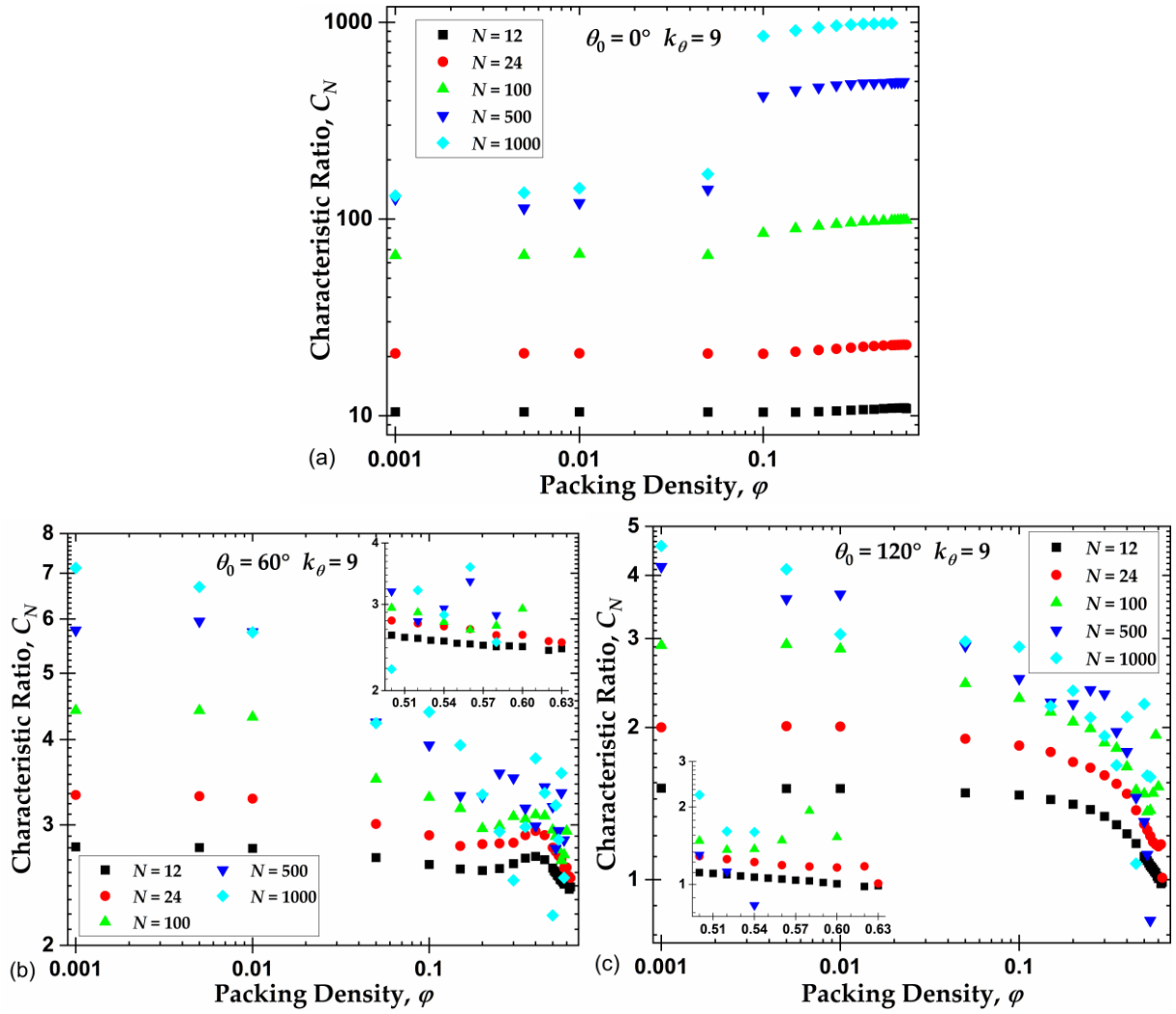


Figure 4.29: Characteristic ratio (C_N) as a function of packing density (ϕ) for semi-flexible polymers of different chain lengths (N) with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0^\circ$ (a), 60° (b), and 120° (c). Insets for (b) and (c) present the characteristic ratio in the marginal and concentrated regimes for freely-jointed chains [16, 33, 34].

As mentioned above, the rest of the semi-flexible systems generally present an evolution with the packing density, regardless of chain length, similar to the four scaling regimes of freely-jointed chains (see Section 2.2), as observed in Figure 4.28 and panels (b) and (c) of Figure 4.29. However, semi-flexible systems with $\theta_0 = 60^\circ$ also present a region of almost constant characteristic ratio (even a small increase) approximately from $\phi = 0.20$ to $\phi = 0.50$, as seen in Figure 4.28 and panel (b) of Figure 4.29. After this intermediate region between the semi-dilute and marginal regimes, the characteristic ratio for systems with $\theta_0 = 60^\circ$ decreases at the same rate of the rest of semi-flexible systems until the concentrated regime is reached. Consequently, and as expected, semi-flexible polymers with $\theta_0 = 60^\circ$ (corresponding practically to extended zig-zag configurations) present a remarkably larger chain size than more coiled conformations.

Given that we employed polydisperse chain systems in the present work through a uniform dispersity in lengths ($N \in [N_{av}(1 - \Delta), N_{av}(1 + \Delta)]$, $\Delta = 0.5$), a dependence of the chain size, as quantified by the characteristic ratio, on chain length (N), can be extracted from a single simulation for every semi-flexible system. Figure 4.30 collects graphs at different packing densities (φ) of the evolution of the characteristic ratio (C_N) as a function of the chain length (N) and the equilibrium bending angles (θ_0). As expected, all semi-flexible systems, except rod-like polymers, decrease in chain size with increasing packing density, while chain size increases with chain length (N) until reaching an asymptotic value (C_∞). This asymptotic value decreases and is established at shorter chain lengths with the increase in packing density.

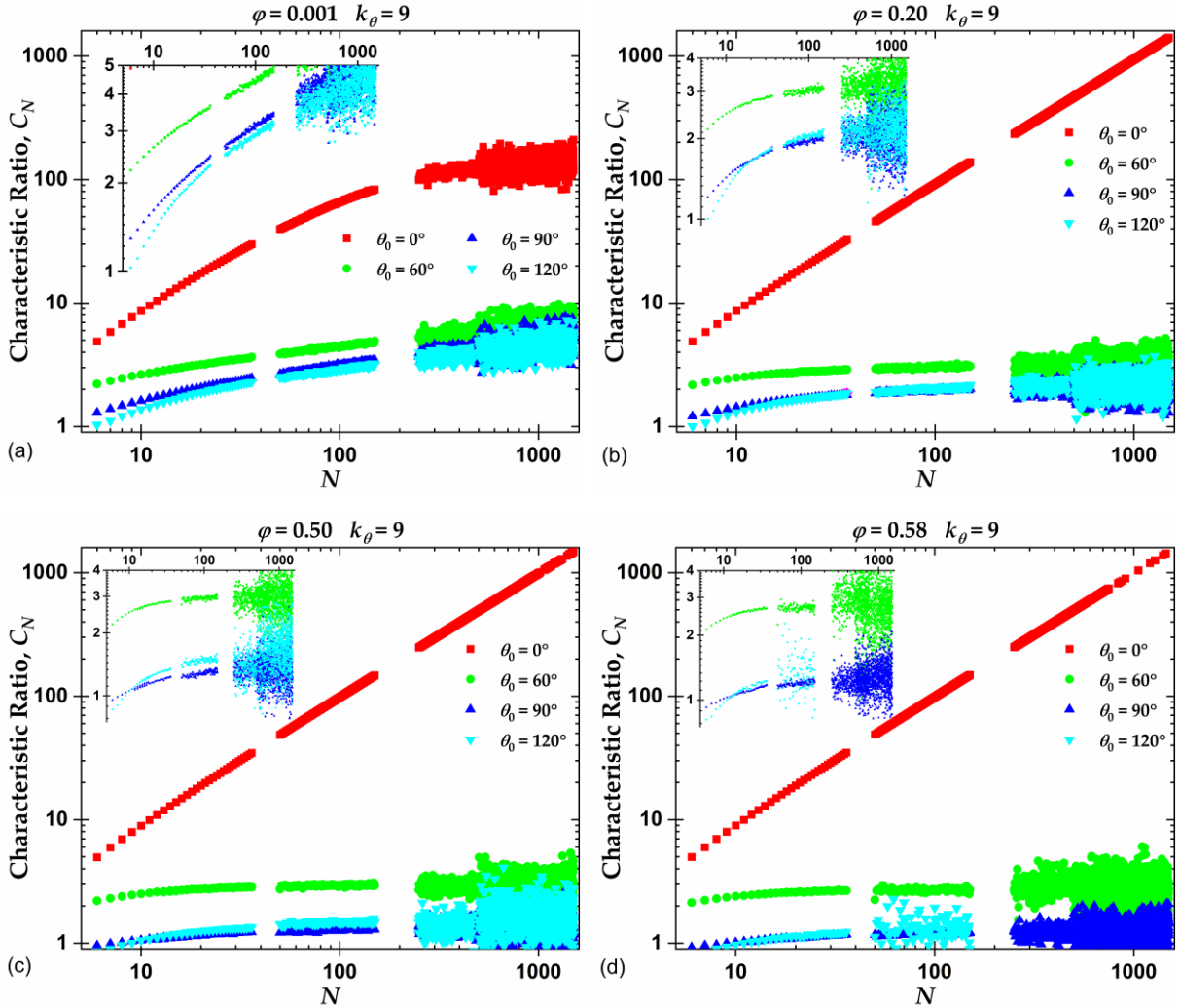


Figure 4.30: Characteristic ratio (C_N) as a function of chain length (N) for semi-flexible chain systems of different sizes (see Table 3.1) with bending constant $k_\theta = 9$ and different equilibrium bending angles (θ_0) at packing densities of $\varphi = 0.001$ (a), $\varphi = 0.20$ (b), $\varphi = 0.50$ (c), and $\varphi = 0.58$ (d). Insets: Zoom of characteristic ratio for $\theta_0 = 60, 90$, and 120° .

For the rod-like polymer systems ($\theta_0 = 0^\circ$), the characteristic ratio follows the same behaviour with chain length at dilute conditions. However, the characteristic ratio, and consequently the chain size, increases linearly with the chain length after the isotropic-to-

nematic transition. Another interesting observation from the insets of Figure 4.30 is that $\theta_0 = 90^\circ$ polymer chains can reach lower chain sizes (and asymptotic value) than chains with the most coiled conformation ($\theta_0 = 120^\circ$) with the increase of packing density and once specific chain lengths are reached. Thus, long right-angle chains can collapse into locally dense configurations as efficiently as the inherently compact chain configurations.

In Figure 4.31, the evolution of the characteristic ratio (C_N) as a function of the chain length (N) is displayed at increasing packing densities (φ) for different equilibrium bending angles (θ_0). As in the previous Figure 4.30, it is clearly shown that semi-flexible systems reach asymptotic values at longer chain lengths (N). These asymptotic values decrease and are established at shorter chain lengths at higher volume fractions, for the only exception is the rod-like polymers, as they establish straight conformations induced by the nematic phase and, consequently, present a linear increase of the chain size with the chain length.

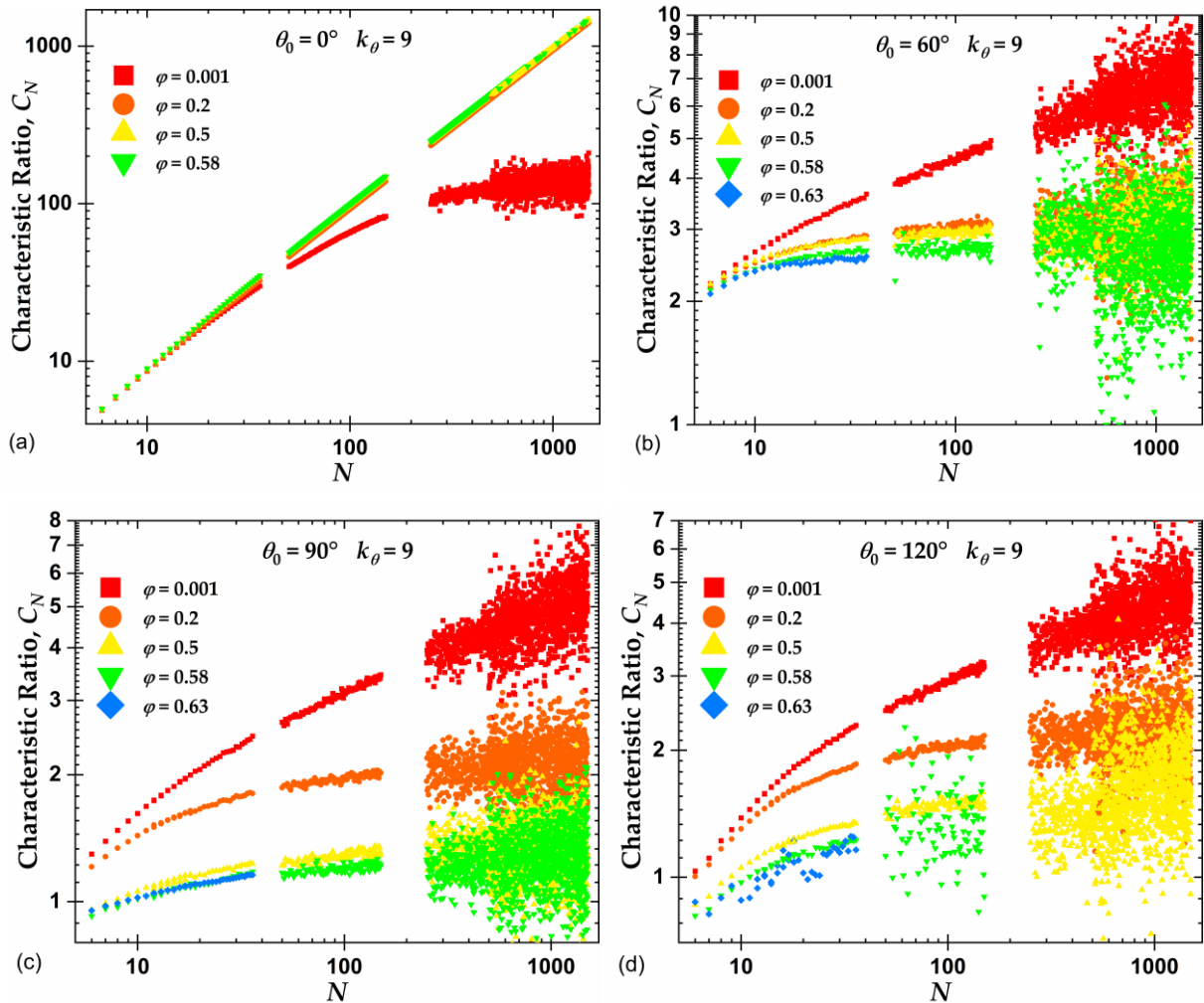


Figure 4.31: Characteristic ratio (C_N) as a function of chain length (N) for semi-flexible chain systems (see Table 3.1) with bending constant $k_\theta = 9$ and equilibrium bending angles $\theta_0 = 0^\circ$ (a), 60° (b), 90° (c), and 120° (d) at different packing densities (φ).

4.3 2D Systems

In a similar way to three-dimensional polymer systems, we studied the packing ability of 2D polymers, as polymeric systems confined in extremely thin films. In particular, we analysed the influence of the concentration or surface coverage (φ_{sup}) and the equilibrium bending angle (θ_0) on the packing of semi-flexible polymers in two dimensions, quantifying the short- and long-range order. As a first reference case, we study the packing ability of thin films of athermal, fully flexible polymers and their monomeric analogues under the same conditions. For both fully flexible and semi-flexible polymers, a critical component to analyse is the local order, which is calculated as the degree of order or crystallinity. Thus, the Characteristic Crystallographic Element (CCE) norm [3, 4] is employed to quantify the similarity of the local structure with respect to the honeycomb (HON), square (SQU), triangular (TRI) crystals, and the pentagonal (PEN) local symmetry in two dimensions. In parallel, the global order of semi-flexible polymeric thin films is analysed through the orientational Long-Range Order (LRO) parameter (q), properly modified to take into account the reduction in the dimensionality of the system.

Toward this, the polymeric systems studied in two dimensions correspond to thin films of 100 chains of tangent hard spheres with average chain length $N_{av} = 12$ (in total, $N_{at} = 1200$ monomers), which are equilibrated through Monte Carlo (MC) simulations at constant volume. For the fully flexible polymers, they are modelled as freely-jointed (FJ) chains. The semi-flexible polymers had a bending constant of $k_\theta = 9$ and equilibrium bending angles of $\theta_0 = 0, 60, 90$, or 120° . As explained previously (see Section 3.2.2), polymeric thin films are obtained from very dilute configurations ($\varphi = 0.05$) in three dimensions through the introduction of confining, flat, and parallel walls in one of the dimensions and the adsorption of monomers on one of the flat walls until the formation of a monolayer. Effectively, the simulation cell is converted into a polymer thin film with a thickness equal to the monomer diameter, i.e. a compact monolayer.

The systems of polymeric thin films are subsequently compressed until the random close-packed (RCP) limit is reached, so no further shrinkage is possible. Practically, the long dimensions of the simulation cell are compressed through a shrinkage algorithm of *Simu-D*. Initially, cell compression is performed isotropically until a surface coverage of 0.70 is reached. Then, the shrinkage changes from isotropic to anisotropic (rectangular) by allowing the two large dimensions of the cell to independently fluctuate until no further compaction is possible. The final cell shapes are characterised by a very small value of anisotropy. For the generation of the monomeric system of hard spheres, the initial configuration is generated by removing all bonds in the maximally compressed fully flexible polymer configuration. The

resulting monomeric system is further compressed through the same shrinkage protocol until no further reduction can be achieved.

Table 4.2 summarises the maximum achieved surface coverage (φ_{sup}^{RCP}) through the shrinkage protocol for the monomeric, fully flexible, and semi-flexible systems to be studied in this section. In order to study the packing ability of 2D polymer systems, constant-volume MC simulations are performed for the different systems at the maximum achieved surface coverage (φ_{sup}^{RCP}) and at selected surface coverages $\varphi_{sup} = 0.50, 0.60$, and 0.70 .

Table 4.2: Maximum achieved surface coverage (φ_{sup}^{RCP}) and reduced surface coverage ($\varphi_{sup}^{RCP} / \varphi_{sup}^{max}$) through the shrinkage scheme of thin films in two dimensions for monomeric and polymeric systems, both fully flexible (freely-jointed, FJ) and semi-flexible chains.

Systems	φ_{sup}^{RCP}	$\varphi_{sup}^{RCP} / \varphi_{sup}^{max}$
Monomers	0.901	0.993
FJ ($k_\theta = 0$)	0.895	0.987
$\theta_0 = 0^\circ$	0.774	0.853
$\theta_0 = 60^\circ$	0.839	0.925
$\theta_0 = 90^\circ$	0.797	0.879
$\theta_0 = 120^\circ$	0.764	0.842

Part of the results in this section were published in: Pedrosa, C.; Martínez-Fernández, D.; Herranz, M.; Foteinopoulou, K.; Karayiannis, N.C.; Laso, M. *Densest packing of flexible polymers in 2D films*. The Journal of Chemical Physics, 2023, **158** (16), 164502. <https://doi.org/10.1063/5.0137115> (article available in [6]).

4.3.1 Monomeric and fully flexible polymeric systems

For fully flexible polymeric and monomeric packings, the maximum surface coverages achieved correspond to $\varphi_{sup}(FJ) = 0.895$ and $\varphi_{sup}(HS) = 0.901$, respectively (see Table 4.2). Taking as reference the maximum possible surface coverage, that of the perfect hexagonal crystal, $\varphi_{sup}^{max} = \varphi_{sup}^{TRI} = 0.907$, the 2D polymer and monomer packings are less dense by just 1.3% and 0.7%, respectively. This small difference is expected to decrease even further if we increase the size of the simulation cell and/or properly tune the number of monomers as explained below.

Figure 4.32 presents computer-generated visualisations of the compression of the 2D polymer systems, initially at intermediate surface coverage ($\varphi_{sup} = 0.60$), to the final (i.e. densest) polymeric and monomeric packings at the maximum achieved surface coverage. Systems are represented with monomers colour-coded according to the parent chain (top panels)

and the local structural similarity (bottom panels), the latter as quantified by the CCE norm. It is interesting to note that the MC suite spontaneously generates final, almost perfectly crystalline structures consisting of 32 rows of 37 monomers that fulfil as closely as possible the condition of a given total number of monomers ($32 \times 37 = 1184$ vs 1200) and simultaneously obey the geometric condition of the ratio of height to width of the hexagon ($32/37 = 0.86486$ vs $\sqrt{3}/2 = 0.86603$), which leads to an almost perfectly square simulation cell. Nearby pairs of rows and monomers per row, like 33×36 , fulfil the first condition slightly better, but widely miss the second ($33 \times 36 = 1188$ but $33/36 = 0.91667$). In a perfect 2D TRI crystal, those two conditions would be fulfilled exactly. However, the impossibility of fulfilling both conditions in a system with $N_{at} = 1200$, be it monomeric or polymeric, prevents full crystallinity from being reached. The faults visible in the two lower right panels of Figure 4.32 and the failure to reach 100% crystallinity are primarily due to the discrepancy between $32 \times 37 = 1184$ and 1200.

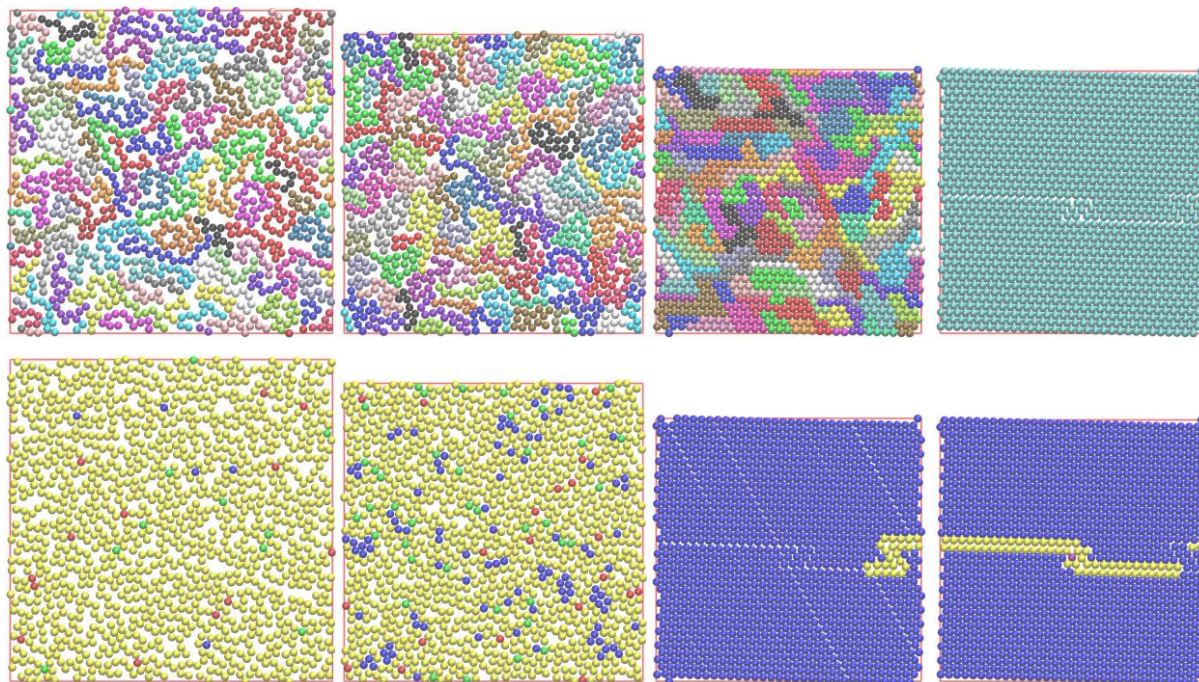


Figure 4.32: Systems in two dimensions at progressively higher surface coverages (φ_{sup}). From left to right: polymer thin films at $\varphi_{sup} = 0.600$, 0.700 , and 0.895 ; monomer thin film at $\varphi_{sup} = 0.901$. Top panels: Monomers are coloured according to the parent chain. For the monomeric system, all monomers are shown in cyan. Bottom panels: Monomers are colour-coded according to their structural environment, as quantified by the CCE norm. Blue, red, purple, and green correspond to TRI-, SQU-, HON-, and PEN-like sites, respectively. Amorphous (AMO) sites are coloured yellow. Images created with VMD visualisation software [295].

As mentioned previously, the exact amount of order present in the system can be quantified through the CCE norm descriptor. Accordingly, the bottom panels of Figure 4.32 host snapshots of thin film configurations at various surface coverages, including the ones with maximum compactness, where the sites are coloured according to their structural similarity to the given reference crystals. At $\varphi_{sup} = 0.600$, the polymer assembly is predominantly

amorphous with a minimal number of crystals mainly of SQU type. At higher surface coverage $\varphi_{sup} = 0.700$, the number of crystallites increases, especially the ones of closely packed TRI character forming small clusters of no more than 6-7 sites. In parallel, pentagonal symmetry emerges and acts as a competitor to the crystal morphologies, in the same way as fivefold symmetry does for the HCP and FCC crystals in 3D [199]. The densest structures correspond to a single TRI crystal with a single, localised defect. Interestingly enough, while the monomeric structure is marginally denser than the polymeric one, it is characterised by a slightly lower degree of order. This is because, on average, the TRI sites are denser and more symmetric than the ones encountered in the polymer packing but the structural defects cover a larger part of the surface. For comparison, if we increase the threshold to $\varepsilon^{thres} = 0.2500$ (0.3000), the corresponding crystallinity becomes 0.980 (0.982) for the chain packing and 0.945 (0.9990) for the monomeric one. A further comparison of the average CCE-norm for the TRI crystal (ε^{TRI}), which is 0.0365 (0.079) and 0.0219 (0.073), for polymers and monomers, respectively, further confirms that the monomer crystal is, on average, structurally better formed than the one made of polymers. The exact numerical values for each crystal and the pentagonal local symmetry can be found in Table 4.3.

Table 4.3: Order parameters (S^X) for the TRI, SQU, and HON crystals, as well as PEN symmetry, and total crystallinity (τ_c^{2D}) for fully flexible chain and monomeric systems, as calculated by the CCE norm descriptor using a threshold value of $\varepsilon^{thres} = 0.245$ [3].

φ_{sup}	S^{TRI}	S^{SQU}	S^{HON}	S^{PEN}	τ_c^{2D}
0.500	3.33×10^{-3}	1.67×10^{-3}	0	0	5.00×10^{-3}
0.600	4.17×10^{-3}	0.0108	0	0.00833	0.0150
0.700	0.0850	0.0167	8.33×10^{-4}	0.0325	0.102
0.895	0.980	0	0	0	0.980
0.901 (monomers)	0.944	0	0	8.33×10^{-4}	0.945

Based on the above, fully flexible athermal polymers can be packed in two dimensions nearly as efficiently as monomeric analogues, reaching a state of almost maximum compactness.

It is also interesting to study how polymer chains behave locally (bonded geometry) and globally (chain size) as their monomers adopt positions that correspond to the sites of the TRI crystal. Figure 4.33 shows the distribution of bending angle (θ), formed by the unit vectors of a triplet of consecutive atoms along the chain backbone, at various surface coverages. Also shown for comparison is the corresponding trend of the same system in bulk 3D under dilute conditions. As density increases, the population of bending angle at $\theta = 120^\circ$ rises, given that the formation of equilateral triangles corresponds to the minimum local free area and, thus,

maximum local surface coverage. This trend is in perfect analogy with that of athermal polymers packing in bulk 3D (see, for example, Fig.1 in Ref. [15]). However, the tendency is distinctly different at $\varphi_{sup} = 0.895$ where populations at $\theta = 0^\circ$, 60° , and 120° dominate since these bending angle configurations are compatible with the occupation of successive sites in the TRI crystal. Noisy peaks of limited intensity appearing near the dominant bending angles correspond to imperfect triangular crystals and the spheres belonging to the small defect-ridden area of the generated system, as seen in Figure 4.32. A further comparison is provided in the inset of Figure 4.33 between the bending angles formed along the chain backbones for the densest polymer packing in 2D and the bending angles, as calculated for the Voronoi neighbours, of the perfect TRI crystal. The observed small difference in the frequency of occurrence suggests that segments of the polymer crystal are constructed by proper positioning of inter- and (non-bonded) intra-chain segments.

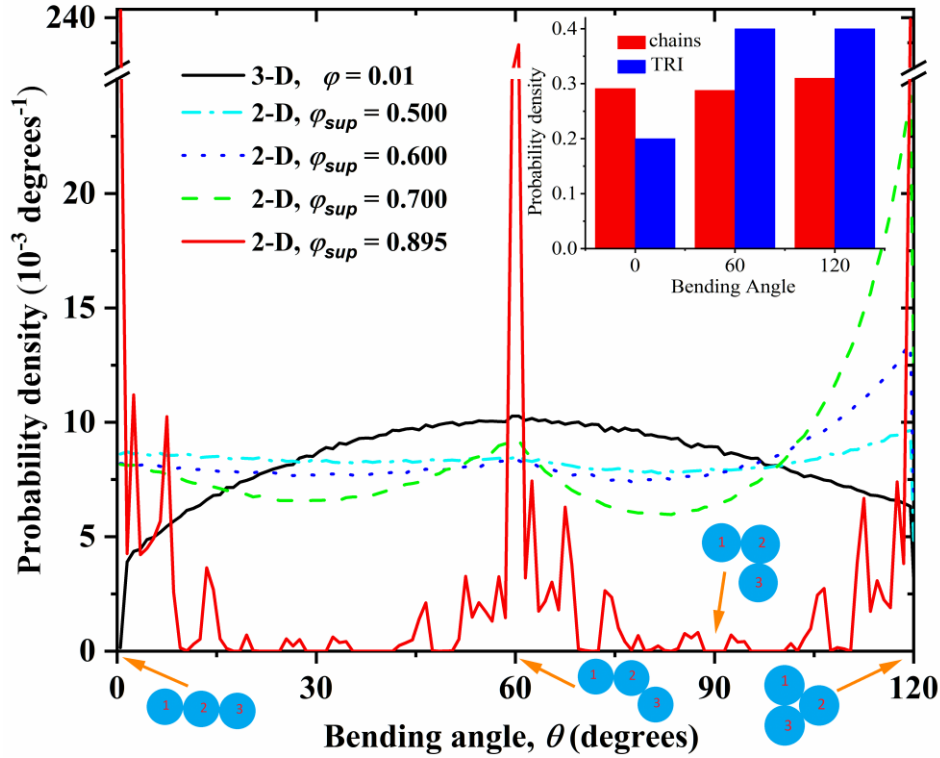


Figure 4.33: Distribution of bending angle (θ) at various surface coverages for the 100-chain, $N_{av} = 12$ freely-jointed systems in 2D. The corresponding distribution of the same system in bulk 3D under dilute conditions ($\varphi = 0.01$) is also shown, together with sketches of the corresponding configurations for selected bending angles. Inset: Comparison of the peaks at 0° , 60° , and 120° as obtained for the densest freely-jointed system in 2D (red) and as calculated between the neighbours of the Voronoi cell of the perfect TRI crystal (blue).

Chain size is quantified by the mean square end-to-end distance, $\langle R^2 \rangle$, and mean square radius of gyration, $\langle R_g^2 \rangle$, where brackets $\langle \rangle$ denote ensemble average over system configurations and chains. A mean-field approximation, based on the concept of excluded volume interaction and chain coiling, as proposed by Flory [42], suggests a relationship of $\langle R_g^2 \rangle \propto N^{2\nu}$, where ν is the Flory exponent given by $\nu = 3/(2 + d)$ and d is the dimensionality of the system. An

exponent of 0.50 is expected for densely packed and collapsed polymer configurations in two dimensions [305].

The main panel of Figure 4.34 shows the dependence of the mean square radius of gyration, $\langle R_g^2 \rangle$, on chain length N . The denser the system becomes, the smaller the size of the polymer chains due to their collapse. This trend can be explained by the spheres adopting an obtuse bending angle of 120° to reduce the local free area, but also the acute 0° and 60° angles to conform with the geometric constraints of the TRI crystal, as seen in the corresponding distribution of Figure 4.33. As a consequence, the shortest average size is observed in the maximally packed polymer crystal of almost perfect triangular character. For comparison, the corresponding trends of 3D polymer packings are also shown at i) the MRJ state in 3D ($\varphi = 0.635$) [14], and ii) in a defect-ridden crystal having a rHCP morphology as formed in constant-volume simulations at $\varphi = 0.58$ [19]. Best linear fits provide the values of $\nu = 0.62$ (2D, $\varphi_{sup} = 0.895$) and 0.57 (3D, $\varphi = 0.635$). The former value lies between the limits of 0.50 (compact and collapsed state) and 0.75 (self-avoiding walk), expected from the analytical predictions in two dimensions [45, 305]. For comparison, at a more dilute state (2D, $\varphi_{sup} = 0.500$), the corresponding Flory exponent is equal to $\nu = 0.705$, according to the present simulations.

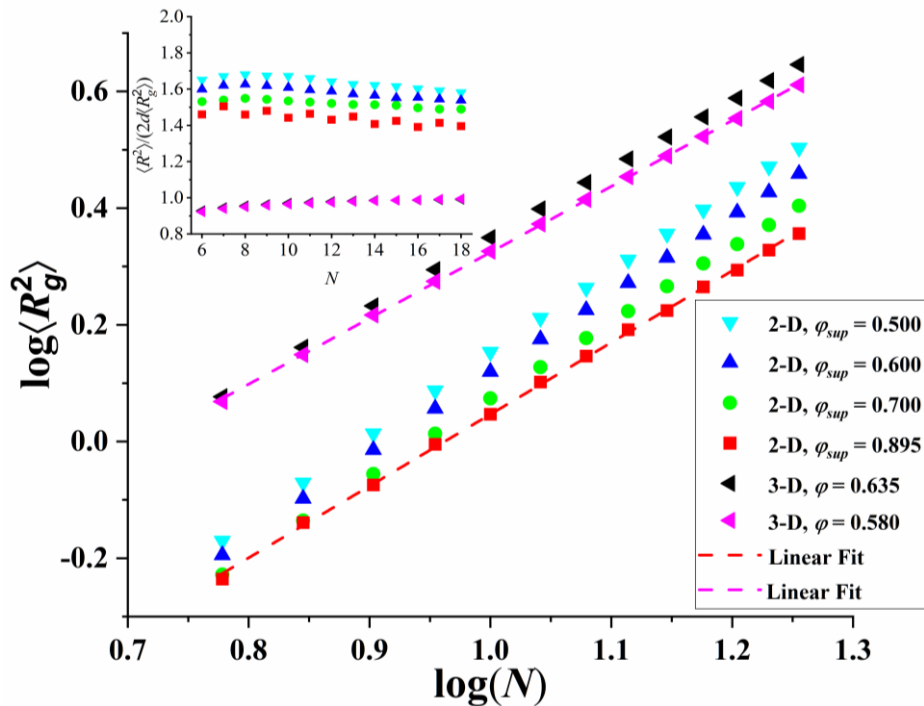


Figure 4.34: Logarithm of the mean square radius of gyration, $\langle R_g^2 \rangle$, as a function of the logarithm of chain length, N , in 2D and 3D at various packing densities, φ , and surface coverages, φ_{sup} . Packing density $\varphi = 0.635$ corresponds to the MRJ state in bulk 3D [14], while $\varphi = 0.58$ corresponds to a polymer crystal of rHCP morphology of alternating layers formed spontaneously in constant-volume simulations as reported in Ref. [19]. Red and purple dashed lines correspond to the best linear fits for 2D ($\varphi_{sup} = 0.895$) and 3D ($\varphi = 0.635$), respectively. Inset: Ratio $\langle R^2 \rangle / (2d \langle R_g^2 \rangle)$ as a function of chain length, where $\langle R^2 \rangle$ is the mean square end-to-end distance and d is the dimensionality of the system.

The inset of Figure 4.34 hosts the ratio $\langle R^2 \rangle / (2d \langle R_g^2 \rangle)$ as a function of chain length, N . Even if the 2D systems studied are characterised by moderate lengths (of average $N_{av} = 12$), both the jammed and the crystal polymer packings in bulk 3D show ideal chain behaviour, as evidenced by $\langle R^2 \rangle / (2d \langle R_g^2 \rangle)$ reaching the value of 1 within minimal statistical uncertainty. In contrast, the maximally dense polymer packing in 2D shows a significant deviation since the corresponding ratio value is approximately 1.4.

4.3.2 Semi-flexible polymeric systems

After studying monomeric and fully flexible polymeric systems, the work is extended to analyse the effect of chain stiffness on the ability of polymers to pack in two dimensions, and especially the influence of the surface coverage (φ_{sup}) and the equilibrium bending angle (θ_0). The local order of the systems is again quantified with the help of the CCE norm, along with the chain conformation and chain size, to compare the results to those obtained for freely-jointed chains and monomers (where available). In the case of semi-flexible polymers in three dimensions, the global order for two-dimensional semi-flexible systems is determined through the nematic LRO parameter (q).

System snapshots at the end of the constant-volume MC simulations in two dimensions are displayed in Figure 4.35 for all the different equilibrium bending angles at progressively higher surface coverage until the random close-packed (RCP) limit is reached. Clearly, the 2D RCP limit itself should, in principle, be strongly dependent on the equilibrium bending angle, especially if the latter is not compatible with the geometry of the TRI crystal. Monomers are coloured according to the parent chain, and the coordinates of their centres are subjected to periodic boundary conditions in the two long dimensions of the simulation cell. Through the shrinkage protocol, the semi-flexible polymeric systems under two dimensions achieved maximum surface coverages, φ_{sup}^{RCP} , (and reduced surface coverages) of 0.7736 (0.853), 0.8387 (0.925), 0.7972 (0.879), and 0.7644 (0.842) for the given equilibrium bending angles of $\theta_0 = 0, 60, 90$, and 120° , respectively (Table 4.2). As a reference, the surface coverage for the ideal TRI, SQU, and HON crystals is approximately 0.907, 0.785, and 0.604, respectively. The latter is too dilute compared to the surface coverage achieved here over the whole range of equilibrium bending angles, so the HON crystal is very rarely encountered, even in the form of isolated ordered sites. Comparing the data on surface coverage from Table 4.2, the following trend is established: $\varphi_{sup}^{RCP}(FJ) > \varphi_{sup}^{RCP}(60^\circ) > \varphi_{sup}^{RCP}(90^\circ) > \varphi_{sup}^{RCP}(0^\circ) > \varphi_{sup}^{RCP}(120^\circ)$. As expected, fully flexible chains can be packed in the most efficient pattern, whose density lies within 1.4% of the densest limit (the perfect TRI crystal). On the other hand, the least dense RCP limit unexpectedly corresponds to semi-flexible polymers with $\theta_0 = 120^\circ$, i.e. one corresponding to the locally fully collapsed conformation.

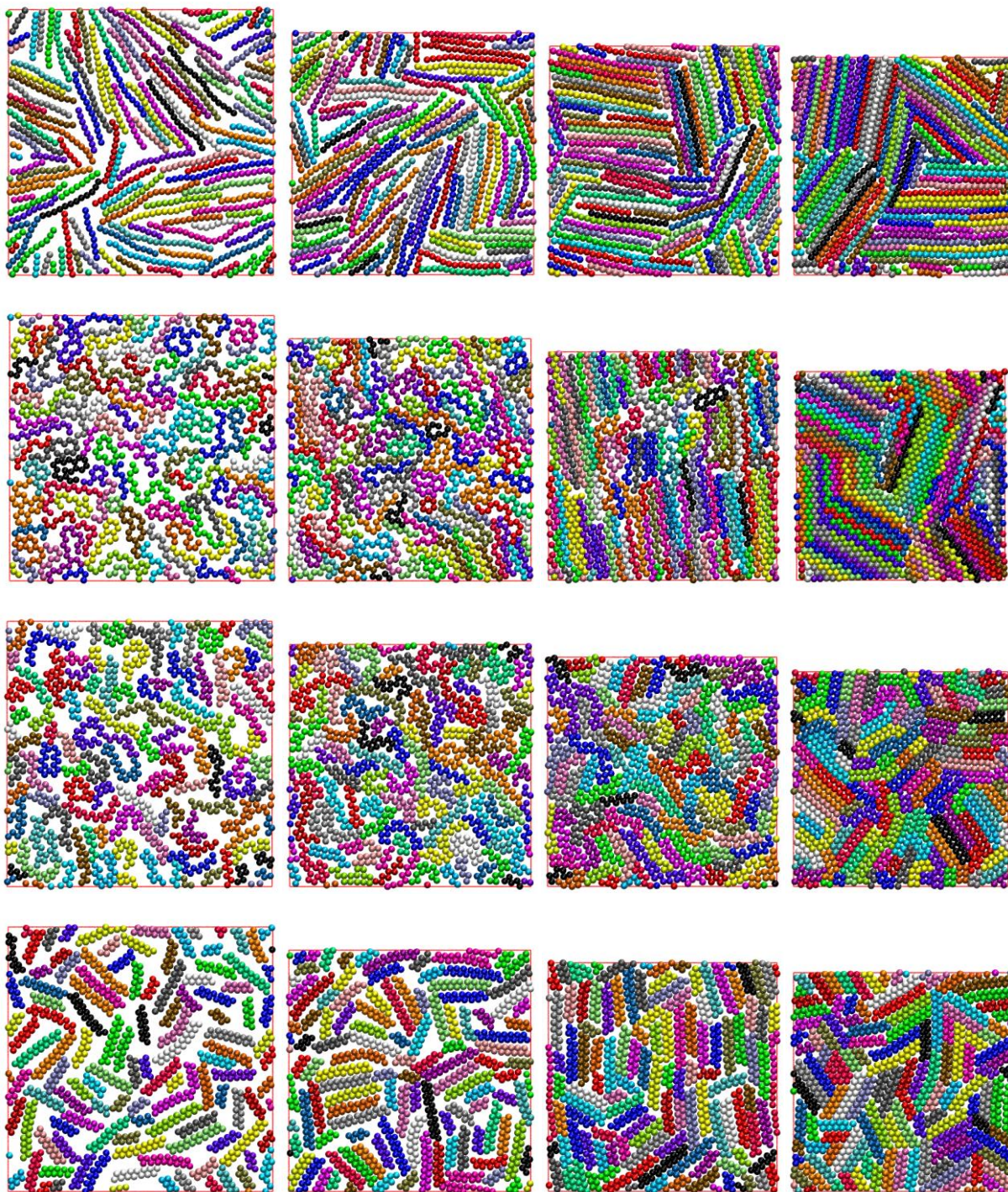


Figure 4.35: Snapshots at the end of the MC simulations of semi-flexible polymer systems in two dimensions for different equilibrium bending angles (θ_0) and at progressively higher surface coverages (φ_{sup}). From top to bottom: $\theta_0 = 0, 60, 90$, and 120° . From left to right: $\varphi_{sup} = 0.50, 0.60, 0.70$, and φ_{sup}^{RCP} . Maximum achieved surface coverages (φ_{sup}^{RCP}) for each θ_0 are collected in Table 4.2. Monomers are coloured according to the parent chains, and the coordinates of their centres are subjected to periodic boundary conditions (PBCs) in the two long dimensions of the simulation cell. Images created with VMD visualisation software [295].

However, the lowest RCP limit for $\theta_0 = 120^\circ$ is somewhat surprising given that the $\theta_0 = 90^\circ$ is the only angle that is not encountered between the nearest neighbour sites in the TRI crystal. Given that i) the average chain length studied here is $N_{av} = 12$, ii) bonded monomers are tangent and, thus, by construction also neighbours, and iii) chain ends are free of bending constraints, approximately 83.3% of the monomers have, at least, two nearest neighbours whose bending conformation is not compatible with the geometry of TRI crystal. Thus, this geometric incompatibility of the 90° bending angle frustrates the formation of the TRI crystal, as bond tangency hinders, in general, athermal crystallisation near the melting transition, compared to the presence of bond gaps [22, 201]. Consequently, it is expected that the corresponding system cannot achieve surface coverages as high as those of polymers whose equilibrium bending angles are compatible with TRI crystals.

However, further geometric arrangements, due to the inter-molecular alignment of chains, could additionally affect the packing ability of semi-flexible polymers. This statement is also relevant in the case of $\theta_0 = 90^\circ$ chains. The RCP limit for semi-flexible polymers of $\theta_0 = 90^\circ$, as calculated from the present MC simulations ($\varphi_{sup}^{RCP}(90^\circ) \approx 0.797$), is higher than the surface coverage of the ideal SQU crystal ($\varphi_{sup}^{SQU} \approx 0.785$). Accordingly, the sphere arrangement for right-angle chains is expected to correspond to a blend of square conformations built through intra-chain conformations, because of the imposed bending constraints, and more compact local packings achieved through inter-chain arrangements. Therefore, in the densest possible state, semi-flexible polymers of $\theta_0 = 90^\circ$ should maximise their external contour available for inter-chain arrangements. Accordingly, chains should adopt extended conformations, and the higher the concentration, the more elongated the corresponding configuration. This is verified by comparing, for example, the snapshots of the left- and right-most panels in Figure 4.35 for $\theta_0 = 90^\circ$. This inter- and intra-chain arrangement is expected to have further and profound complications in the observed and global order of the chains, as will be demonstrated in the continuation.

As a first analysis of the global order under two dimensions, Figure 4.36 shows snapshots at the end of the MC simulations for all the different equilibrium bending angles at progressively higher surface coverages. Chains are represented by blue lines, and vectors of the largest (semi)axis of the inertia ellipsoid are coloured red, with a length proportional to the corresponding length of the axis. Furthermore, Figure 4.37 presents the dependence of the nematic long-range order (LRO) parameter (q) on the surface coverage (φ_{sup}) for all semi-flexible systems studied, including the LRO parameter of freely-jointed chains for comparison. The mean value of q , averaged over all frames of the equilibrated part of the simulation trajectory, is represented together with the minimum and maximum values of q over the equilibrated part of the MC trajectory as a qualitative representation of the stability of the systems with respect to the global order.

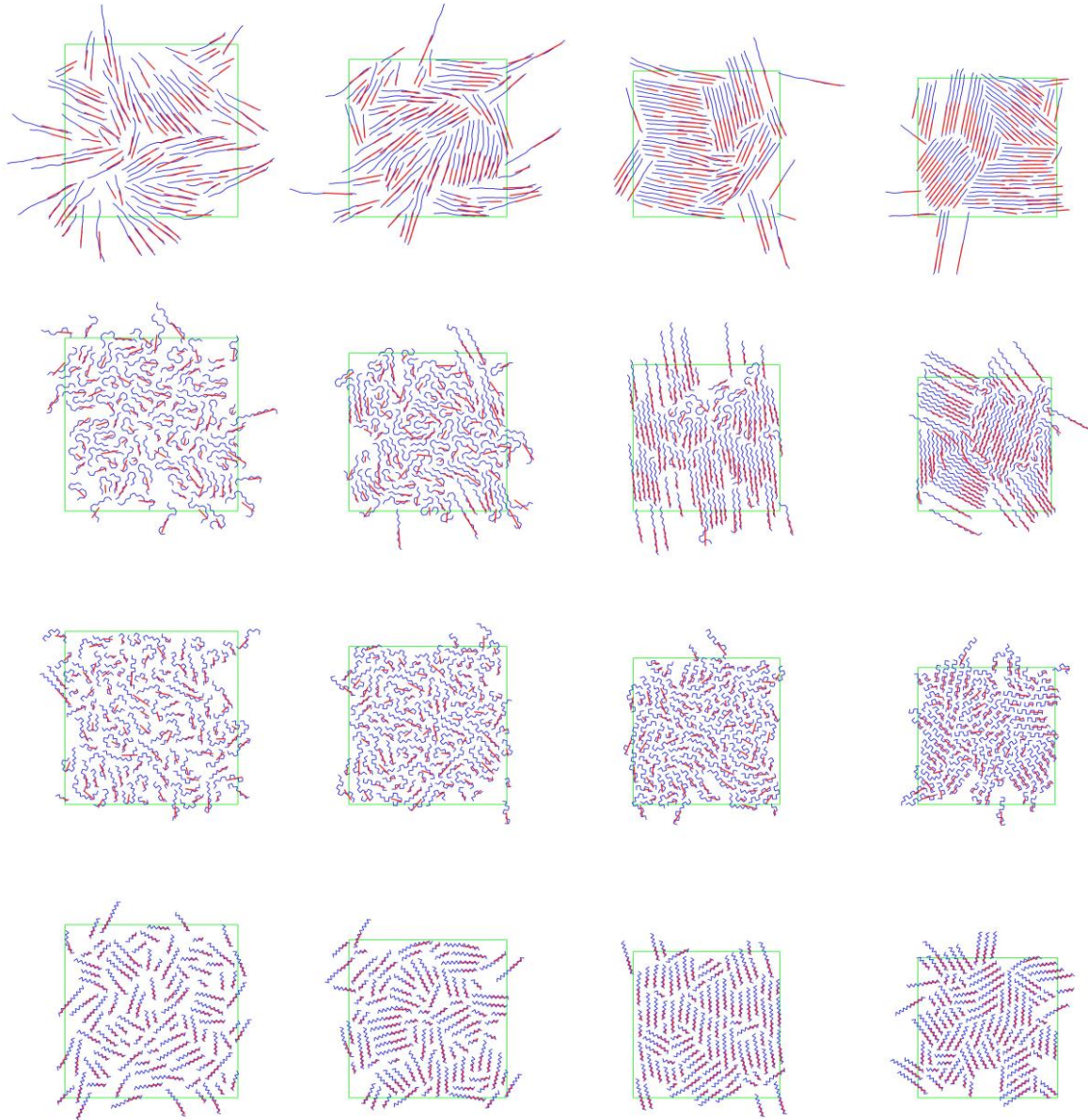


Figure 4.36: Snapshots at the end of the MC simulations on semi-flexible polymer systems in two dimensions.

Chains are represented by lines (bonds) and coloured blue. Also shown in red is the vector of the largest (semi)axis of the inertia ellipsoid, with a length proportional to the corresponding length of the axis. From top to bottom: $\theta_0 = 0, 60, 90$, and 120° . From left to right: $\varphi_{sup} = 0.50, 0.60, 0.70$, and φ_{sup}^{RCP} for each θ_0 (collected in Table 4.2). Images created with VMD visualisation software [295].

Unexpectedly, rod-like polymer systems follow a decreasing trend in the global LRO with increasing surface coverage (see Figure 4.37). Despite this trend, snapshots of rod-like ($\theta_0 = 0^\circ$) and zig-zag chains of acute ($\theta_0 = 60^\circ$) or obtuse ($\theta_0 = 120^\circ$) bending angles in Figure 4.36 show that chains tend to align mutually parallel and form clusters with different directions. This prevailing behaviour at the RCP limit could correspond to the establishment of an orientational tetratic order, where each pair of chains is either mutually parallel or perpendicular [306]. The current global-order analysis tool cannot identify and quantify the tetratic order of the systems. Thus, the present LRO descriptor needs to be expanded so as to

gauge the orientational long-range order in 2D through two scalar order parameters: the nematic and the tetratic order parameters (see explanation in Future Plans).

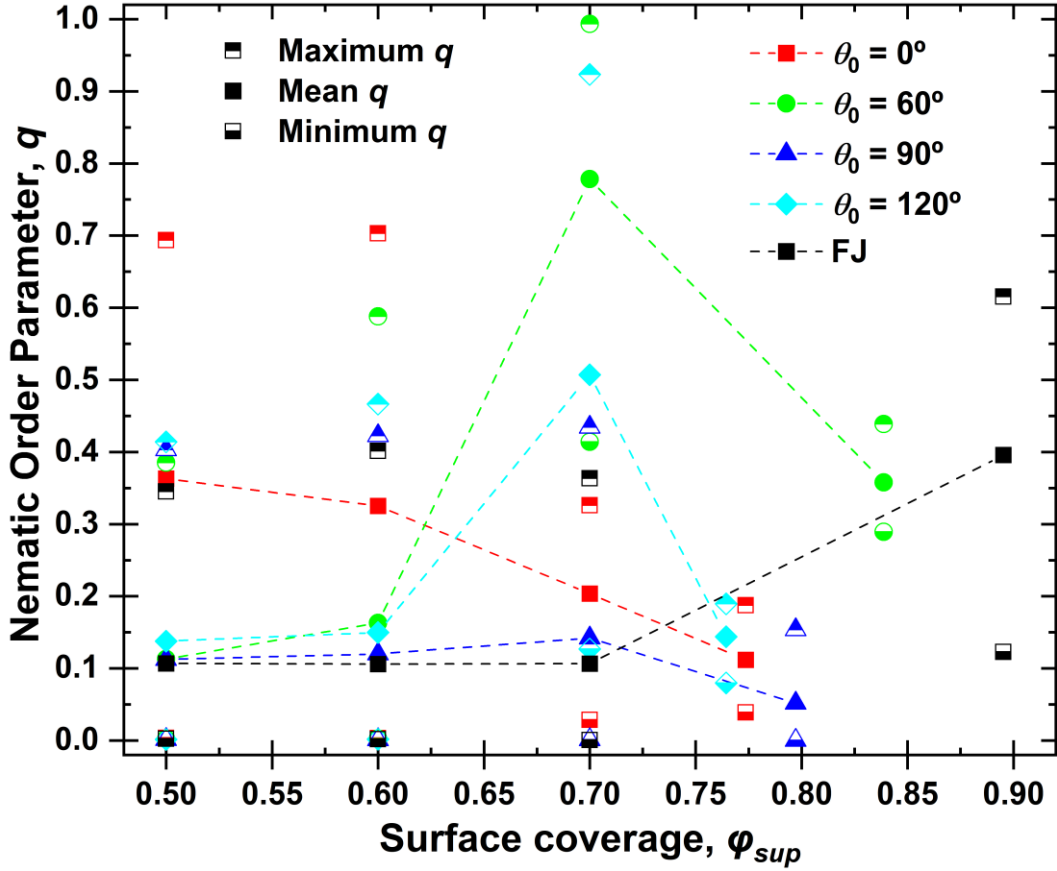


Figure 4.37: Evolution of the LRO parameter (q) as a function of surface coverage (ϕ_{sup}) for the different equilibrium bending angles (θ_0) of 100-chain, $N_{av} = 12$ semi-flexible systems in two dimensions, including a comparison with the freely-jointed (FJ) chains. Semi-filled points correspond to minimum and maximum observed values, and filled points correspond to the average value over the equilibrated trajectory. Dashed lines connecting points of mean value serve as visual aid.

Focussing on rod-like systems, Ref. [257] has demonstrated that spherocylinders confined to a plane show a nematic phase when their aspect ratio is higher than a threshold value $L/D > 7$, where L is the length and D the diameter (the limit of $D \rightarrow 0$ corresponding to needles [256]). Shorter rods show an isotropic phase where chains are aligned either side-by-side or perpendicular to each other [257]. In our rod-like polymer case, dispersity in chain lengths is enforced, combined further with a distribution of bending angles around the equilibrium value. Thus, our computer-generated samples deviate from the ideal, fixed-shape rods of the aforementioned study. Still, we can attempt a comparison of the aspect ratio as a function of surface coverage and N by considering that $D = \sigma = 1$ and $R(N) = N - 1 = L$. For $\theta_0 = 0^\circ$, and at all surface coverages studied, including one of the RCP limit, approximately 23% of the chain population have aspect ratio $L/D = R(N)/\sigma \leq 7$, corresponding to lengths $N = 6, 7$, and 8. This could potentially make the observed nematic phase unstable compared to systems with significantly longer chains. The analysis in Ref. [255] for infinitely thin rods

(needles) demonstrates that rod length dispersity significantly affects phase behaviour, with long and short rods stabilising and weakening, respectively, the nematic phase.

On the other hand, semi-flexible systems that do not present orientational ordering in three dimensions ($\theta_0 = 60$ and 120°) show in two dimensions a certain degree of long-range order at $\varphi_{sup} = 0.70$ in nematic phases, which can reach high values of the nematic LRO parameter ($q \geq 0.9$) with some system configurations. This requires that semi-flexible chains, especially $\theta_0 = 60^\circ$, predominantly adopt extended conformations while corresponding bending angle constraints are fulfilled; for example, chains of $\theta_0 = 60^\circ$ form maximally-extended, zig-zag conformations. In parallel, all systems present a decrease in the LRO when they reach the RCP limit, except for the freely-jointed chains. Given that the RCP limit is intimately related to the concept of randomness, this is an important finding. In three dimensions, RCP can be quantified by gauging the densest structures and selecting among them the ones with the least local order or, equivalently, of maximum disorder. In two dimensions, the situation is different given that the RCP limit is quite close to the maximum densest limit that corresponds to the TRI structure, so the RCP limit is characterised by a high degree of local order, in relative terms much higher than the corresponding one in 3D. The distinguishing feature of the 2D RCP can thus be the significant reduction of long-range order, as quantified here by the nematic order parameter. The unexpected increase of LRO for freely-jointed chains when the RCP limit is reached could be related to groups of chains selecting specific directions during the formation of the TRI crystal with a high degree of crystallinity, as was observed in Figure 4.32.

Interesting trends can be established by studying the evolution of the nematic order parameter (q) over the MC simulation as presented in Figure 4.38. It must be noted that the rest of the semi-flexible systems, not shown here, exhibit a stable value of the nematic order parameter over the whole simulation trajectory. The panel (a) of Figure 4.38 focuses on rod-like chains ($\theta_0 = 0^\circ$) at surface coverage of $\varphi_{sup} = 0.50$. For this system, the nematic order parameter shows very large fluctuations between a maximum value of $q \approx 0.84$, corresponding to a predominantly nematic phase, and a minimum value of $q = 0$, indicative of isotropic behaviour. Figure 4.39 shows snapshots for the rod-like system at $\varphi_{sup} = 0.50$ that corresponds to configurations with minimum ($q = 0.004$), mean ($q = 0.363$), and maximum ($q = 0.836$) observed values of q , where chains are represented as blue lines and vectors of the largest semi(axis) of the inertial ellipsoid, as red lines. Such very large fluctuations correspond to an unstable nematic phase, which is expected since a significant percentage of rod-like chains possess an aspect ratio that is below the identified threshold for the formation of stable nematic phases in two dimensions [257], as explained above.

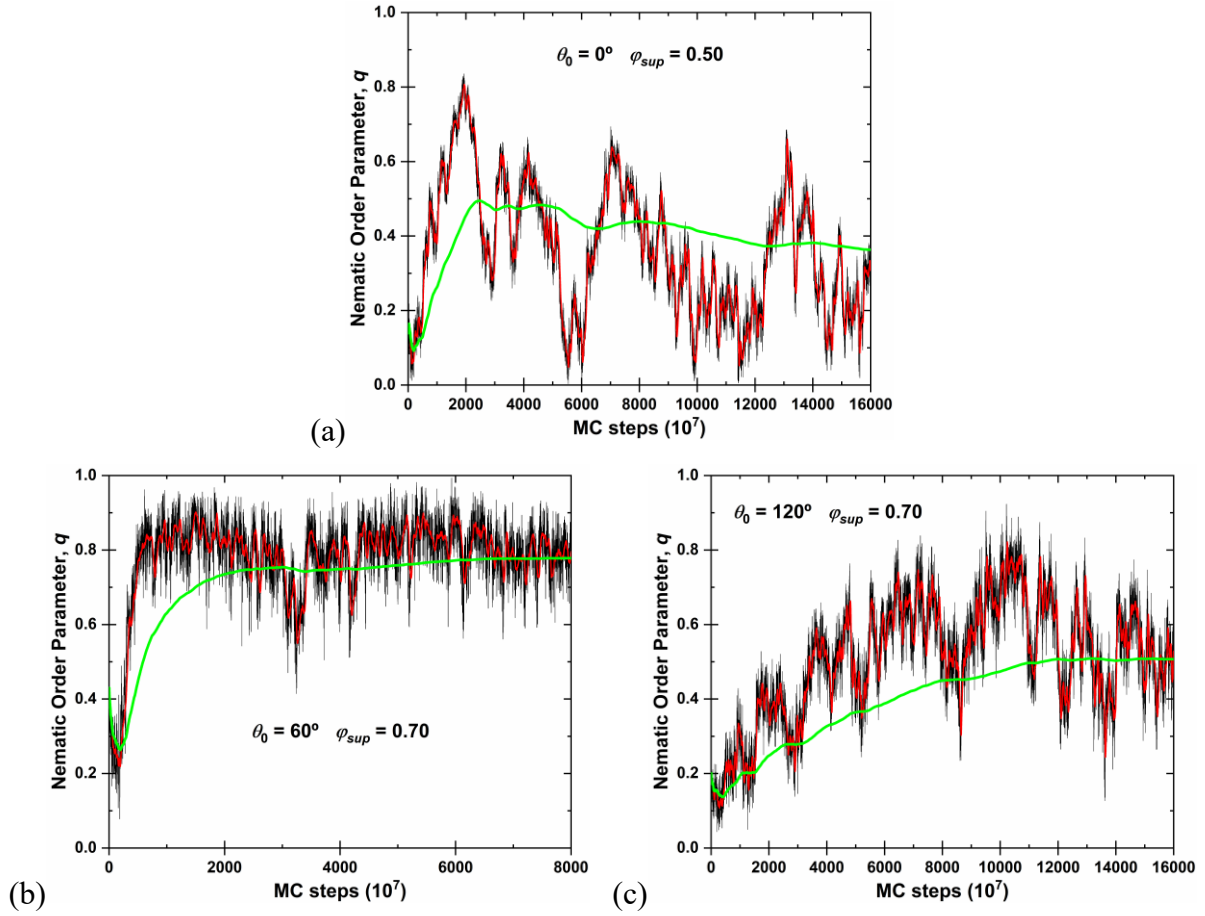


Figure 4.38: LRO parameter (q) as a function of MC steps for selected simulated 100-chain, $N_{av} = 12$ systems: (a) $\theta_0 = 0^\circ$ and $\varphi_{sup} = 0.50$; (b) $\theta_0 = 60^\circ$ and $\varphi_{sup} = 0.70$; (c) $\theta_0 = 120^\circ$ and $\varphi_{sup} = 0.70$. Black, red, and green lines correspond to instantaneous value, simple running average (with a period of 50 frames), and cumulative running average, respectively. In all cases, 1 frame corresponds to 10^7 MC steps.

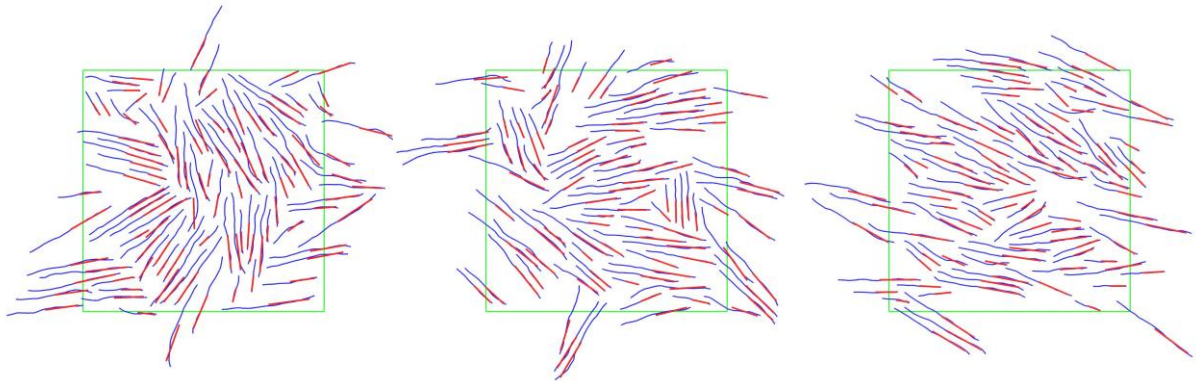


Figure 4.39: Snapshots of the rod-like system of $\theta_0 = 0^\circ$ at $\varphi_{sup} = 0.50$ corresponding to the configurations with minimum (left: $q = 0.004$, frame #5544), mean (middle: $q = 0.363$, frame #14872) and maximum (right: $q = 0.836$, frame #1927) value of the LRO parameter. Chains are shown in unwrapped coordinates and are represented by blue lines (bonds). Also shown in red is the vector of the largest (semi)axis of the inertia ellipsoid, with a length proportional to the corresponding length of the axis. The corresponding evolution of q as a function of MC steps can be seen in the panel (a) of Figure 4.38. Images created with VMD visualisation software [295].

On the other hand, the semi-flexible system of $\theta_0 = 60^\circ$ at $\varphi_{sup} = 0.70$ (panel (b) in Figure 4.38) shows a clear isotropic $\rightarrow$ nematic transition with the mesogens (zig-zag chains) adopting stable configurations once the nematic phase is established. Indicative snapshots of the long-range ordering transition of the zig-zag chains can be seen in Figure 4.40. A similar isotropic-nematic transition is also observed for the semi-flexible system of $\theta_0 = 120^\circ$ at $\varphi_{sup} = 0.70$ (panel (c) in Figure 4.38), although the nematic phase is more unstable and presents a lower mean LRO than the semi-flexible polymers of $\theta_0 = 60^\circ$. Figure 4.41 shows snapshots of the configurations corresponding to the minimum ($q = 0.0435$), mean ($q = 0.560$), and maximum ($q = 0.923$) observed values of q for the semi-flexible polymer system of $\theta_0 = 120^\circ$ at $\varphi_{sup} = 0.70$.

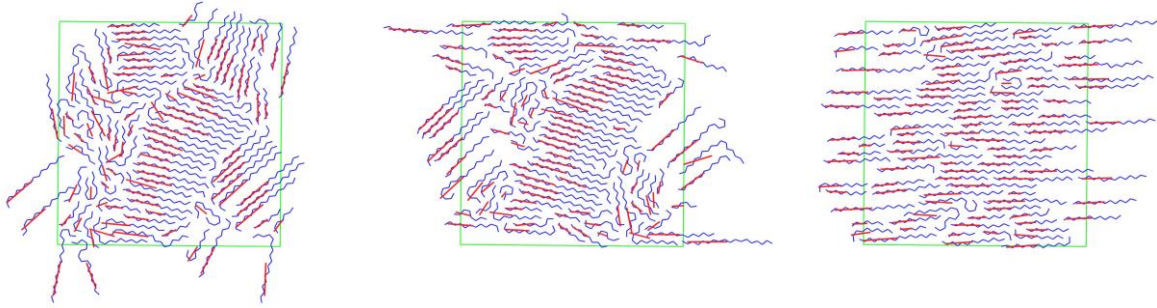


Figure 4.40: Snapshots along the isotropic-nematic transition for the polymeric system of $\theta_0 = 60^\circ$ at $\varphi_{sup} = 0.70$. From left to right: $q = 0.0777$ (frame #186), $q = 0.507$ (frame #307), and $q = 0.994$ (frame #5932). 1 frame corresponds to 10^7 MC steps. Chains are shown in unwrapped coordinates and are represented by blue lines (bonds). Also shown in red is the vector of the largest (semi)axis of the inertia ellipsoid, with a length proportional to the corresponding length of the axis. The corresponding evolution of q as a function of MC steps can be seen in the panel (b) of Figure 4.38. Images created with VMD visualisation software [295].

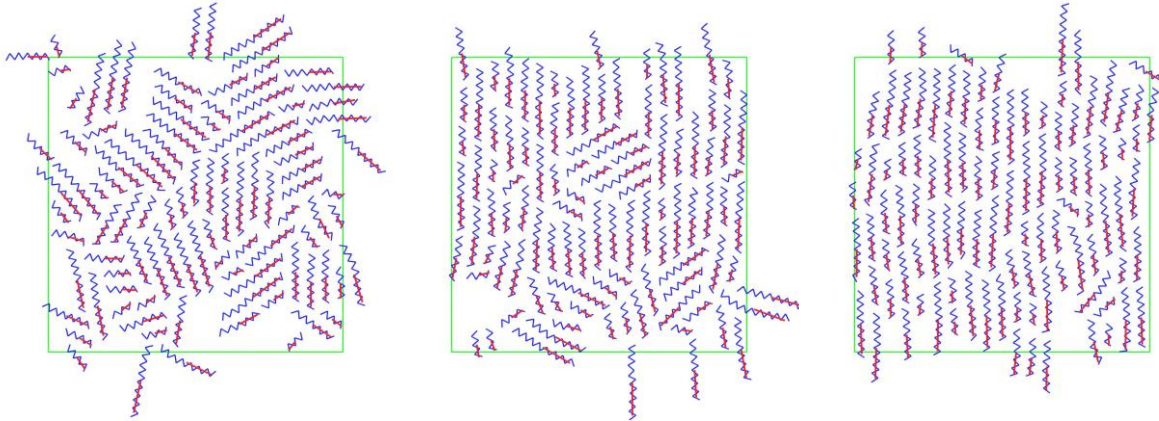


Figure 4.41: Snapshots along the isotropic-nematic transition for the polymeric system of $\theta_0 = 120^\circ$ at $\varphi_{sup} = 0.70$. From left to right: the minimum observed value ($q = 0.0435$, frame #211), approximately the mean value ($q = 0.560$, frame #12473), and the maximum observed value ($q = 0.923$, frame #10216). 1 frame corresponds to 10^7 MC steps. Chains are shown in unwrapped coordinates and are represented by blue lines (bonds). Also shown in red is the vector of the largest (semi)axis of the inertia ellipsoid, with a length proportional to the corresponding length of the axis. The corresponding evolution of q as a function of MC steps can be seen in the panel (c) of Figure 4.38. Images created with VMD visualisation software [295].

An essential element in the identification of the crystal phase, the MRJ state, or the RCP limit is the quantification of local order. As for fully flexible polymers, the CCE norm descriptor [3, 4] is employed to quantify the structural similarity to the triangular (TRI), square (SQU), and honeycomb (HON) crystals as well as the pentagonal (PEN) symmetry, adopting a threshold of $\varepsilon^{thres} = 0.245$ for all the calculations. Figure 4.42 presents the evolution of the total crystallinity (τ_c) of the 2D semi-flexible systems as a function of the surface coverage for the different equilibrium bending angles, including along the evolution of freely-jointed chains for comparison. Furthermore, Figure 4.43 shows CCE-based system snapshots at the end of the MC simulations at different surface coverage, including the densest ones achieved, for each equilibrium bending angle. Monomers with TRI, SQU, HON, and PEN similarity are coloured blue, red, purple, and green, respectively. Monomers labelled as amorphous, or more precisely as “unidentified”, are coloured yellow.

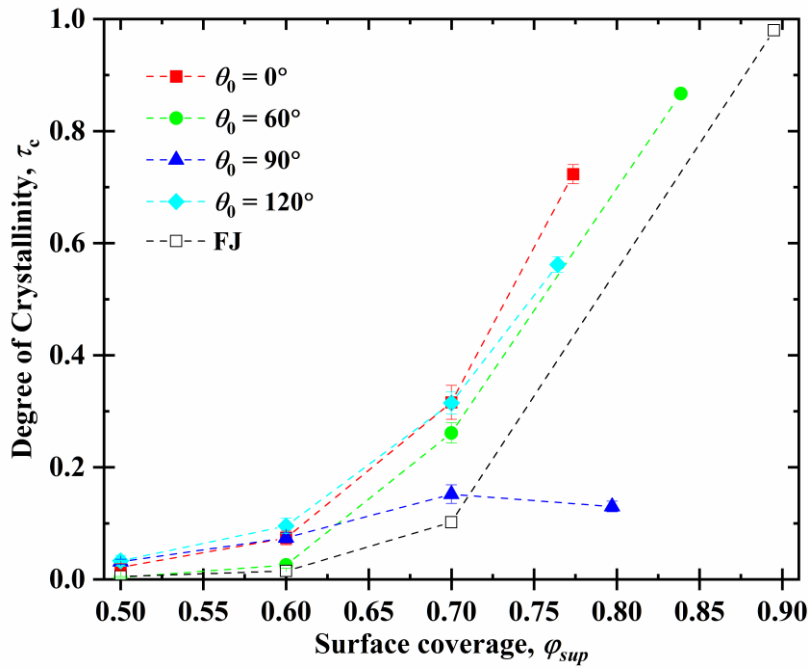


Figure 4.42: Degree of crystallinity (τ_c) as a function of surface coverage (φ_{sup}) for the different equilibrium bending angles (θ_0) of 100-chain, $N_{av} = 12$ semi-flexible systems in two dimensions, including a comparison with the freely-jointed (FJ) chains. Dashed lines connecting points serve as visual aid.

At the lowest surface coverage ($\varphi_{sup} = 0.50$), all systems are predominantly amorphous and the number of sites with a crystal structure is very low, i.e. the degree of crystallinity tends to zero. As surface coverage increases, crystallinity increases, and ordered sites start to form small and isolated clusters. These clusters grow significantly in size as concentration further increases, as can be observed at $\varphi_{sup} = 0.70$ in Figure 4.43. Finally, at the RCP limit, all systems exhibit the highest local order, with the crystallinity being higher, the denser the RCP limit for the corresponding system. Given the very high values of surface coverage, the RCP limit for $\theta_0 = 0^\circ$, 60° , and 120° corresponds to a TRI crystal, ridden with

defects in the form of amorphous sites and free of isolated clusters of other ordered morphologies.

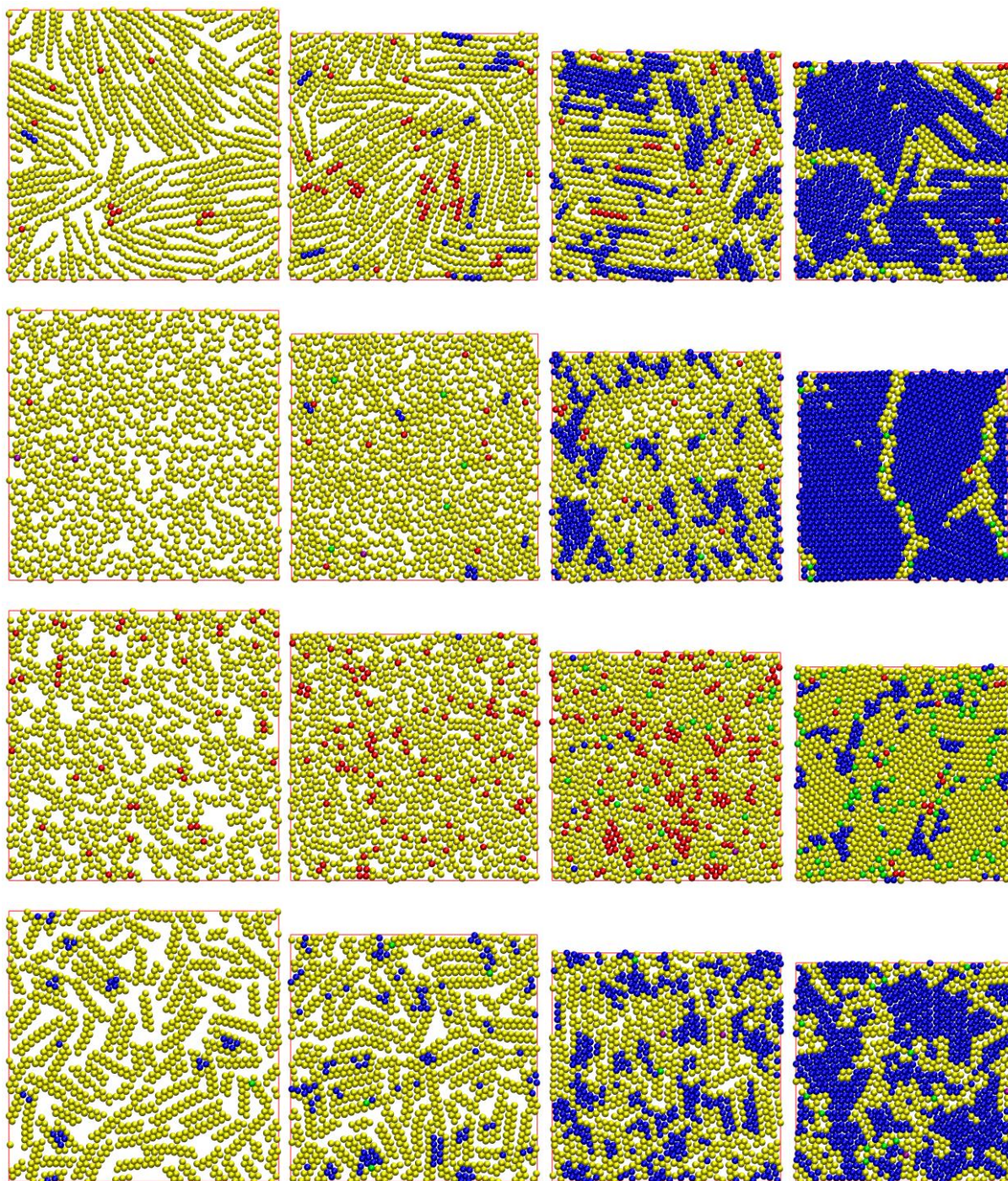


Figure 4.43: Snapshots at the end of the MC simulations on semi-flexible polymer systems in two dimensions. Monomers are coloured according to their crystal similarity by the CCE norm descriptor: blue, red, purple, and green colours correspond to TRI, SQU, and HON crystals, and PEN local symmetry, respectively. Amorphous or unidentified (AMO) sites are coloured yellow. From top to bottom: $\theta_0 = 0, 60, 90$, and 120° . From left to right: $\varphi_{sup} = 0.50, 0.60, 0.70$, and φ_{sup}^{RCP} . Maximum achieved surface coverages (φ_{sup}^{RCP}) for each θ_0 are collected in Table 4.2. Images created with VMD visualisation software [295].

The only exception to the general trend dictating that RCP shows the highest local order is the right-angle chain system. This is expected given that $\theta_0 = 90^\circ$ is incompatible with the geometry of the adjacent sites in the TRI crystal. Furthermore, the bending constant ($k_\theta/k_B T = 9 \text{ rad}^2$) is strong enough so as not to allow angle distortions which could lead to bending conformations of 60° or 120° , which are elements of the connectivity of the TRI crystal. It is interesting to note (Figure 4.43) that, while the system remains primarily amorphous throughout the range of surface coverages, the established crystals adopt the order of the SQU crystals for $\varphi_{sup} = 0.50, 0.60$, and 0.70 . Furthermore, the higher the concentration, the higher the order of SQU (and crystallinity), as seen in Figure 4.42. However, as the system transits to the RCP state, the pattern changes drastically, the SQU sites disappear almost completely and get replaced by small clusters of TRI character, while crystallinity decreases. Due to the RCP surface coverage ($\varphi_{sup}^{RCP}(90^\circ) \approx 0.797$) being higher than that of the pure SQU crystal ($\varphi_{sup}^{SQU} \approx 0.785$), the resulting packing is necessarily a blend of intra-molecular square packing, imposed by the right-angle bending constraints, and inter-molecular arrangements that fill the gaps in the square spacing to maximise the local density. The net result is a configuration that is significantly less ordered, at least with respect to the TRI reference crystal. This can be clearly seen in the structural details of Figure 4.44 corresponding to a segment of the polymer packing at $\varphi_{sup}^{RCP}(90^\circ)$, as established at the end of the MC simulation. Sphere monomers are coloured according to the parent polymer so as to identify the intra- and inter-chain local arrangements. Square and triangle shapes are drawn to indicate the formation of intra- and inter-molecular squares and intermolecular triangles, filling the gaps between the vertices of the squares. In addition, it can be seen that a significant fraction of the squares is distorted because the bending angles follow a distribution around the equilibrium bending angle, as explained below.

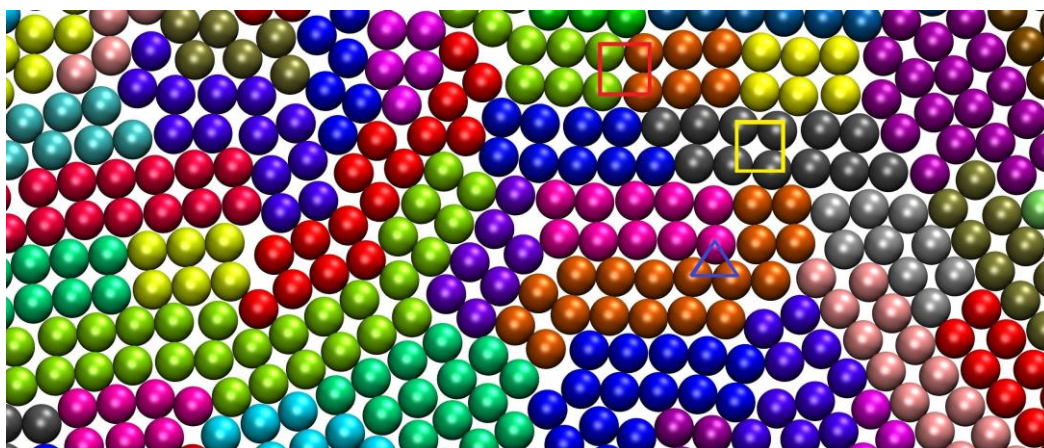


Figure 4.44: Detail of the snapshot at the end of the MC simulation for the semi-flexible system with $\theta_0 = 90^\circ$ at $\varphi_{sup}^{RCP}(90^\circ) \approx 0.797$. Monomers are coloured according to the parent chain. Yellow and red squares indicate intra- and inter-molecular local arrangements, respectively, leading to the formation of a square. Blue triangle indicates interchain triangular packing. Image created with VMD visualisation software [295].

The distributions of bending angles for the semi-flexible polymeric systems studied are shown in Figure 4.45 at various surface coverages. As for semi-flexible polymers in three dimensions, the harmonic spring constant employed of $k_\theta/k_B T = 9 \text{ rad}^{-2}$ allows the bending angles to fluctuate in an interval of approximately $\pm 20^\circ$ around the equilibrium bending angle (θ_0). The bending angle distribution becomes progressively narrower from $\varphi_{sup} = 0.50$ to 0.70 for all equilibrium angles, except for 90° where the distribution is practically unaffected by the change of concentration. Thus, because packing promotes the formation of TRI structures (densest limit), the distributions become narrower for angles corresponding to neighbouring sites of the TRI crystal.

For semi-flexible chains, both polymer size and shape are dominated by constraints imposed by chain connectivity and, to a lesser degree, by concentration. This is in contrast to the behaviour of freely-jointed chains, for which four distinct scaling regimes can be identified on the dependence of chain size on volume fraction from dilute to nearly jammed packings [16, 33]. Because bond lengths are, within a very small numerical tolerance, kept to $l = \sigma$ (tangency) while a single layer is formed with a thickness equal to the monomer diameter, all torsion angles are forced to adopt the values 0° or $\pm 180^\circ$. Therefore, this combination of chain geometry, whose bending angle distribution is dominated by the harmonic bending potential as seen in Figure 4.45, along with surface coverage leads to a non-trivial effect of chain size, considering also the different equilibrium bending angles.

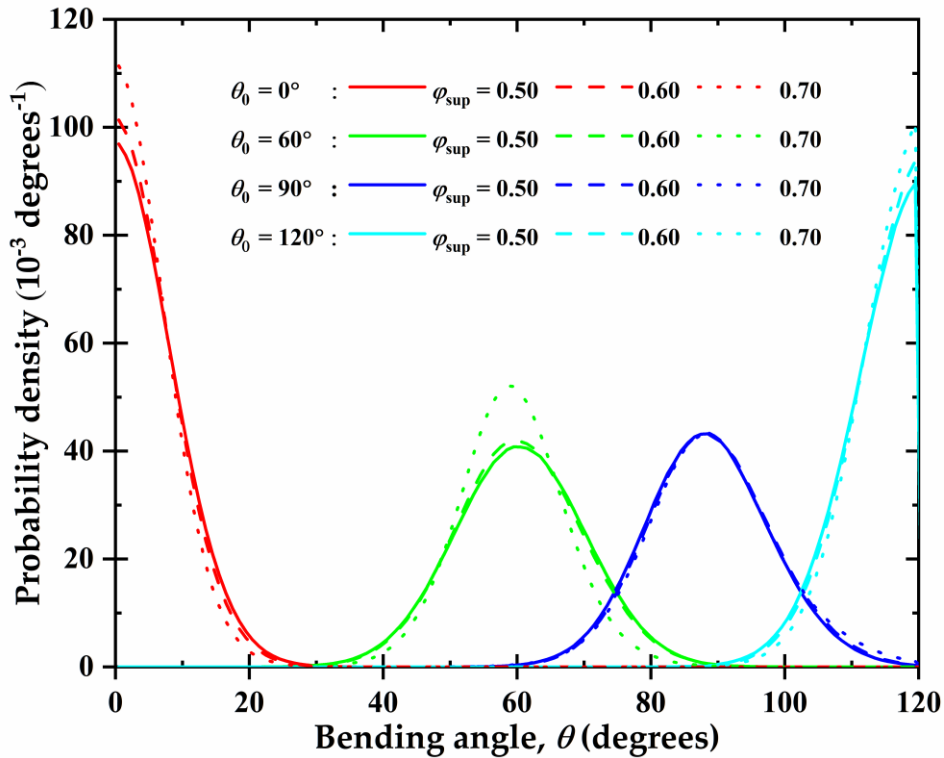


Figure 4.45: Distribution of bending angle (θ) for the 100-chain, $N_{av} = 12$ semi-flexible systems in 2D at surface coverages of $\varphi_{sup} = 0.50, 0.60$, and 0.70 for different equilibrium bending angles (θ_0).

Chain size of semi-flexible polymers under two dimensions is quantified again through the mean square end-to-end distance, $\langle R^2 \rangle$, and mean square radius of gyration, $\langle R_g^2 \rangle$, as presented in Figure 4.46. Furthermore, since simulations are performed on systems with chain length dispersity ($N \in [6,18]$) and chain-connectivity-altering moves guarantee robust sampling of long-range polymer conformations, we can further analyse the effect of chain length on size. Left and right panels present the dependence of $\langle R^2 \rangle$ and of the ratio $\langle R^2 \rangle / \langle R_g^2 \rangle$, respectively, on the number of bonds per chain ($N - 1$) at a surface coverage of $\varphi_{sup} = 0.70$ for all equilibrium bending angles, including a comparison with the freely-jointed (FJ) chains from above. The middle panel shows the dependence of $\langle R_g^2 \rangle$ on $N - 1$ for $\theta_0 = 60^\circ$ at various surface coverages.

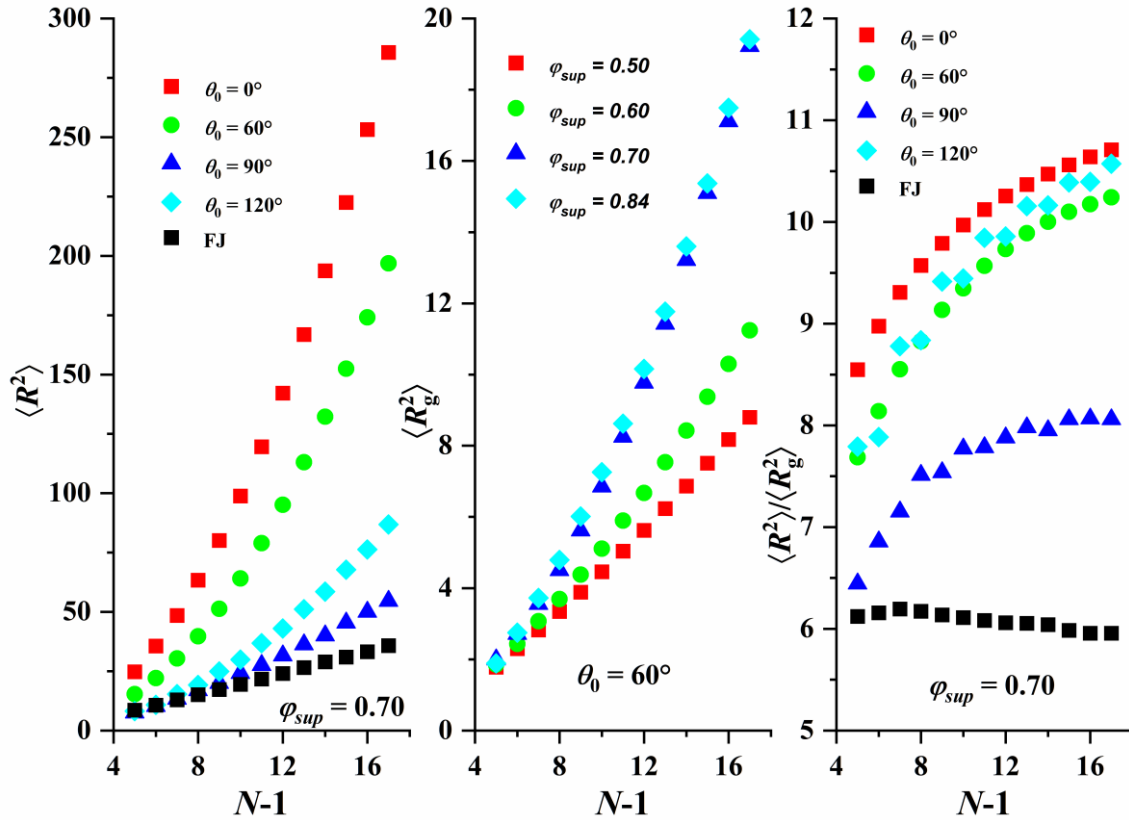


Figure 4.46: (Left) Mean square end-to-end distance, $\langle R^2 \rangle$, as function of number of bonds ($N-1$) at a surface coverage of $\varphi_{sup} = 0.70$ for different equilibrium bending angles (θ_0) of 100-chain, $N_{av} = 12$ semi-flexible systems in two dimensions, including a comparison with the freely-jointed (FJ) chains. (Middle) Mean square radius of gyration, $\langle R_g^2 \rangle$, as function of $N-1$ at different surface coverages (φ_{sup}) for $\theta_0 = 60^\circ$. (Right) Ratio $\langle R^2 \rangle / \langle R_g^2 \rangle$ as a function of $N-1$ for different equilibrium bending angles at $\varphi_{sup} = 0.70$.

Acute bending angles of $\theta_0 = 0^\circ$ and 60° lead to longer sizes while the freely-jointed chains present the most compact systems. As surface coverage increases, the chain size increases, but there is no appreciable difference in the radius of gyration between $\varphi_{sup} = 0.70$ and $\varphi_{sup}^{RCP}(60^\circ) \approx 0.839$. With respect to the ratio $\langle R^2 \rangle / \langle R_g^2 \rangle$, the freely-jointed chain system reaches a plateau value very close to 6 after a couple of bonds, followed by the right-angle

system ($\theta_0 = 90^\circ$) for which $\langle R^2 \rangle / \langle R_g^2 \rangle \approx 8$. The remaining systems show a systematic increase in the ratio with the increasing number of bonds, suggesting that ideal polymeric behaviour appears for longer chains. For comparison, the limits of fully flexible and very stiff chains in the worm-like (Porod-Kratky) model correspond to $\langle R^2 \rangle / \langle R_g^2 \rangle = 6$ and 12, respectively [307].

The critical Flory exponent (ν) can be extracted from the dependence of chain size on chain length, through $\langle R_g^2 \rangle \propto (N - 1)^{2\nu}$, considering the number of bonds instead of the number of monomers, given the short chains studied here. We recall that the value of $\nu = 0.75$ corresponds to self-avoiding walks in two dimensions and considering excluded volume interactions and chain coiling [43]. The maximum chain extensibility corresponds to an all-trans, rod-like and zig-zag configuration according to which $R_{max} = (N - 1) \cos(\theta_0/2)$, providing a scaling exponent of $\nu = 1$. On the other limit, the densely packed and fully collapsed polymers correspond to $\nu = 0.5$ [305].

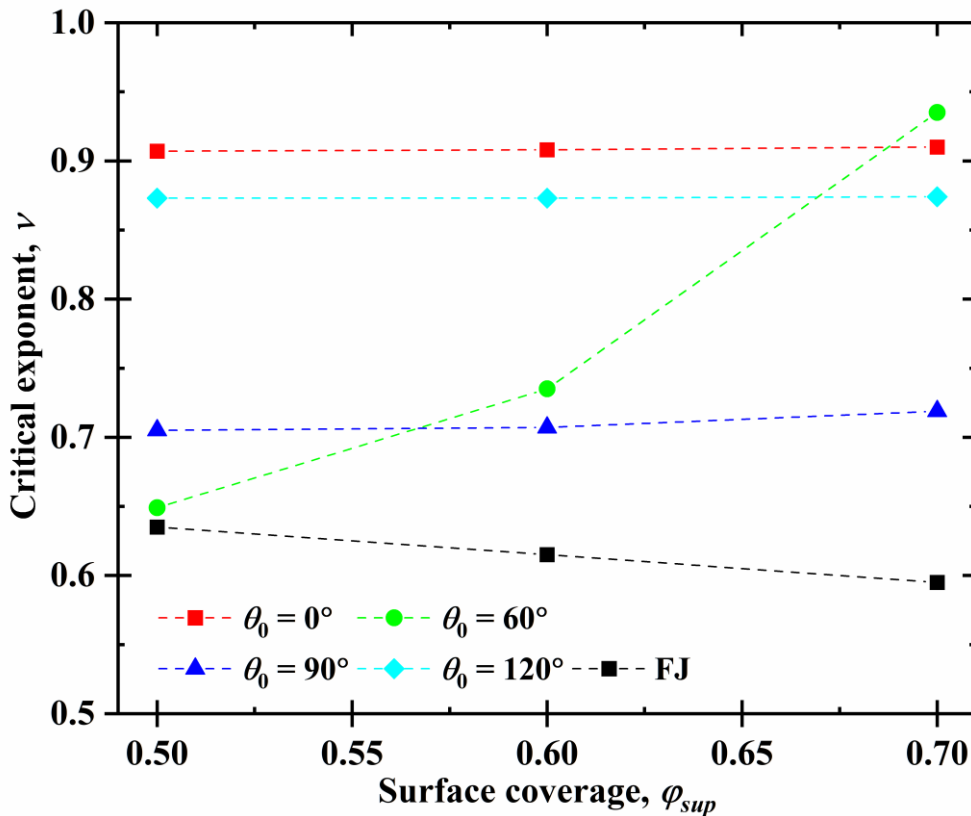


Figure 4.47: Critical exponent (ν) as a function of surface coverage (ϕ_{sup}) for the different equilibrium bending angles (θ_0) of 100-chain, $N_{av} = 12$ semi-flexible systems in two dimensions, including a comparison with the freely-jointed (FJ) chains. Dashed lines connecting points serve as visual aid.

Figure 4.47 shows the dependence of the critical exponent (ν) on surface coverage for semi-flexible polymers of different equilibrium bending angles, including a comparison with fully flexible chains under the same conditions. Rod-like systems corresponding to $\theta_0 = 0^\circ$ show a Flory exponent which is independent of concentration and, approximately, equal to

0.91. This value is slightly lower than the expected one corresponding to the ideal rods of $\nu = 1$. This small deviation is clearly attributed to the bending angles that follow a distribution around the equilibrium bending angle, as seen in Figure 4.46, rather than being exactly equal to 0° . The locally compact system of $\theta_0 = 120^\circ$ also shows a high value of the critical exponent, which is again unaffected by surface coverage. Right-angle chains ($\theta_0 = 90^\circ$) are characterised by significantly lower values of $\nu \approx 0.7$, independently of surface coverage. In contrast, the scaling exponent for freely-jointed chains shows a decrease as surface coverage increases as a result of progressive chain collapse. The strongest effect of surface coverage is encountered for $\theta_0 = 60^\circ$, as the critical exponent markedly increases until it reached a value of $\nu \approx 0.935$ at $\varphi_{sup} = 0.70$. This trend is strongly related to the formation of a nematic phase in which chains adopt fully extended zig-zag conformations.

Chapter 5: CONCLUSIONS

In the present doctoral thesis, the simulation study of chain stiffness for hard-sphere polymers has extracted several conclusions about the local (at the level of monomers) and global (at the level of chains) structure, phase behaviour, self-organisation, crystallisation, and random packing, in two (2D) and three (3D) dimensions. Specifically, the study has analysed the effect of the equilibrium bending angle (θ_0), the packing density (φ), and, to a lesser extent, the average chain length (N_{av}) on the structure of athermal, semi-flexible polymers in a wide range of concentrations, from very dilute conditions to the Random Close-Packed (RCP) limits in two and three dimensions. One prominent result of the present thesis is the identification of the RCP limit in 2D and 3D as a function of the equilibrium bending angle.

The results obtained here were compared with those for fully flexible, freely-jointed chains, considered to be the reference system and which was studied extensively in the past by our research group [6, 14-21, 23-25, 33, 34]. Semi-flexible polymers were modelled as linear chains of tangent hard spheres in which chain stiffness is practically realised through a harmonic bending potential that depends on a bending constant (k_θ) and an equilibrium bending angle (θ_0). The bending angles ranged from fully extended (rod-like polymers) to fully compact (coiled) configurations of triplets, specifically being $\theta_0 = 0, 60, 90, 108$, and 120° , while the bending constant was set equal to $k_\theta/k_B T = 9 \text{ rad}^{-2}$ in all semi-flexible cases. Polymer systems in three dimensions were represented under bulk conditions following Periodic Boundary Conditions (PBCs) in every dimension, while two-dimensional systems were modelled as extremely-confined thin films of monolayers of polymer chains.

The development of the present thesis has been made possible by the application of extensive Monte Carlo (MC) simulations under constant volume and temperature conditions (NVT ensemble) through the *Simu-D* software [2], which was developed by the host Laboratory of Simulation of Materials (LSM). *Simu-D* software is a simulator-descriptor MC suite for the generation, equilibration, and characterisation of complex systems based on polymers under a plethora of conditions, including extreme ones such as jammed packing densities, extreme confinement, or nanofillers whose size is significantly larger than the monomer one. The simulator part of *Simu-D* carries out the generation and equilibration of general systems through

a wide collection of advanced MC algorithms (moves), such as standard localised (executed in a configurational bias pattern), chain-connectivity-altering, cluster-based, and identity-exchange moves for blends and solutions, and volume fluctuation moves, which change the size of the simulation cell.

Independently of average chain length or dimensionality, simulations were performed to generate progressively denser semi-flexible systems from configurations at very dilute conditions through a standard shrinkage algorithm. Simulation cells were periodically and isotropically compressed, following an overlap-free criterion, until the target packing density for the denser system was reached. This shrinkage approach can generate semi-flexible system configurations up to the RCP limit. On the other hand, the two-dimensional (2D) systems were created from dilute three-dimensional (3D) systems under the same conditions using an adsorption approach: Bulk dilute systems are first confined by parallel, flat, and impenetrable walls imposed in one dimension, and then individual monomers and polymer chains are strongly attracted and adsorbed on one of the flat surfaces until a monolayer of thickness equal to monomer size is created. Similar to 3D systems, thin-film systems were compressed by the shrinkage algorithm to generate denser configurations until the corresponding RCP limit was reached. The systems generated at different concentrations were then equilibrated through constant-volume MC simulations, again executed through the *Simu-D* suite.

A key aspect of this thesis is to analyse and identify the phase behaviour and gauge the structure of semi-flexible polymer systems. Consequently, discriminating descriptors were applied to determine the order of the systems at the local and global levels. The Characteristic Crystallographic Element (CCE) norm [3, 4], integrated into the descriptor part of the *Simu-D* suite [2], allows us to gauge the local order at the level of monomers. The CCE norm descriptor quantifies the similarity of the local structure to ideal reference crystals in two or three dimensions and is thus able to identify phase transitions. To analyse the global structure, the orientational Long-Range Order (LRO) of the chains was implemented [226], which identifies the presence of isotropic or nematic phases. Thus, the global order, at the level of chains, is measured through the orientational LRO parameter (q) [5].

Extensive MC simulations have provided a collection of results on the phase behaviour of semi-flexible polymers, with shorter chains, as a function of the packing density (φ) and the equilibrium bending angle (θ_0). The analysis of the global LRO revealed the formation of prolate mesogen, nematic mesophase (PRO) for rod-like ($\theta_0 = 0^\circ$) polymer chains at rather low packing densities and of oblate mesogen, nematic mesophase (OBL) for right-angle ($\theta_0 = 90^\circ$) chains at high packing densities. Through a comparison of rod-like polymer systems with different average chain lengths (N_{av}), the isotropic-to-nematic transition was clearly observed for all rod-like systems at packing densities lower than the solidification point for hard-sphere polymers and monomers. Eventually, all rod-like systems reached a practically perfect nematic

phase ($q \rightarrow 1$), independently of chain length. Furthermore, the longer the average chain length, the more dilute the state in which the transition takes place. The behaviour observed for the isotropic-to-nematic transition for rod-like polymers agrees with the results of previous independent studies [227-230].

Moreover, a rich one-dimensional phase diagram as a function of packing density was identified where, once a critical volume fraction is reached, all semi-flexible polymer chains crystallise in close-packed morphologies, including random hexagonal close (rHCP) ones of single or multiple stacking directions, or almost perfect face-centred cubic (FCC) and hexagonal close-packed (HCP) crystals for the case of rod-like polymers. Although all the semi-flexible systems studied here show crystallisation, the equilibrium bending angle significantly affects the corresponding melting point. Although equilibrium bending angles of 108° and 120° favour the crystallisation compared to the freely-jointed model, chains with $\theta_0 = 90^\circ$ showed a behaviour that almost coincides with the fully flexible chains. The acute angle of 60° was found to hinder crystallisation, forcing nucleation and growth to take place at higher concentrations.

During the crystallisation, the structure of semi-flexible systems, except for rod-like polymers, appreciably changes in specific polymer conformations and intra-molecular radial arrangements, depending on the equilibrium bending angle. The characteristic polymer conformations obtained after the disorder-order transition presented sharp maxima and minima at values that promote the formation of HCP/FCC crystallites. However, the characteristic intra-molecular arrangements for each equilibrium bending angle are generally not enough to complete the geometric elements of HCP and FCC structures. Thus, inter-chain monomers cover positions in the local environment that are not accessible by the corresponding polymer conformations. Consequently, the total radial arrangement in the crystalline phase is very similar for all semi-flexible systems, independent of equilibrium bending angle, and further matches that of fully flexible polymers [18, 20]. Therefore, the monomer arrangement produced in the disorder-order transition for semi-flexible polymers can be considered universal and, at total consideration, independent of the equilibrium bending angle, finally giving rise to crystals of random hexagonal close-packed (rHCP) structure.

Through a simultaneous analysis of the dependence of global and local order on concentration, three distinct regimes were identified in a one-dimensional phase diagram for rod-like polymers, specifically with $N_{av} = 12$, in 3D, and a delay was observed between global and local self-organisation: i) AMO-ISO ($\varphi \leq 0.15$), where the system is amorphous and isotropic; ii) AMO-PRO ($0.20 \leq \varphi \leq 0.45$), where the packing is amorphous at the local level and nematic at the global; and iii) CRY-PRO ($\varphi \geq 0.50$), where the system shows crystallinity in the form of HCP and FCC closed-packed morphologies of varied levels of perfection, as well as a perfect nematic ordering at the global orientational level. In the case of right-angle chains,

a synchronous establishment of local and global order was observed, thus splitting the behaviour into two distinct regimes; i) AMO-ISO ($\varphi \leq 0.56$), where the system is amorphous and isotropic; and ii) CRY-OBL ($\varphi > 0.56$), where the system consists of rHCP crystals in a nematic mesophase of oblate mesogens.

In parallel to the study of phase behaviour, the influence of chain stiffness on the structure and chain conformations of random (as opposed to ordered) packings of semi-flexible polymers in three dimensions was also investigated, exploring the whole volume fraction range and with an emphasis on the four distinct scaling regimes (dilute, semi-dilute, marginal, and concentrated), as for freely-jointed chains [33]. Semi-flexible polymer systems of different equilibrium bending angles (θ_0) and average chain lengths (N_{av}) were compressed until the random close-packed limit was reached. A strong effect of the equilibrium bending angle and the average chain length was observed on the maximum achieved packing densities (φ^{RCP}), similar to the one reported by Hoy for freely-rotating chains [218]. The maximum achieved packing density increases with the equilibrium bending angle, reaching generally maximum values with $\theta_0 = 90^\circ$, and decreases with average chain length. However, we need to remind the reader that the RCP limits reached strongly depend on the generation protocol and, in this work, the RCP limit was identified as the state where no further compression is possible, i.e. the acceptance rate of compression tends to zero even for infinitely low amplitudes, after a prolonged simulation time.

An important aspect of the conformational analysis is the study of the local chain conformations, which dictate not only the local arrangement but also the global size of the chains. At dilute and semi-dilute packing densities, chain conformations are only governed by the equilibrium bending angle and intra-molecular constraints, with a preference for extended conformations. As the concentration increases and the marginal and concentrated regimes are reached, compact configurations are favoured with characteristic conformations that depend on the equilibrium bending angle. Thus, equilibrium bending angles compatible with these compact conformations ($\theta_0 = 60$ and 120°) improve the stiffness of the bonds, while the rest of systems, such as $\theta_0 = 90$ and 108° , are “distorted” to produce bending arrangements that optimise local packing. Rod-like polymers are an exception to this behaviour. Extended conformations of rod-like polymers are kept and even are further stiffened as concentration increases after the establishment of the nematic phase due to the inter-molecular interactions. On the other hand, inter-chain packing is independent of chain stiffness, regardless of the packing density. However, rod-like polymers are again an exception, where the establishment of the nematic ordering, as the packing density increases and the chains begin to interact between themselves, leads to the formation of a characteristic 2D hexagonal ordered structure in the perpendicular plane to the nematic director, in agreement with independent studies by Shakirov and Paul [206]. With respect to the effect of chain length, no appreciable effect was

observed on chain conformations and inter-chain packing, regardless of packing density and equilibrium bending angle. An exception to this rule is the concentrated regime, where longer chains present slight variations in chain conformation distributions because of the proximity to the maximally random jammed (MRJ) state.

The global size of the chains, quantified by the characteristic ratio (C_N), is clearly influenced by the local conformational rearrangements, especially at high concentrations. For semi-flexible polymers, the dependence of chain size on concentration presents, as packing density increases, an approximately similar behaviour to the four scaling regimes as established for freely-jointed chains [33], except for systems with $\theta_0 = 0$ and 60° . Furthermore, the trend in chain size for each equilibrium bending angle is independent of the average chain length. Rod-like polymers present a constant chain size at dilute conditions until the isotropic-to-nematic transition, when stiffness and chain size increase with packing density until the maximum extension is reached. The inter-chain alignment along the whole polymer contour, which gives rise to the nematic phase, enforces straight configurations. On the other hand, although semi-flexible polymers with $\theta_0 = 60^\circ$ generally follow a similar behaviour to the rest of the equilibrium bending angles, they present a region of almost constant characteristic ratio (even a small increase) between $\varphi = 0.20$ and 0.50 . In the concentrated regime, semi-flexible chains with $\theta_0 = 60^\circ$ show a remarkably larger chain size than the more coiled semi-flexible systems ($\theta_0 = 90, 108, \text{ and } 120^\circ$). In addition, right-angle chains present systematically smaller chain sizes than the most coiled conformation ($\theta_0 = 120^\circ$) as packing density increases and once a specific chain length is reached. Thus, long right-angle chains can collapse into locally dense configurations as efficiently as the inherently compact chain configurations.

Regarding two-dimensional (2D) systems, semi-flexible polymers are compared against thin-film systems of athermal, fully flexible polymer chains and their monomeric analogues under the same conditions. As a first reference case, extremely-confined packings of freely-jointed chains of tangent hard spheres were compressed from dilute conditions until the RCP limit was reached, so that no further shrinkage was possible. At the maximum surface coverage, freely-jointed chains form a crystal of predominantly triangular (TRI) character. Therefore, packings of freely-jointed chains ($\varphi_{sup}^{RCP}(FJ) = 0.895$) can be packed nearly, if not, as efficiently as monomeric analogues ($\varphi_{sup}^{RCP}(HS) = 0.901$) at a maximum surface coverage that approaches the state of maximum order and compactness exhibited by the triangular crystal ($\varphi_{sup}^{max} = \varphi_{sup}^{TRI} = 0.907$). In parallel, simple geometric arguments suggest that even denser packings can be achieved by properly tuning the number of monomers in the simulation cell to comply with the geometric condition of the height-to-width ratio of the perfect hexagon. Furthermore, it should be noted that the compression rate profoundly affects the class of structures obtained, enhancing or inhibiting crystallisation and thus the state of jamming [308].

Systems of semi-flexible athermal polymers extremely confined in monolayers were also compressed until no further shrinkage was possible, providing as a first result the trends on the densest configurations according to which: $\varphi_{sup}^{RCP}(FJ) > \varphi_{sup}^{RCP}(60^\circ) > \varphi_{sup}^{RCP}(90^\circ) > \varphi_{sup}^{RCP}(0^\circ) > \varphi_{sup}^{RCP}(120^\circ)$. Employing simple calculations, the RCP limit in three dimensions is observed to be approximately 13.6% less dense compared to the maximum achievable density of the HCP and FCC ideal crystals. However, in two dimensions and based on the present results, the RCP limits range from the highest one of the freely-jointed chains, which is just 1.3% lower than the maximum achievable surface coverage of the ideal TRI crystal, to the least dense one of the compact, zig-zag chain configurations of $\theta_0 = 120^\circ$, approximately 15.8% less concentrated than φ_{sup}^{max} . As for three-dimensional systems, the packing ability is intimately related to the bond geometry of the chains and their size, imposed primarily by the equilibrium bending angle and secondarily by the surface coverage.

A wealth of distinct behaviours, but also universal trends, could be recognised. Packings of right-angle ($\theta_0 = 90^\circ$) chains represent an exception by remaining locally amorphous (disordered) and globally isotropic throughout the range of surface coverages analysed. Interestingly enough, the RCP limit for right-angle chains exceeds the maximum surface coverage of an ideal square crystal, i.e. $\varphi_{sup}^{RCP}(90^\circ) \approx 0.797 > \varphi_{sup}^{SQU} \approx 0.785$. In parallel, the equilibrium bending angle of $\theta_0 = 90^\circ$ is incompatible with the geometric elements of the TRI crystal. This combination explains the disordered/isotropic state of the right-angle chain packing, compared to the rest of the systems. Universal behaviour is observed for the rest of the semi-flexible systems: crystallinity increases monotonically as surface coverage increases and reaches its maximum at the RCP limit. This is in sharp contrast to three-dimensional systems, where the disorder prevails at the RCP limit. This discrepancy can be attributed to the protocol-dependence nature of the RCP limit in 2D and 3D, but also to the difficulty of crystal formation in 3D compared to 2D due to the increased coordination number at sufficiently high densities.

Another interesting trend was observed with respect to global order. For rod-like polymers, given the short chains studied here, the nematic phase is highly unstable, fluctuating between configurations of high nematic order and apparent isotropic configurations. Zig-zag chains of acute ($\theta_0 = 60^\circ$) or obtuse ($\theta_0 = 120^\circ$) bending angles show the following transition as surface coverage increases: isotropic $\rightarrow$ nematic $\rightarrow$ isotropic (or tetratic order, see discussion in Future Plans), with the latter being the prevailing state at the RCP limit. However, visual inspection of semi-flexible systems at the RCP limit gives the impression of an orientational tetratic order, where each pair of chains is either mutually parallel or perpendicular [306]. Thus, the global-order analysis tool requires to be improved to identify and quantify the global tetratic order in polymer systems. Subsequently, the global structure of two-dimensional semi-flexible

systems will be analysed again to quantitatively confirm the presence or absence of tetratic order.

On the basis of the results presented in the present work, athermal polymers in two dimensions possess a richness of multi-scale structural behaviour, which is not encountered by the monomeric analogues and which appears to be even more complex than the one exhibited by the three-dimensional analogues under bulk conditions.

Chapter 6: FUTURE PLANS

The work initiated in the present doctoral thesis has allowed the Laboratory of Simulation of Materials (LSM) to open various new research lines in the field of molecular simulations, especially on highly idealised polymer-based systems. Most of them take advantage of the newest features and applications developed for *Simu-D* [2] in recent years.

The present study on semi-flexible polymers of tangent hard spheres, in two and three dimensions, is further expanded at present to treat and analyse other characteristic features that could not be included here due to time and resource constraints. Some indicative examples include: i) the exhaustive analysis of the local structure of the computer-generated configurations focusing on the Voronoi polyhedron (3D) or polygon (2D) of the semi-flexible chains, ii) the extraction of the primitive path network and the identification of entanglements between chains, iii) the effect of intensity (constraint) of chain stiffness (k_θ), iv) the effect of confinement on the isotropic-to-nematic transition, etc. Among them, one of the most interesting endeavours is to explore further the short- and long-range behaviour of right-angle ($\theta_0 = 90^\circ$) polymers. Interestingly, in 3D right-angle polymer chains are rearranged during the crystallisation of the systems to form ordered oblate mesogens that give rise to a nematic ordering, as can be observed in Figure 4.6, while in 2D ordering is not easily reached due to the incompatibility of the bending angle with the neighbour geometry of the triangular crystals. Through a deeper study of the nematic ordering and analysis of chain shape, we want to extract a greater understanding of the origin and mechanism after the oblate mesogens of right-angle chains.

Regarding two-dimensional (2D) semi-flexible polymer systems, a pending issue to be addressed is to expand the long-range orientation analysis, specifically by including the identification of tetratic order [254-257, 306]. As seen in Figure 4.36 and Figure 4.37, two-dimensional semi-flexible polymers at the random-close packed (RCP) limit present a non-nematic state after the establishment of (more or less stable) nematic order at lower surface coverages, as quantified by the nematic order parameter. However, visual inspection of Figure 4.36 shows regions of chains that tend to align mutually parallel and form clusters with

different orientations. This behaviour may be indicative of the formation of an orientational tetratic order, where the chains show two mutually perpendicular alignments [306].

Therefore, these 2D semi-flexible polymers require the extension of the orientational-order analysis tool that can identify and quantify the degree of orientational Long-Range Order (LRO) through two order parameters in 2D [306]: first, the already analysed nematic order parameter (q_2), being equal to unity when all chains are perfectly aligned parallel to the nematic director $\mathbf{n}$; and second, the tetratic order parameter (q_4), which is equal to unity when each pair of chains is either mutually parallel or perpendicular [306]. While the nematic order parameter (q_2) is calculated by the second-order tensor $\mathbf{Q}$, as has already been explained in the Section 3.4.2, the tetratic order parameter (q_4) requires the adoption of the formalism of a fourth-order tensor, the tetratic order tensor ($\mathbf{T}$), as follows [254]:

$$\mathbf{T} = 4(\langle \mathbf{u} \mathbf{u} \mathbf{u} \mathbf{u} \rangle - \mathbf{I}) \quad (6.1)$$

where $\mathbf{u}$ is the unit vector along the largest semiaxis of the inertia ellipsoid of a chain (considering all of its monomers as points of unit mass) and so the components of the tensor $\mathbf{T}$ are given by

$$T_{ijkl} = 4 \left[(u_i u_j u_k u_l) - \frac{1}{8} (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \right]. \quad (6.2)$$

The tetratic order tensor from Equation (6.1) has major and minor symmetries: $T_{ijkl} = T_{jikl} = T_{ijlk} = T_{klij}$. The 4th order tensor components are represented in a 4×4 matrix $\tilde{\mathbf{T}}$ following the steps of Ref. [254], condensing pairs of sub-indices i, j and k, l ($1 \leq i, j, k, l \leq 2$) of the tetratic order tensor to two sub-indices α and β ($1 \leq \alpha, \beta \leq 4$) according to the scheme:

$$ij, kl = 11, 12, 21, 22 \rightarrow \alpha, \beta = 1, 2, 3, 4 \quad (6.3)$$

The $\tilde{\mathbf{T}}$ matrix is subsequently diagonalised and its eigenvalues are related to the order parameters q_2 and q_4 , according to Ref. [254], as:

$$\begin{aligned} m_1 &= \frac{1}{2} \left[q_4 + (15q_2^2 + q_4^2)^{1/2} \right] \\ m_2 &= 0 \\ m_3 &= -q_4 \\ m_4 &= \frac{1}{2} \left[q_4 - (15q_2^2 + q_4^2)^{1/2} \right] \end{aligned} \quad (6.4)$$

The sum of the eigenvalues, shown in Equation (6.4), of the tetratic order tensor $\tilde{\mathbf{T}}$ is zero.

Therefore, the nematic order parameter, q_2 , is derived from the eigenvalues of the $\mathbf{Q}$ tensor, while the eigenvalues of the $\tilde{\mathbf{T}}$ matrix can be used to obtain the tetratic order parameter,

q_4 ($0 \leq q_4 \leq 1$), either from the third eigenvalue ($q_4 = -m_3$) or from the combination of first and fourth eigenvalues ($q_4 = m_1 + m_4$).

However, the tetratic order parameter, on its own, is not sufficient to identify a tetratic phase and thus requires further calculation of the nematic order parameter. Consequently, by determining both orientational order parameters q_2 and q_4 , we can determine and quantify the orientational LRO of the systems. In fact, the ideal nematic case, where all chains are orientated parallel to the director, corresponds to both $q_2 = q_4 = 1$. The ideal tetratic phase, where the chains show two perpendicular alignments, corresponds to the limit of $q_2 = 0$ and $q_4 = 1$. Finally, the isotropic state corresponds to $q_2 = q_4 = 0$.

Another current research line is to study the primitive paths and the inter-chain topological constraints (entanglements) for semi-flexible polymer systems with different equilibrium bending angles. The primitive path of a polymer chain immersed in a sea of obstacles is the shortest path connecting the chain ends that does not violate the topological constraints on it, i.e. other chains. The analysis of primitive path networks and universal entanglement behaviour [33] allows for a better understanding of the different states of polymers, from melts and solutions to glasses and jammed amorphous solids, and the corresponding polymer dynamics and rheology [44, 45, 147]. For this reason, the efficient topological Z1 algorithm [35, 309-312] is used to solve the problem of the shortest multiple disconnected path minimising the Euclidean length and extracting information about the entanglements of the chains.

Previous works of LSM have already analysed the primitive paths, entanglements, and knots (intramolecular topological constraints) for freely-jointed chains of tangent hard spheres from very dilute conditions up to the MRJ state [15, 16, 18, 33]. Here, the Z1 topological algorithm is used to extract the primitive paths and topological constraints of computer-generated structures by MC simulations of semi-flexible polymer systems with different equilibrium bending angles, as can be seen in Figure 6.1 for a system of $N_{av} = 100$ with $\theta_0 = 90^\circ$.

In addition, new research lines consist of analysing the behaviour and structure of semi-flexible polymers under new more complex conditions, using the present work as a reference case. These analyses can be realized due to the ability of *Simu-D* to simulate polymer-based systems under a plethora of different conditions, including extreme ones [2]. Thus, semi-flexible polymer chains, both in 2D and 3D, are currently studied under different conditions, such as thermal systems, confinement, blends of polymers and monomers, etc.

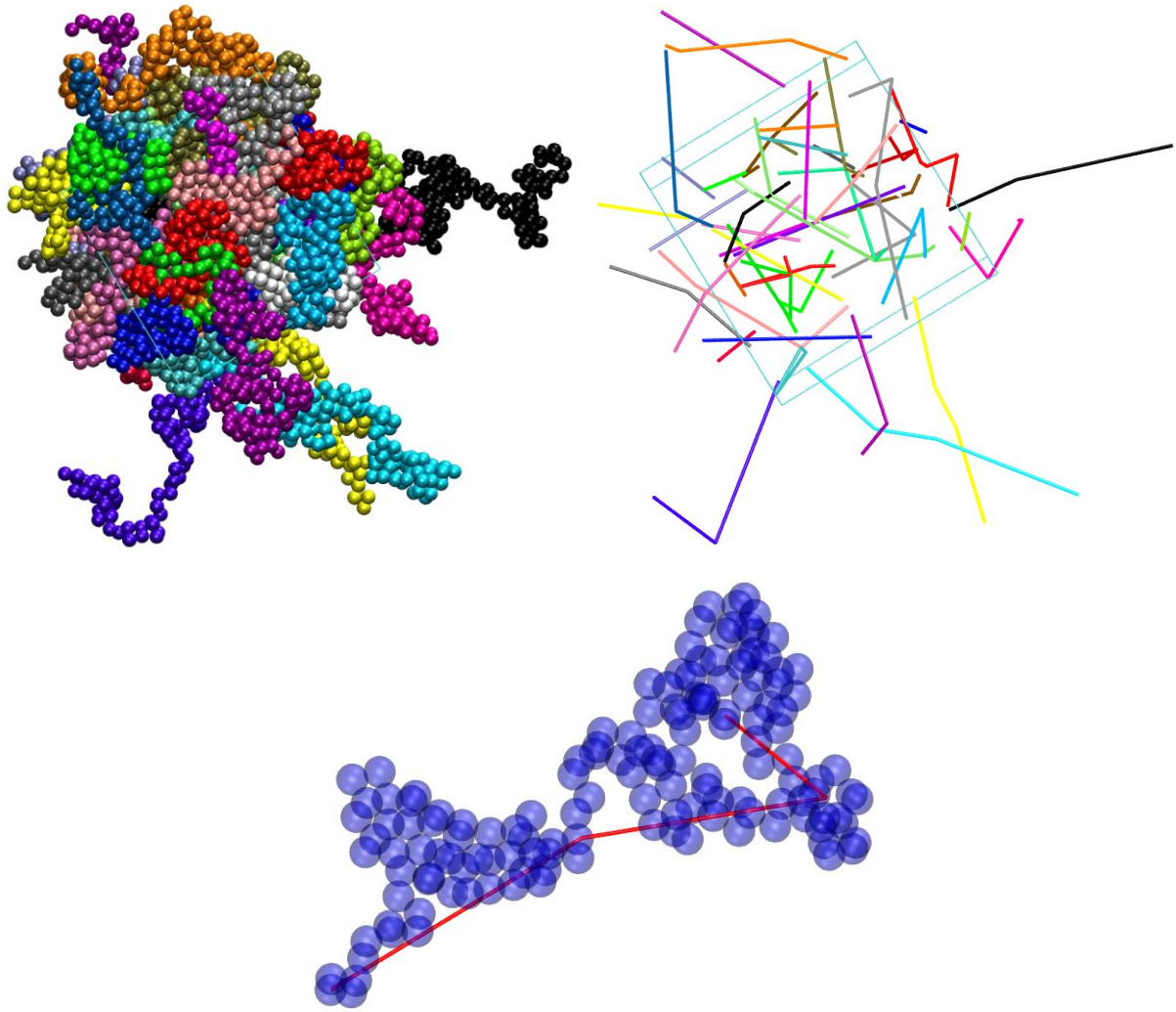


Figure 6.1: (Top left) Representative configuration of a 48-chain, $N_{av} = 100$ semi-flexibly polymer system with equilibrium bending angle $\theta_0 = 90^\circ$ at a packing density $\varphi = 0.45$. Coordinates of sphere centres are unwrapped in space and monomers are coloured according to parent chain. (Top right) Primitive path network of the right-angle semi-flexible system, after application of the Z1 topological algorithm [35, 309-312]. Primitive paths are represented as lines coloured according to the parent chain and entanglement coordinates are unwrapped in space. (Bottom) Arbitrary selected atomistic chain and its corresponding primitive path. Monomers are shown as blue transparent spheres and the primitive path is represented as a sequence of connected red lines. Each change in the direction of the primitive path practically corresponds to an entanglement. Images created with VMD visualisation software [295].

Recently, attractive, fully flexible polymer chains of tangent hard spheres were simulated in two and three dimensions to demonstrate a hierarchical modelling approach for the design and morphological fine-tuning of crystals of colloidal polymers with short attractive interactions [32]. A phase diagram of polymer chains in two and three dimensions was determined by controlling the intensity (ε) and range (σ_2) of attraction for the Square-Well (SW) potential. Thus, by tuning the attraction range, which can be considered a single parameter for the materials design, a rich collection of crystal structures was obtained, including face-centred cubic (FCC), hexagonal close-packed (HCP), simple hexagonal (HEX), and body-centred cubic (BCC) crystals and a Frank-Kasper phase in three dimensions, and triangular and

square crystal structures in two dimensions. These dominant crystal structures were predicted by a proposed geometric neighbours (GN) model, which is based on the concept of cumulative neighbours of ideal crystals as a function of the attraction range (σ_2). The more neighbours packed within a radius equal to the attraction range, the lower the potential energy and (ignoring entropic differences between polymorphs) the more stable the corresponding ideal crystal.

Currently, efforts are placed into gauging the phase behaviour of semi-flexible polymers interacting with the SW potential, both in bulk systems (3D) and in extremely-confined thin films (2D). However, this model is more challenging than for freely-jointed chains because of the combination of two different energetic potentials: the pair-wise, SW potential and the bending angle potential. Furthermore, one should consider the compatibility of the enforced bending angle with the neighbour geometry of the expected crystals. Early results in three dimensions reveal that the equilibrium bending angle plays a significant role in the final crystal structure, being able to promote or suppress the nucleation and growth of specific crystals. For example, chains with $\theta_0 = 60^\circ$ suppress the crystallization of BCC and HEX structures because of the incompatibility of the bending angle with these crystals. **Figure 6.2** presents some snapshots of resulting structures for attractive rod-like ($\theta_0 = 0^\circ$) polymers with different attraction ranges, including a spiral-like exotic structure.

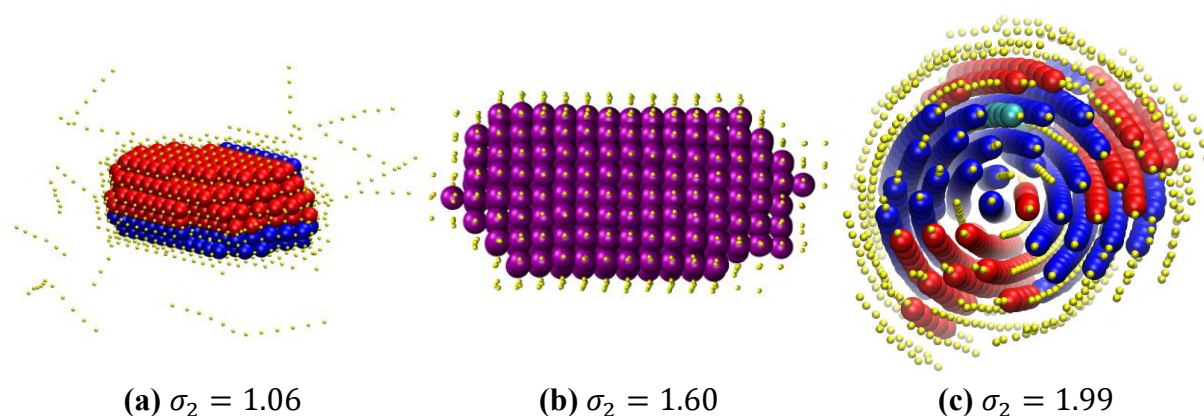


Figure 6.2: Computer-generated snapshots of attractive rod-like polymers of $N_{ch} = 100$ and $N_{av} = 12$. Attractive interaction counts with an intensive $\varepsilon = -0.6$ and interaction ranges of (a) $\sigma_2 = 1.06$, (b) $\sigma_2 = 1.60$, and (c) $\sigma_2 = 1.99$. Monomers are coloured according to the CCE norm similarity: HCP (blue), FCC (red), BCC (cyan), HEX (purple), and FIV (green). Amorphous sites, or more precisely “unidentified” ones, are coloured yellow with reduced dimensions for visual clarity. Images created with VMD visualisation software [295].

Another topic that has been commonly studied in previous works of LSM is monomeric and polymeric systems confined in one or more dimensions [25-30]. These studies are expanded to analyse the influence of confinement on the local and global order of semi-flexible polymers, especially rod-like polymers. For this reason, semi-flexible polymers are simulated under confinement in one (plates), two (tubes), and three (full confinement) dimensions, exploring the effect of the confining walls, the interwall distance, and the packing density on the

structures. Figure 6.3 presents examples of rod-like systems confined in one and two dimensions.

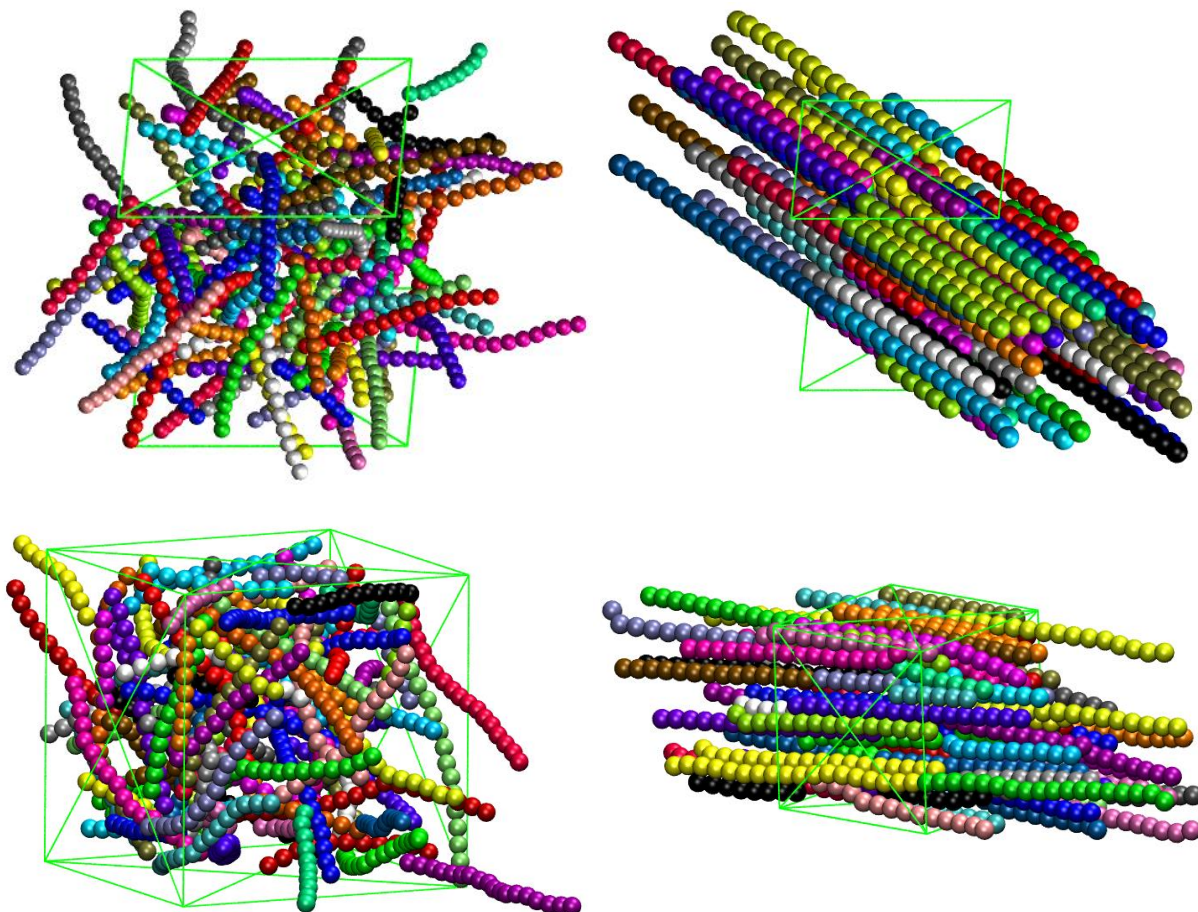


Figure 6.3: Representative snapshots of rod-like polymer systems of $N_{ch} = 100$ and $N_{av} = 12$ at (**left column**) $\varphi = 0.10$ and (**right column**) $\varphi = 0.56$ confined under (**top row**) one dimension and (**bottom row**) two dimensions. Coordinates of sphere centres are unwrapped in space and monomers are coloured according to parent chain. Flat, parallel, and impenetrable walls are applied as confining agents and are indicated by the crossing green lines. Images created with VMD visualisation software [295].

Further efforts include the simulation of mixtures of polymers and individual monomers of the same chemical composition (here hard spheres of uniform size), taking advantage of the newest Identity Exchange Moves (IdExMs) included in *Simu-D* [2] (see Section 3.3.4). Mixtures of monomers and polymer chains, both fully flexible and semi-flexible, are simulated to analyse the crystallisation, structure, phase behaviour, and phase separation as a function of different parameters, such as the packing density and the monomer concentration or chains-monomers ratio. For example, in Figure 6.4, two blends of monomeric hard spheres and rod-like polymer chains are represented at different packing densities. While the system is isotropic and separation between both phases does not exist at lower densities, the rod-like chains of the system tend to align among them, generating a separated phase from monomers, as packing density increases.

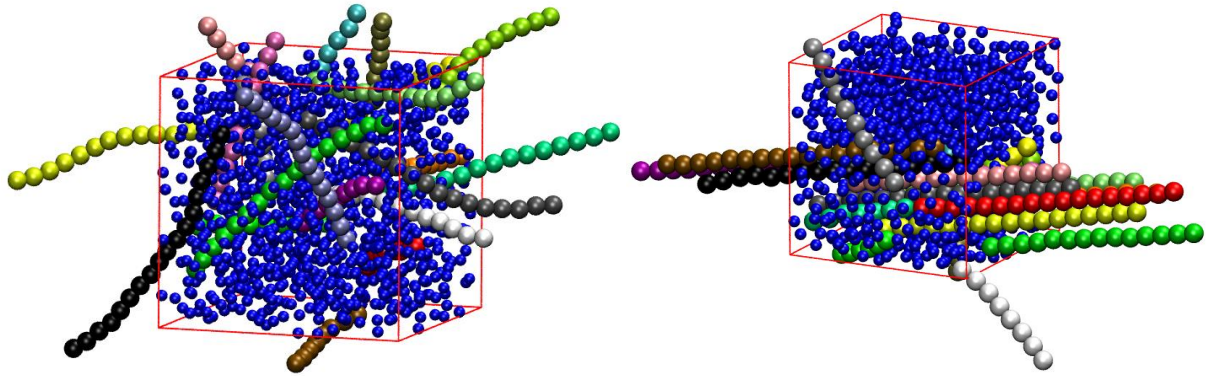


Figure 6.4: Computer-generated visualisations of blends of 960 individual monomers and 20 rod-like polymer chains with $N_{av} = 12$ at (**left panel**) $\phi = 0.20$ and (**right panel**) $\phi = 0.45$. Individual monomers are coloured blue with reduced dimensions for visual clarity. Chain monomers are coloured according to the parent chain, and coordinates of its centres are unwrapped in space. Images created with VMD visualisation software [295].

Finally, in the future, it is projected to work with even more complex polymer-based systems, such as Polymer Nanocomposites (PNCs). The latest version of *Simu-D* can currently simulate systems of polymer nanocomposites with nanofillers of different shapes (spheres and cylinders), sizes, and concentrations. Additionally, the modular construction of *Simu-D* allows, with some investment in programming, the creation and simulation of more different features with regard to PNCs, such as new shapes like pellets. Thus, the aim is to study the effects of nanofillers on the structure and self-organisation phenomena, such as phase separation or crystallisation, of the polymer matrix. These polymer matrices can be freely-jointed or semi-flexible chains. For example, we can analyse the influence of the presence of nanocylinders on the orientational nematic ordering of a polymer matrix conformed by rod-like polymer chains, as can be seen in Figure 6.5.

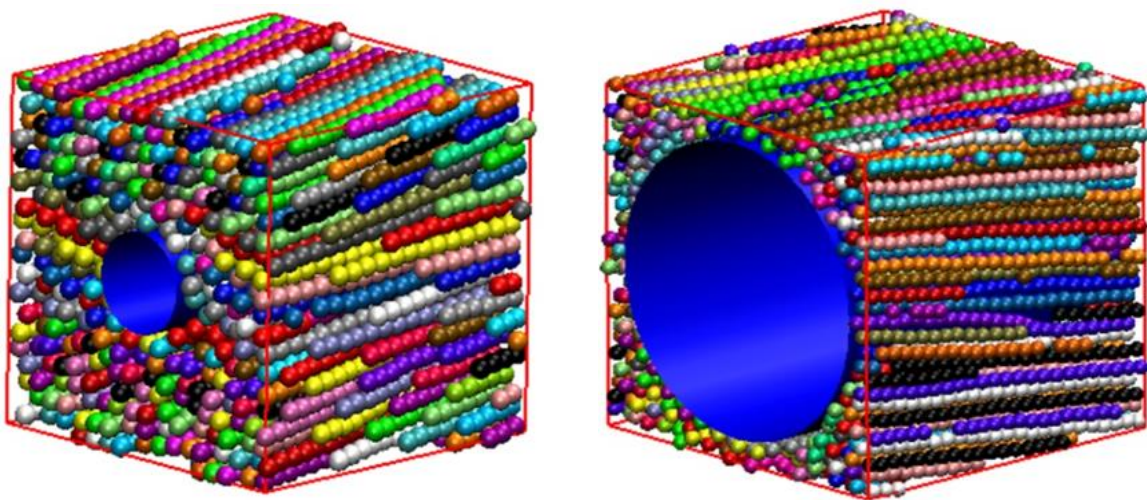


Figure 6.5: Snapshots of polymer nanocomposites formed by a nanocylinder of infinite length and a polymer matrix of $N_{ch} = 48$, $N_{av} = 100$ rod-like chains at a packing density of $\phi = 0.54$. Diameters of nanocylinders are (**left panel**) 5 times larger than the monomer diameter (5σ) and (**right panel**) 20 times the monomer diameter (20σ). Polymer chains are under periodic boundary conditions (PBCs), and monomers are coloured according to the parent chain. Images created with VMD visualisation software [295].

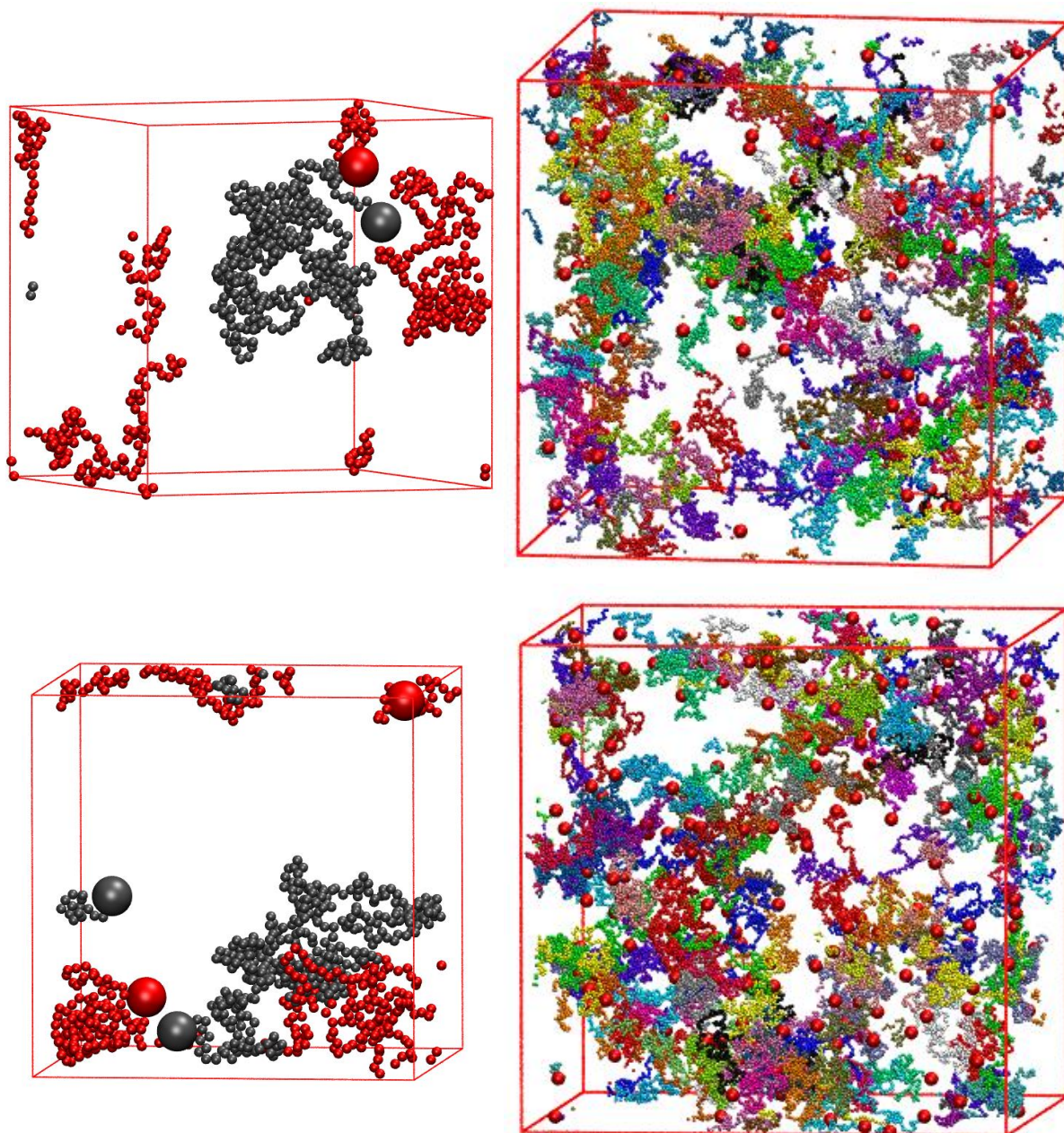


Figure 6.6: Snapshots of polymer nanocomposite systems of freely-jointed polymer chains grafted onto nanoparticles, whose diameter is 4 times monomer diameter (4σ). Systems are formed by 100 chains of average chain length $N_{av} = 400$ with (**top row**) one end anchored onto a nanoparticle and (**bottom row**) both ends anchored onto different nanoparticles. (**Left column**) Two tethered chains with monomers and nanoparticles coloured according to the parent chain. (**Right column**) Systems at $\phi = 0.01$ with monomers coloured according to parent chain and nanoparticles coloured red. All chains are subject to periodic boundary conditions (PBCs). Images created with VMD visualisation software [295].

Among polymer nanocomposites, linear chains terminally grafted onto nanoparticles have raised remarkable interest. Understanding the fundamentals of their behaviour can help to improve efficiency in technological processes, such as the stabilisation of colloidal suspensions or polymeric surfactants, used in different industries. There are various possibilities here: a polymer chain is anchored by one of its two ends onto a nanoparticle; a polymer chain is anchored by both ends onto the same nanoparticle; and a polymer chain is anchored by its ends

to two distinct nanoparticles. Some representative systems can be seen in Figure 6.6. The core of this research line is born from a collaboration with Prof. Mukta Tripathy of the Indian Institute of Technology Bombay (IITB), which counts with ample experience in this kind of polymer-based systems [313] through analytical studies employing the Polymer Reference Interaction Site Model (PRISM) theory and advanced coarse-graining techniques. Therefore, one of the goals of the project is to conduct numerous MC simulations in *Simu-D* of terminally grafted-nanoparticle systems, varying the chain length, size of the nanoparticles, and effective packing density, to analyse the potential of mean force (PMF) of the system between nanoparticles and between nanoparticles and anchored polymer chains.

Chapter 7: REFERENCES

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