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Glossary of terms relating to modeling and simulation of polymers

IUPAC Recommendations 2026*

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Abstract: This document gives definitions of terms related to computational and modeling studies of polymeric materials. The terms and methods covered by this document are characterized by different degrees of resolution, such as molecular dynamics and Monte Carlo simulations of both atomistic and coarse-grained polymer models. Most of the terms defined herein apply to particle-based methods, which retain at least some degree of molecular-level information. Thus, continuum-level theories and computational methods are excluded, while electronic structure methods are included to some extent. Modeling of polymerization and other chemical reactions are excluded. The list is restricted to the most commonly encountered terms.

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1 INTRODUCTION

The molecular-level simulation of polymers has grown over the years into a broad subject, located at the interface between computational chemistry and physics [1–7], on the one hand, and the statistical mechanics of polymers and related soft materials [8–15] on the other. It is a rapidly growing research field, thanks to the increasing power and accessibility of computers, the wide availability of both commercial and free, often open-source computational software, and the unique insights and advantages that can be obtained from their application. The prediction of properties of specific materials and the design of materials with specific properties have long been a scientific Holy Grail. While this holds for all areas of chemistry and materials science, the role of simulation and modeling in polymers is particularly significant due to their inherent complexity. The nearly infinite possibilities to modulate their structure make statistical and modeling approaches essential, even to gain a rough interpretation of experimental data. But polymer modeling faces specific challenges arising from the extremely broad range of time- and length-scales that characterize these materials. These are related to the possible presence of "morphological constraints" (the amount and size of crystalline regions within a semicrystalline polymer, or the degree of nanoparticle dispersion within a cross-linked matrix, for example) and to the important role played by non-equilibrium states in polymeric materials (quenched amorphous phases, for example). These features of polymeric materials often require the adoption and integration of multiple modeling approaches.

The main aim of the present work, with all the above in mind, is defining the fundamental terminology relating to modeling and simulation of polymers, in order to facilitate consistency and precise understanding between scientists coming from the broad range of disciplines involved.

The terms in the present document are arranged in alphabetical order within four logical groupings:

- General terms: chemistry, physics, and polymer-science terms, the relevance of which to polymer modeling and simulation prompts inclusion in the present document in order to augment its self-sufficiency.
- Models: in the context of particle-based models, the degrees of freedom, geometry, and interactions that define the physical structure and properties of a system.
- Methods: numerical procedures designed to sample the configuration or phase space or the dynamical/kinetic properties of a model, under equilibrium or non-equilibrium conditions.
- Data analysis: the concepts and methods that can be used to interpret the results of a simulation.

Terms in the present document cover definitions relating to polymer science, physical chemistry, computational chemistry, and physics. The document does not include terms that are either very advanced or very specialized. Also, the terminology

associated with statistical mechanics and its application to polymers has mostly been limited herein to terms that are more relevant for simulations or computational approaches.

We have attempted to keep definitions as compact as possible, while notes are used to specify relevant details within the specific context and supply examples. For consistency, pertinent satisfactory definitions in the context of polymer science that are given in other IUPAC publications have been maintained as much as possible, but notes were added, discarded, or adapted to the modeling and simulation context of the present document. Important terms from other documents are reproduced in order to make the present document reasonably self-contained. The main sources are IUPAC's Compendium of Chemical Terminology [16], i.e., the so-called 'Gold Book', and the 2nd edition of the Compendium of Polymer Nomenclature and Terminology [17], i.e., the so-called 'Purple Book'. Other relevant, more specific IUPAC documents that have been used include those on macromolecular conformations, polymer solutions, and amorphous bulk polymers [18], on aggregation and self-assembly [19], on computational organic chemistry [20], on chemical kinetics [21], on stereochemistry [22], and on physical organic chemistry [23]. Many recent developments in molecular simulation rely on concepts from data science and machine learning, which share a lot of terminology with chemometrics. We have not included them here, since this subject has been extensively covered in another recent document [24]. Except for IUPAC documents, we decided to keep references mostly confined to books, given the basic nature of the terminology we considered. The terms defined in the present document and acceptable synonyms are printed in bold. Terms in italics are defined elsewhere in this document or, when they appear with a reference, possibly only or also in other IUPAC documents [16–24].

2 GLOSSARY OF TERMS

2.1 GENERAL TERMS

2.1.1 Chain segment

segment

Group of contiguous skeletal atoms in a polymer molecule, including their side groups, if any, such that the chain can be represented as a connected sequence of segments.

Note 1: In an *atomistic model* of a polymer, it comprises all the atoms spanning an appropriate section of a chain. In a *coarse-grained model* of a polymer, it may correspond to one or more contiguous *particles*.

Note 2: A Kuhn segment [18] corresponds to a single link of an equivalent *freely jointed chain*.

Note 3: Usage of the simple term "segment" is advisable only when there is no possible ambiguity with its common geometrical meaning (a straight line connecting two end points).

Note 4: Adapted from [18].

2.1.2 Collective coordinate

Function of the coordinates of the *particles* within a system or a part of it, providing a coarse-grained description of its *configuration* or of a dominant mode of motion.

Note 1: Examples may be a vibrational or relaxation *normal mode*, the deviation from planarity of a conjugated molecular backbone, the end-to-end distance or radius of gyration [18] of a polymer chain, a *reaction coordinate*, etc.

Note 2: An appropriate choice of collective coordinates is essential to evaluate expediently the key properties of models resulting from simulation procedures and orient interpretation or further simulations. The choice of suitable collective coordinates is also crucial for the construction of *machine learning potentials*.

Note 3: The *potential of mean force* represents the free energy of a system, as a function or one or more collective coordinates.

2.1.3 **Configuration** (stereochemical)

Spatial arrangements of atoms within a molecular entity that distinguishes stereoisomers, the isomerism between which is not due to *conformation* differences.

Note 1: In the present document, use of the term according to the present definition will always be completed by the specification "(stereochemical)". This in order to distinguish it from the *configuration (in statistical mechanics)*. This is not generally the case in scientific literature, where no specification is usually given and the term's meaning can be assessed from the context.

Note 2: The configuration (stereochemical) of a molecule and its stereocenters do not usually change in the course of a simulation, specifically with *atomistic models*. Exceptions may occur in systems described by *ab initio molecular dynamics* or with *reactive force fields*, which are designed to allow formation and breaking of chemical bonds and changes in a *particle*'s type and valence (e.g., from sp^3 to sp^2 and vice versa in the case of carbon atoms).

Note 3: Different *topologies* may in principle be possible for macromolecules with a given configuration (stereochemical).

Note 4: Adapted from ref. [22], differences being limited to specifying the context in which the definition applies.

2.1.4 **Configuration** (in statistical mechanics)

Positions of all the *particles* of a system, providing a complete description of its compositional and geometrical structure.

Note 1: The present definition originates from classical statistical mechanics, as it is the one commonly used in the context of molecular simulations. It is distinct and should not be confused with *configuration (stereochemical)*, and with the arrangement of electrons in orbitals that is specific to atomic structure and quantum chemistry, as defined in configuration (electronic) [23] and used in configuration interaction [16], for example.

Note 2: For a molecule, it depends on its position and orientation in space and its molecular geometry. The configuration of a system of several molecules is the collection of the configurations of all the molecules.

Note 3: In the present document, use of the term according to the present definition is the default, and the specification "(in statistical mechanics)" will be omitted, just as in general scientific literature where the term's meaning can be assessed from the context.

2.1.5 **Configuration space** (in statistical mechanics)

Collection of all *configurations* available to a system of *particles*.

Note: The dimensionality of the configuration space of a system is equal to the number of its *degrees of freedom*.

2.1.6 **Conformation** (stereochemical)

Spatial arrangement of the atoms within a molecular entity, affording distinction between stereoisomers which can be interconverted by rotations about formally single bonds, inversions at trigonal pyramidal centers or other polytopal. rearrangements.

Note 1: For a molecule, like a polymer chain in a crystalline polymorph, the term is often used to indicate the set of torsion angles defining its tridimensional structure. For example, isotactic polypropylene adopts enantiomeric three-fold helical conformations characterized by $(TG^{+})_3$ or $(TG^{-})_3$ main chain torsion angle [22] sequences in its crystalline □, □□ and □ phases.

Note 2: Whereas in the general use (e.g., in physics), it is essentially a synonym of configuration and references the general shape of an object, in chemistry, and more specifically in stereochemical contexts, its use is more restricted and distinct from *configuration (stereochemical)*.

Note 3: Adapted from ref. [22], differences being limited to specifying the context in which the definition applies.

2.1.7 **Conformer**

One of a set of stereoisomers [22], each of which is characterized by a *conformation* corresponding to a distinct potential energy minimum.

Source: [22], page 2204

2.1.8 **Constraint**

Mathematical equality imposed on the *phase space* variables of a system, limiting their variation.

2.1.9 **Degree of freedom** (in statistical mechanics)

In *configuration space*, a Cartesian or other *generalized coordinate* that, together with other such coordinates, provides an unambiguous, non-redundant specification of the microscopic *configuration* of the system under consideration.

Note 1: The provided definition is specific to molecular modeling and derives from its use in classical mechanics. It is distinct from the one in ref. [16], which originates from statistics.

Note 2: In *phase space*, the configurational degrees of freedom are augmented by their time derivatives (velocities) or momenta.

Note 3: In *molecular dynamics* simulations, a few additional degrees of freedom may be used to describe the physical coupling of the system to the environment (e.g., positions and momenta of the *thermostat* and *barostat* variables).

2.1.10 Detailed balance

Principle by which, in a system at equilibrium, each molecular process has an exact counterpart in the reverse direction, and the rate of every chemical process is exactly equal to the rate of the reverse process.

Note 1: In *Monte Carlo* simulations, the term refers to the condition where any given move and its reverse are carried out with equal a priori probabilities at any step.

Note 2: It represents a more restrictive condition than the closely related principle of *microscopic reversibility at equilibrium*.

Note 3: Adapted from ref. [21].

2.1.11 Distribution function (in statistical mechanics)

A normalized function giving the probability that a random variable assumes a specific value or else that it falls within a range of values.

Note 1: It may be discrete, i.e., take on only a finite or countable set of values of the random variable(s), or continuous, i.e., take on any intermediate value of the random variable(s), in a given range. An example of the former is the molar mass distribution of a polymer, an example of the latter is the distribution of end-to-end distances of a polymer chain. Even when the distribution is intrinsically discrete, it is often convenient to regard it as continuous or to model it by a distribution function that is inherently continuous.

Note 2: It may be integral (or cumulative), i.e., give the proportion of the population for which a random variable is less than or equal to a given value. Alternatively, it may be differential (or a probability density function), i.e., give the possibly infinitesimal proportion of the population for which the random variables are within a possibly infinitesimal interval of their ranges.

Note 3: Normalization requires that: (i) for a discrete differential distribution function, the sum of the function values over all possible values of the random variable(s) be unity; (ii) for a continuous differential distribution function, the integral over the entire range of the random variable(s) be unity; (iii) for an integral (cumulative) distribution function, the function value at the upper limit of the random variable(s) be unity.

Note 4: Adapted from [16].

2.1.12 Ensemble (in statistical mechanics)

Collection of points in the *phase space* of a system, all of which are characterized by the same values of thermodynamic variables that determine its macroscopic state at equilibrium, depending on its mode of coupling to the environment.

Note 1: All the statistical mechanical ensembles are equivalent in the thermodynamic limit of an infinite system at equilibrium. A specific ensemble may be preferable to others when simulating a system, depending on the experimental conditions that are mimicked by the simulations or by numerical techniques (e.g., *molecular dynamics* or *Monte Carlo*) adopted for a specific problem.

Note 2: Examples of types of ensembles that are commonly encountered in polymer simulations are the *NVE* or *microcanonical ensemble*, the *NVT* or *canonical ensemble*, the *NPT* or *isothermal-isobaric ensemble*, and the *μVT* or *grand-canonical ensemble*.

2.1.13 **Entanglement** (in polymer science)

Restriction to chain motion arising from the inability of macromolecular chains to cross through one another, producing a transient or permanent network junction over the time scale of observation.

Note 1: An entanglement may be permanent (e.g., within a polymer network) or have a long but finite lifetime (e.g., within a melt of long linear chains). Only the permanent entanglements, such as those between concatenated ring-like chains, strictly preserve the system's *topology*.

Note 2: Though the non-crossing condition is often seen as involving two chains at a time, entanglements in polymer systems largely arise from complex, many-chain interactions.

Note 3: Entanglements can also occur within single chains (knots) and in their interaction with other extended objects, such as nanoparticles and nanotubes.

Note 4: The tube model [18] arises from a *mean-field theory* for the effect of a large number of entanglements on the motion of a long chain. An individual entanglement may also be described and modeled by a slip-link or slip-spring, namely a cross-link that can slide along contours of neighboring polymer chains.

Note 5: The presence of entanglements affects the diffusion and relaxation of polymer chains (e.g., by *reptation* in the case of long linear chains), and results in the appearance of a plateau modulus on time scales shorter than the lifetime of the entanglements themselves.

Note 6: Within a simulation, the entanglements associated with a specific *configuration* of a collection of interacting polymer chains may be identified by a *primitive path analysis*.

Note 7: Adapted from ref. [18]

2.1.14 **Ergodicity** (in statistical mechanics)

Property of a system by which, for long enough observation times, the time spent by the system in the neighborhood of a *phase space* point is proportional to the equilibrium probability of that point in the appropriate *ensemble*.

Note 1: For an ergodic system, the temporal averages and the ensemble averages of its properties, obtained by a large number of independent *molecular dynamics* simulations, should yield equivalent results.

Note 2: In the context of simulations, ergodicity is a combined property of the system and of the numerical method used to model its behavior.

2.1.15 Excluded volume of a macromolecule

macromolecular excluded volume

Volume from which a macromolecule in a dilute solution effectively excludes all other macromolecules.

Note 1: The excluded volume of a macromolecule depends on the thermodynamic quality of the solvent [18], and it is not a measure of the geometrical volume of the macromolecule. It results from all the intramolecular and intermolecular *excluded volumes of the segments* within the interacting chains.

Note 2: A non-zero macromolecular excluded volume is obtained under good solvent conditions, when the second virial coefficient A_2 [18] is positive and can be taken as a measure of the volume spanned by a macromolecule.

Source: IUPAC recommendation [18], entry 3.2.9.

2.1.16 Excluded volume of a segment

segmental excluded volume

Volume from which a *chain segment* of a macromolecule in solution effectively excludes all other segments, i.e., those belonging to the same macromolecule as well as those belonging to other macromolecules.

Note 1: The excluded volume of a segment depends on the thermodynamic quality of the solvent [18] and is not a measure of the geometrical volume of that chain segment.

Note 2: Within a model or a simulation, the *excluded volume interactions* between the segments can have different mathematical representations, depending also on the resolution adopted in the description of the system.

Source: IUPAC recommendation [18], entry 3.2.8.

2.1.17 Generalized coordinate

One of the coordinates in a minimal set which can be used to describe the state of a system, taking into account the *constraints* restricting the system's evolution.

Note 1: The number of independent generalized coordinates equals the number of *degrees of freedom* of a system.

Note 2: A complete set of generalized coordinates univocally represents the *configuration* of a system. Such a set is not unique, and many equivalent representations exist.

2.1.18 Global minimum

Point or region in the *configuration space* of a system for which a given property, often the potential energy or the free energy, reaches its absolute minimum value.

Note 1: Any deviation of model coordinates from those defining it will determine an increase of the value of the property under consideration. The deviation itself may be arbitrarily small in an off-lattice model, whereas it is necessarily finite in a *lattice model*.

Note 2: The global minimum of a system may depend on computational model used to describe it, and on the presence of *constraints* or *restraints* on the variables defining its microscopic state.

Note 3: A system may have a single global minimum, or multiple minima with identical values of considered property. In the latter case, the minima are said to be degenerate.

Note 4: Proving that a minimum is a global minimum requires an exhaustive search of the configuration space of a system, comparing the property of this and other, alternative local minima. A systematic search and enumeration of all minima of a system may be possible only in special, simple cases (e.g., small molecules or lattice models).

Note 5: In complex systems, it may be difficult or even impossible to identify the global minimum with certainty, typically due to a very large number of possible local minima, some of which may be degenerate. Computational algorithms such as *simulated annealing* have been explicitly developed in order to address such difficult global optimization problems.

Note 6: Several local minima of the potential energy may participate to the same global minimum of the free energy, when these can quickly interconvert compared to the time scale of an experiment or a simulation.

2.1.19 Holonomic constraint

Constraint involving only the *particle* coordinates and possibly time.

Note: A simple example is the requirement that a certain bond length or interatomic distance remains constant during a *molecular dynamics* simulation.

2.1.20 Internal coordinate representation

Specification of a molecular structure in terms of atom types, bond lengths, bond angles, dihedral angles or other suitable combinations of *particle* coordinates, such that the representation is independent of the position and orientation of the molecule in space.

Note 1: For the common case of a non-linear molecule with N atoms, there are 3N-6 independent internal coordinates. For a linear molecule, there are 3N-5 independent internal coordinates. Six additional coordinates (five for linear molecules) need to be specified to properly place and orient the molecule in three-dimensional space.

Note 2: The so-called Z-matrix, adopted with slight differences by several computational codes, is an example: for the first atom in a list only the atom type needs to be defined, from the second also a bond length, from the third also a bond angle, while each additional atom is described by the atom type, a bond length, a bond angle and, generally, by a dihedral or torsion angle.

Note 3: In special cases (e.g., linear or highly symmetric molecules), some internal coordinates may be specified with respect to one or more additional fictitious particles ("dummy" or "ghost" atoms).

2.1.21 Markov chain

Sequence of states, each belonging to a set called the state space, such that the probability of observing a state at a particular location in the sequence only depends on the states that precede it.

Note 1: In an *n*-th order Markov chain, the probability of observing a state depends on the *n* states immediately preceding it in the sequence. The most common case is the first order Markov chain, in which the probability of observing a state depends only on the state immediately preceding it.

Note 2: Markov chains provide the basis for many *Monte Carlo* simulation methods. In Monte Carlo simulations of a system of *particles*, the state space usually coincides with the *configuration space*.

2.1.22 Mean-field theory

Theory reducing the difficult exact evaluation of interactions in a multi-body system to a simpler but approximate evaluation of an average effective interaction of a body with its surroundings.

Note 1: In general, mean-field theories are valid in situations where it is possible to neglect the effect of correlations or fluctuations within a system.

Note 2: Mean-field approximations can be applied both to quantum mechanical and to classical many-particle systems. Examples are the *Hartree–Fock theory* for the electronic structure of atoms, molecules and materials, the van der Waals theory for fluids and their phase equilibria, and the *polymer self-consistent-field theory* for inhomogeneous polymer systems, such as blends, block copolymers and interfaces.

Note 3: In the context of polymer modeling and simulation, the "bodies" in the definition may be any kind of *particle*, such as atoms, coarse-grained *chain segments* or whole polymer chains, as well as electrons.

Note 4: One important example of mean-field theory for polymers is Flory's treatment of *excluded volume interactions*, for a polymer chain in a good solvent [9,12,13]. The theory gives the exponent ν, within the *scaling* law the dependence of a chain's root-mean-square radius of gyration (R_g) [18] on the number of segments N:

$$R_g \sim N^{\nu}$$

where the scaling symbol "~" indicates the omission of a proportionality constant with the dimension of length. The result, for the general case of a polymer chains in d dimension, is:

$$\nu = \frac{3}{d+2}$$

This gives $\nu = 0.6$ when $d = 3$, in good agreement with computer simulations and the more exact result from *polymer renormalization group theory*, $\nu = 0.588$. The result for $d = 2$, relevant for polymer chains strongly confined in one direction, is $\nu = 0.75$, which is exact.

Source: IUPAC recommendation [18], entry 3.1.11.

2.1.23 Microscopic reversibility at equilibrium

Principle by which, in a system at equilibrium, any molecular process and its reverse process occur, on the average, at the same rate.

Note 1: In *Monte Carlo* simulations, the requirement that a process and the reverse of that process may occur through a finite sequence of trial moves with equal probabilities is sufficient and necessary to ensure microscopic reversibility.

Note 2: It represents a more general, weaker condition than the closely related *detailed balance* principle.

Note 3: Adapted from ref. [21].

2.1.24 Non-bonded interaction

Attraction or repulsion between atoms or *particles* that are not covalently linked to each other, affecting the thermodynamic stability of the chemical species concerned.

Note 1: The atoms may belong to the same or to different molecules. In the first case, they should not be directly bonded to each other, nor share covalently bonded neighbors. The 1–4 interactions between next-nearest neighbors, that largely affect the relative energies of the *rotamers* of a polymer chain, depend in general on a combination of bonding and non-bonding effects, which may not be always rigorously separated.

Note 2: When two *chain segments* are widely spaced apart within a macromolecule, this corresponds to a *long-range intramolecular interaction*.

Note 3: Adapted from ref. [16].

2.1.25 Non-holonomic constraint

Constraint involving the *particles*' velocities, possibly in addition to the particles' coordinates and time.

Note: Simple examples are the requirement that particular atoms move at a constant speed, or that the total kinetic energy of the system remains constant during a simulation.

2.1.26 Normal mode

Collective coordinate describing the mode of motion of a molecule or a group of *particles*, which occurs with a characteristic time scale or frequency, and is essentially uncoupled from the motion of other normal modes or other parts of the system.

Note: Normal modes arise in different contexts, being typically obtained from the analysis of certain linearized equations of motion. See, for example, *vibrational normal mode analysis* and *relaxation normal mode analysis*.

2.1.27 **Particle** (in polymer modeling and simulation)

Fundamental physical entity, with a non-zero mass and whose internal structure is neglected, used to construct the model of a molecular system.

Note 1: In a classical model or simulation, a particle is usually spherically symmetric and has at most three translational *degrees of freedom*. Rotational degrees of freedom are usually neglected, when the particle is spherical and its mass is assumed to be concentrated at its center.

Note 2: In some cases, such as *electrostatic models* with multipolar charge distributions or systems based on the *Gay–Berne potential*, a particle may be non-spherical and have up to three additional degrees of freedom associated with its rotation in space.

Note 3: In polymer simulations, the highest level of detail that can presently be expected corresponds to the positions and velocities of each atom, and possibly also the overall electron density. Hence, although the electron [16] is a legitimate elementary particle [16], and electrons are explicitly included in *ab initio molecular dynamics*, in polymer simulations electrons are normally excluded when referring to "particles".

Note 4: Examples of particles are atomic nuclei, whole atoms and small rigid molecules. In a *coarse-grained model*, a particle may correspond to a well-defined group of atoms or to a generic polymer *chain segment*.

Note 5: In a *lattice model*, the particles correspond to the individual units that may occupy the nodes of the lattice.

Note 6: Within this document, the specifier "(in polymer modeling and simulation)" will be omitted when referring to particles.

2.1.28 **Phase space** (in statistical mechanics)

Collection of states available to a system, defined by the positions and momenta of all of its constituent *particles*.

2.1.29 **Potential energy surface (PES)**

energy hypersurface

Function specifying the dependence of the potential energy of a molecular system on its *configuration*, electronic state, and environment.

Note 1: Within the adiabatic approximation, it represents the potential energy of a molecular system (total energy minus the kinetic energy of the nuclei) as a function of the coordinates of all nuclei contained in it.

Note 2: The notion of hypersurface is used to stress the multidimensionality of PESs. In a molecular system consisting of N atomic nuclei, the number of independent coordinates that fully determine a PES is equal to $3N$-6 (or $3N$-5 if the system is linear).

Note 3: The PES of a molecular system may be obtained within the Born–Oppenheimer approximation [20] by (approximate) solution of the electronic Schrödinger equation. *Density functional theory* aims mainly at the electronic ground state of a system, whereas other electronic structure methods may provide the PES also for some excited states. The PES for excited states and the transitions between them are relevant for some polymer-related systems or processes, such as photochemical reactions, or charge- and energy-transport in photoactive and semiconducting polymers.

Note 4: The opposite of the derivatives of the PES with respect to the *particle* coordinates represent the forces on the atoms.

Note 5: *Force fields* generally aim to provide a simple representation of the PES for the electronic ground state of a system, possibly also far away from its minima in the case of *reactive force fields*.

Note 6: The concept of potential energy surface may be extended to include the *potential of mean force*, i.e., to a free energy depending on a small number of *collective coordinates*. The dependence of the potential energy surface on the environment arises from the neglected degrees of freedom, such as the coordinates of the solvent molecules in an *implicit solvent model*.

Note 7: The characteristics of a system's PES are fundamental in determining its physical and chemical properties. Examples are whether it is rugged or smooth, and the energies, number and types of its *stationary points* (minima and saddle points).

Note 8: Adapted from ref. [20].

2.1.30 Reptation

Effectively snake-like Brownian motion of linear chain molecules or long linear sections of more complex macromolecules along their coarse-grained contour, arising from the chains' inability to cross through one another and thereby form *entanglements*.

Note 1: It typically occurs in concentrated polymer solutions and in bulk amorphous polymers.

Note 2: It is an important example of the consequences of *topology* and entanglements for the properties of polymers. It manifests itself only above a critical molecular mass, which depends on the chemical structure of the polymer.

Note 3: The coarse-grained contour of a chain undergoing reptation may be identified with the center of a tube confining it. The tube model [18] arises from a *mean-field theory* for the effect of a large number of entanglements on the motion of a long chain.

Note 4: In a simulation, the coarse-grained contour of the polymer chains and the number of entanglements formed by them may be identified by a *primitive path analysis*.

Note 5: Adapted from ref. [18].

2.1.31 Restraint

Bias applied to the *phase space* variables of a system that limits their values.

Note 1: A common way of introducing a restraint is through an additional fictitious potential energy term, such as a *harmonic potential* acting on a *collective coordinate*.

Note 2: Input for restraints may come from experimental data, such as diffraction/scattering data NMR data, or from the desire to explore by simulation a certain region in the *configuration space* of the system.

Note 3: A stiff restraint (e.g., a harmonic potential with a very large force constant) may be used to approximate a *constraint*.

2.1.32 Rotamer

rotational isomer

One of a finite set of *conformers* arising from restricted rotation about one single bond.

Source: IUPAC recommendation [22], page 2217.

2.1.33 **Rotational isomeric state** (in polymer science)

Rotamer defined by a relative rotation about a skeletal bond of a single-strand *chain*.

Note: States are typically identified with the minima on the PES for a molecular fragment (e.g., one *trans* and two *gauche* for a C–C single bond).

Source: IUPAC recommendation [18], entry 1.9.

2.1.34 **Scaling** (in polymer science)

Relationship between two physical quantities (P and Q), such that a relative change in one produces a relative change in the other, according to a power law:

$$\frac{P}{P_0} = \left(\frac{Q}{Q_0}\right)^{\alpha}$$

where P_0 and Q_0 are reference values with the units of P and Q, and α is the characteristic exponent of the scaling law.

Note 1: A scaling law may also be written by combining P_0 and Q_0 within a single constant C_0:

$$P = C_0 Q^{\alpha} \qquad \text{where} \qquad C_0 = P_0 Q_0^{-\alpha}.$$

Following de Gennes' notation [9, page 26], the constants may also be neglected when writing a scaling law, replacing the equal sign "=" by a tilde "∼" as the scaling symbol:

$$P \sim Q^{\alpha}.$$

Note 2: An important example of scaling law in polymer science is the connection between molar mass M [18] and the root-mean-square end-to-end distance R_{ee} [18] of a flexible linear chain in dilute solution:

$$R_{ee} \sim M^{\nu}$$

where the scaling exponent ν is independent of the polymer but depends on the quality of the polymer-solvent pair: ν = 1/3 for the globular state in a poor solvent, ν = 1/2 for the unperturbed theta state [18], ν ≈ 0.588 ≈ 3/5 for the expanded state in a good solvent. The scaling law implies that, upon doubling the molar mass, the average size of a macromolecule increases by a factor $2^{1/3} \approx 1.26$ in a poor solvent, by $2^{1/2} \approx 1.41$ in a Θ solvent, by $2^{0.588} \approx 1.50$ in a good solvent.

Note 3: A scaling law may be valid only for a limited range of the variables, possibly spanning several orders of magnitude. For example, the scaling laws for the end-to-end distance is only valid above a certain polymer-dependent molar mass M (mathematically, when $M \to \infty$). Other examples are the scaling laws for the viscosity η of monodisperse linear polymer melts:

$$\eta \sim M \quad (\text{for } M \ll M_c) \qquad \text{and} \qquad \eta \sim M^{3.4} \quad (\text{for } M \gg M_c)$$

where M_c is a polymer-dependent critical molar mass. There is no simple scaling law in the transition region, when $M \approx M_c$ ("crossover regime").

Note 4: Scaling transformations associated with a systematic, hierarchical *coarse-grained* description of a system find an important application in *polymer renormalization group theory*.

2.1.35 Self-consistent field (SCF)

Computational approach to a many-body problem, wherein an approximation to the solution is used as an input to obtain an improved solution, until the input and output of the calculations are identical within a given tolerance (self-consistency condition).

Note 1: The self-consistent field approach is often applied in combination with an approximate *mean-field theory* for the inter-particle interactions. However, one could also seek a self-consistent field solution to a more complicated system of equations, not based on the mean-field approximation.

Note 2: The quantum mechanical *Hartree–Fock theory* and *density functional theory* equations are generally solved by a self-consistent iterative procedure. In this case, one seeks a solution for the electron density function [20] and the associated energy of a molecular system.

Note 3: A classical, *polymer self-consistent field theory* can also be formulated and is typically applied to inhomogeneous systems such as polymer blends and interfaces.

2.1.36 Stationary point

Point in the *configuration space* of a system, such that gradient of the *potential energy surface* is zero at that point.

Note 1: At a stationary point, the conservative forces on all the *particles* are also zero.

Note 2: The important stationary points of a system are its minima and its saddle points, depending on its Hessian matrix (second derivatives of the potential energy with respect to the particle coordinates). The minima correspond to locally stable structures, the saddle points to transition states connecting different minima.

Note 3: The concept of stationary point may be extended beyond the potential energy surface, to other scalar functions of the particles' coordinates. For example, the free energy, or measures of the volume or surface area of a macromolecule (see *solvent-accessible surface* and *solvent-excluded surface*).

Note 4: In the case of the *lattice model*, stationary points can still be defined, using finite differences in order to approximate the gradient of the potential energy.

2.1.37 **Topology** (in polymer modeling and simulation)

Ensemble of properties of a molecule or a collection of molecules that are preserved under continuous deformations, such as stretching, bending and rotation about bonds, but without any breakage, rearrangement, or mutual crossing of bonds.

Note 1: The topology of a system does not usually change in the course of a simulation. An important exception is represented by systems described by *reactive force fields* on *ab initio molecular dynamics*, which allow formation and breaking of chemical bonds.

Note 2: A polymer simulation with *soft-core potentials* may also allow changes in the topology, because bond crossing *configurations* have relatively low energies and they may occur frequently.

Note 3: The term topology may also be used to indicate the large-scale architecture of a single macromolecule, for example whether it is linear, branched, star-shaped, ring-like, and so on. Thus, the topology of a polymer model may also change during its preparation, for example in the construction of a network by cross-linking of precursor linear chains.

Note 4: To the extent that conservation of topology precludes *chain segments* from crossing through one another, topological restrictions on chain motions arise, which are called *entanglements*. These may be permanent, or temporary but long-lived. The temporary entanglements do not preserve the topology of the macromolecules, in a strict mathematical sense. However, they affect its physical and dynamical properties, for example through *reptation* in a melt of long linear chains.

Note 5: The term is sometimes used in a looser sense in the case of macromolecules, to refer to macroconformations, possibly also of linear main chains, characterized by different numbers of loops, knots, folds etc., which in order to interconvert do not require bond cleavage, but substantial changes in some *collective coordinate*.

2.1.38 **Virial**

internal virial

In an equation of state, the non-ideal contribution $\langle W \rangle$ arising from interparticle forces:

$$PV = Nk_{\mathrm{B}}T + \langle W \rangle$$

where P is the pressure, V the volume, T the temperature, N the number of *particles*, k_B Boltzmann's constant, and the angular brackets ⟨⟩ indicate an average over a thermodynamic *ensemble*.

Note 1: The first term on the right-hand-side of the equation is the ideal contribution to the pressure, associated with the particles' thermal motion.

Note 2: The mathematical expression of W is:

$$W = -\frac{1}{3}\sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i U$$

where U is the potential energy, $\boldsymbol{r}_i$ the coordinates of particle i, ∇_i the gradient operator with respect to $\boldsymbol{r}_i$.

Note 3: These expressions can be generalized to describe all the components of the stress tensor, which are important in the description of anisotropic systems such as many crystals, liquid crystals, and polymers subject to deformation.

2.2 MODELS

2.2.1 Ab initio model

first-principles model

Quantum mechanical description of a molecular system, based on an approximate numerical solution of the Schrödinger equation or its relativistic extensions for the electrons, excluding the use of any experimental information apart from the values of the fundamental physical constants.

Note 1: An ab initio model may include all the electrons within a molecular system, or only the valence ones. When the core electrons of an atom are excluded from a calculation, their effect on the valence electrons can be modeled by suitable *effective core potentials*.

Note 2: Examples of numerical methods that may be used within an ab initio model for the electronic structure are *Hartree–Fock theory* and *density functional theory*.

2.2.2 Atomistic model

all-atom (AA) model

explicit-atom (EA) model

Representation of a molecular system or a part of it, characterized by a one-to-one correspondence between *particles* and atoms.

Note 1: The potential energy of the system and forces among the atoms that derive from it may be described by an empirical *force field*, by a quantum mechanical model for the system's electronic structure (see e.g., *ab initio model* and *semiempirical model*), or by a combination of the two approaches, as in a *QC/MM model*.

Note 2: A *united-atom model* is very close to an atomistic model, but contains some coarse-graining elements as it keeps most hydrogen atoms implicit.

2.2.3 Bead-spring model

bead-and-spring model

Generic *coarse-grained* representation of a flexible polymer, in which the constituting *particles* interact by spherically symmetric potentials, and the connectivity of the polymer is described by simple potential energy functions among the bonded particles.

Note 1: The interactions among bonded particles may be derived both from *harmonic* or from anharmonic potential energy terms, respectively, giving linear and non-linear springs. The widely used model obtained by

combining the *Weeks–Chandler–Andersen potential* and a *finitely extensible non-linear elastic potential* is known in the literature as Kremer-Grest model.

Note 2: Sometimes potential energy terms associated with bond bending are included in simulations of a bead-and-spring model, to impart some chain stiffness.

Note 3: In the limit of infinitely stiff springs with a non-zero bond length, or when there are *constrains* keeping the bond lengths at a fixed value, it leads to the *bead-rod model*.

Note 4: A bead-spring model may be used in combination with a simple model for the *non-bonded interactions* among the particles (e.g., a *Lennard-Jones potential* or a Weeks–Chandler–Andersen potential), or may exclude any non-bonded interactions, as in the Rouse theory [18] for the dynamics of polymer chains.

Note 5: A *Gaussian chain* model corresponds to a bead-and-spring model without non-bonded interactions, in which the springs are harmonic and their force constants are proportional to the thermodynamic temperature.

2.2.4 Bead-rod model

Generic *coarse-grained* representation of a flexible polymer, in which the constituting *particles* interact by spherically symmetric potentials, and the connectivity of the polymer is described by bonds generally of fixed length.

Note: It is equivalent to a *bead-spring model* with non-zero bond lengths and infinitely stiff springs. Unlike a *freely-jointed chain* model, it may include *non-bonded interactions* among the beads and potential energy terms associated with bond bending, to impart some chain stiffness. Unlike a *self-avoiding random walk chain*, the interactions among the beads are not limited to repulsive *excluded volume interactions* and may include an attractive part.

2.2.5 Bonded potential

Contribution to the potential energy of a molecular system, which depends on two or more *particles* being directly connected by a bond (first nearest-neighbors, 1–2 interaction), or being connected to the same atom (second nearest-neighbors, 1–3 interaction), or being connected to two different atoms that are bonded to each other (third nearest-neighbors, 1–4 interaction).

Note 1: A bonded potential may change in value due to changes in the molecular geometry, but it typically persists throughout a simulation conducted with conventional *force fields*. Exceptions may occur in simulations conducted with *reactive force fields* or some *coarse-grained models* allowing bond breaking and formation.

Note 2: In simulations based on *ab initio models* or *semiempirical models*, there is no a priori separation between *non-bonded interactions* and bonding contributions to the potential energy of a system.

2.2.6 **Boundary condition** (in polymer modeling and simulation)

Constraint or *restraint* on the *phase space* variables in *particle*-based simulation, associated with the thermodynamic state of a system and its interaction with the environment, which limits the range of their possible independent values.

Note 1: The use of *periodic boundary conditions* is an example of constraint, the use of a "wall" to confine the particles is an example of restraint. An example of potential defining a wall is provided within a note to the *Hamaker potential*.

Note 2: In a three-dimensional system, different types of boundary conditions may be defined along different spatial directions.

Note 3: This definition is specific to particle-based theories and simulations. In continuum models, which are typically based on the solution of partial differential equations for one or more functions (e.g., the fluid velocity field, the electrostatic potential, etc.), the boundary conditions specify the values of these function or their derivatives at the boundaries of the computational domain, on specific surfaces or at infinity.

2.2.7 **Buckingham potential**

exp-6 potential

Model that describes the *non-bonded interaction* between two spherical *particles*, using an exponentially decaying function to represent the repulsion at close distances and an inverse sixth power to represent the attraction at longer distance.

Note 1: Its form is:

$$V_{\mathrm{B}}(r) = A_{ij}\exp\left(-B_{ij}r\right) - \frac{C_{ij}}{r^6}$$

where r is the interparticle distance, and A_{ij}, B_{ij}, and C_{ij} are positive parameters which depend on the particle types. The second term in the potential, that is, responsible for the dispersion or London forces [16] among the particles, may be modified (e.g., to become a distance-independent constant) at short interparticle distances, to prevent the unphysical divergence of $V_{\mathrm{B}}(r)$ to $-\infty$ when $r \to 0$.

Note 2: It is an example of *short-range potential*. It can be used as an alternative to the *Lennard-Jones (LJ) potential*.

2.2.8 **Coarse-grained (CG) model**

Low-resolution representation of a molecular system, in which the number of its *degrees of freedom* is reduced by abandoning an *atomistic model*, or any more detailed model.

Note 1: A generic CG model is obtained by specifying the connectivity and interactions of large polymer-like molecules, without any reference to an underlying atomistic model. This approach is adequate for the exploration of generic, universal properties that characterize the large-scale, long-time behavior of polymers. The *bead-spring model* and *bead-rod model* are examples of such generic models.

Note 2: A non-generic CG model is obtained by grouping the atoms of a chemically realistic model into a smaller number of *particles* (*mapping*). The interaction potentials—and, sometimes, also the equations of motion—for these particles are defined in order to reproduce selected thermodynamic, structural, and dynamical properties of the specific system. These properties may be derived either from reference simulations with an atomistic model or from experiment, or both. An atomistic model may also be recovered from the coarse-grained one by *reverse mapping*.

Note 3: The concept can be applied in a hierarchical fashion, for example, using a single soft sphere to approximate a CG polymer chain, which in turn approximates an atomistic polymer chain.

2.2.9 Combination rule

Collection of mathematical expressions providing an approximate set of parameters for the interaction between unlike *particles* (e.g., A and B), from the analogous parameters describing the interactions between particles of the same type (A-A and B-B).

Note 1: Examples of commonly used combination rules that apply to the *Lennard-Jones potential* are, for the interaction energies:

$$\varepsilon_{AB} = \sqrt{\varepsilon_{AA}\varepsilon_{BB}} \quad \text{(geometric average)}$$

and for the effective diameters:

$$\sigma_{AB} = \sqrt{\sigma_{AA}\sigma_{BB}} \quad \text{(geometric average)}$$

or

$$\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 \quad \text{(arithmetic average).}$$

Note 2: Combination rules may be used also in other contexts. For example, the Flory–Huggins χ parameter [18] for a polymer-polymer or polymer-solvent pair may be approximately obtained from the solubility parameters [18] of the individual components.

2.2.10 Concurrent multiscale model

Multiscale model wherein different parts of a system are described within the same simulation using different computational methods or degrees of detail.

Note 1: The constituent parts may overlap to some extent, with some portions of the simulated system described at the same time with two different models.

Note 2: The partitioning may be either *particle*-based or space-based, and it may be either static or dynamic (i.e., change in the course of a simulation).

Note 3: Examples of concurrent multiscale models are:

- *QC/MM models*.
- *Particle*-*continuum* coupling (e.g., atomistic or coarse-grained molecular dynamics and finite element simulations).
- Adaptive Resolution Molecular Dynamics Simulations (AdResS).

2.2.11 Continuum model

Representation of a system or a part of it, which is based on classical macroscopic physics and neglects all atomic or molecular level aspects.

Note 1: A continuum description may be used in a molecular simulation to describe the interaction of the system with its environment, such as the solvent or its physical boundaries.

Note 2: Simulations adopting an *implicit solvent model* provide examples of this type of application where solvent molecules are replaced by a medium characterized by a small number of macroscopic properties (e.g., permittivity, density, viscosity, etc.).

Note 3: A continuum model is usually specified by a set of partial differential equations (e.g., the Maxwell equations for electromagnetic phenomena, or the Navier-Stokes equation for fluid flow) and the associated boundary conditions. If the model does not admit exact analytical solutions, a discretization must be introduced in order to obtain numerical solutions to it, for example by the finite-difference or finite-element methods.

2.2.12 Coulomb potential

Model for the electrostatic interaction between two charged, point-like *particles* in a homogeneous medium.

Note 1: Its mathematical expression is:

$$V_{\mathrm{C}}(r) = \kappa \frac{q_i q_j}{r}$$

where r is the inter-particle distance, q_i and q_j are the particles' electric charges, and κ is a constant inversely proportional to the permittivity of the surrounding medium.

Note 2: It is an example of *long-range potential*.

Note 3: It can be generalized to account for non-point-like or non-spherical charge distributions on each particle.

2.2.13 **Cut-off** (in polymer modeling and simulation)

Value of a parameter within a theory or simulation, determining the neglect of certain contributions to the energy or other properties of a system, or a change in the strategy to compute them beyond that value of the respective parameter.

Note 1: When the cut-off parameter corresponds to an interparticle distance, it may be referred to as "distance cut-off" or "interaction cut-off". In a simulation based on *force fields*, this may be different for different types of atom pairs and also for different components of the interactions (e.g., the *Lennard-Jones* and the *Coulomb potential* for the interaction between two atoms). The interaction potential may be modified also below the cut-off distance, to ensure continuity of the potential and possibly also its derivatives. The *Weeks–Chandler–Andersen potential* is an example of the application of a cut-off to the Lennard-Jones potential.

Note 2: Distance cut-offs are often applied in the simulation of systems with *periodic boundary conditions*, for the evaluation of *short-range potentials*. The *minimum image convention* automatically introduces a cutoff at a distance that, for an cubic cell, is equal to half of the periodic cell length.

Note 3: In the case of periodic systems with *long-range potentials*, the interaction between *particles* at distances beyond the cut-off may be recovered by "reciprocal" or "k-space" summations (*Ewald summation* and related methods). In this case, the cut-off is actually a distance parameter that determines how the full interaction is computed.

Note 4: Some simulation protocols adopt a "group cut-off" scheme, whereby the interaction energy between two atoms is included or neglected depending on the distance between the centers-of-mass of the groups to which they were assigned.

2.2.14 **Delta-function pseudopotential**

Model for the short-range interaction between the *chain segments* of macromolecular chains, which is non-zero only when these occupy the same position in space.

Note 1: Its mathematical expression is:

$$U(\boldsymbol{r}_i - \boldsymbol{r}_j) = u\delta(\boldsymbol{r}_i - \boldsymbol{r}_j)$$

where $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ are the *particles*' coordinates, δ is the Dirac delta-function and u is a prefactor that determines the strength of the interaction.

Note 2: The prefactor u is proportional to the second virial coefficient [16] among the polymer segments, and it is also related to the Flory–Huggins χ parameter [18]:

$$u = v(1 - 2\chi)$$

where v is the effective volume of a segment. Like χ, it may depend on the thermodynamic state of the system, namely temperature, pressure, solvent, and other factors. It is positive in a good solvent ($0 \leq \chi < 1/2$), when the repulsive *excluded volume interaction* among the segments prevails over any mutual attraction, it vanishes in the theta state [18] ($\chi = 1/2$), and it is negative in a poor solvent ($\chi > 1/2$). In the latter case, there is a net attractive interaction between two segments.

Note 3: If $w(R)$ is the *potential of mean force* between two polymer segments at a distance $R = |\boldsymbol{R}|$, the prefactor u is approximately given by (in the common three-dimensional case):

$$u(T) = -\frac{1}{2}\iiint f(R,T)\mathrm{d}^3\boldsymbol{R} = -2\pi\int_0^\infty f(R,T)\mathrm{d}R$$

where its dependence on temperature T has been explicitly indicated. Here $f(R,T)$ is the Mayer f-function:

$$f(R,T) = \exp\{-w(R)/k_\mathrm{B}T\} - 1$$

and k_B is the Boltzmann constant.

Note 4: It is typically used within the *Edwards Hamiltonian* and *polymer self-consistent field theory*.

Note 5: It should not be confused with the *effective core potential* of electronic structure theory.

2.2.15 Edwards Hamiltonian

Sum of the entropic contribution deriving from the linear connectivity of a *Gaussian chain* and the contribution from *excluded volume interactions* between all pairs of *chain segments*, within a continuous representation of a flexible polymer chain.

Note 1: Its mathematical expression is:

$$H(\boldsymbol{r}) = \frac{3}{2l_\mathrm{K}}\int_0^L \mathrm{d}p\left(\frac{\mathrm{d}\boldsymbol{r}(p)}{\mathrm{d}p}\right)^2 + \frac{u}{2l_\mathrm{K}^2}\int_0^L \mathrm{d}p\int_0^L \mathrm{d}q\,\delta[\boldsymbol{r}(p) - \boldsymbol{r}(q)]$$

where l_K is the Kuhn segment length [18] and L is the contour length [18] of the chain, $\boldsymbol{r}(p)$ is the position of the segment corresponding to the curvilinear coordinate p along the chain's contour, and u is the prefactor of the pairwise *delta-function pseudopotential*.

Note 2: It is the classical equivalent of the quantum mechanical Hamiltonian of an electron in a potential, with the kinetic energy of the electron mapped onto the chain entropy and the potential mapped onto the inter-segment interaction.

Note 3: It can be generalized to describe the interaction among multiple chains.

2.2.16 Effective core potential (ECP)

pseudopotential

Approximate potential accounting for the effect of the core electrons on the valence electrons of an atom, allowing the elimination of the former from a quantum chemical calculation.

Note 1: It is valid for properties, such as chemical bonding or low-energy excitations that are predominantly determined by the valence electrons.

Note 2: In parallel to reducing the number of electrons, an ECP allows also a reduction of the size of the *basis set*. This can lead to substantial reductions in the numerical effort required to obtain electronic energies, wavefunctions, and densities, especially for heavy elements with a large number of core electrons.

2.2.17 Electrostatic model

Specification of charge distribution within a molecular system, and of the way in which the energy and forces associated with this charge distribution should be computed.

Note 1: In simulations based on atomistic or coarse-grained *force fields*, the simplest electrostatic models consider a single point charge at the center of each *particle* (if the particles are charged). In this case, the charged particles interact by a *Coulomb potential*. Other electrostatic models may employ off-center charges, dipoles, or higher moments of the charge distributions (multipoles) at the location of the atoms or other positions. These quantities may be fixed or be susceptible to change due to polarization [20] effects.

Note 2: The specification of the electrostatic model requires also other information, beyond the charge distribution. Examples are the permittivity of the medium and the ionic strength of an electrolyte solution (for calculations based on an *implicit solvent model*), the method used to compute the electrostatic interactions (e.g., by *Ewald summation* or some other method) and other specific settings of the method (e.g., the value of the *cut-offs* for the interactions).

Note 3: In simulations based on *ab initio* or *semiempirical models* for the electronic structure, the charge distribution and therefore also the electrostatic model derive from the computed electron density.

Note 4: In some cases, the term is used restrictively, to indicate a model in which the charge distribution is static, i.e., it is not affected by an applied electric field or by a change in the system's *configuration*. In this sense, the term indicates the opposite of a *polarizable model*.

2.2.18 Excluded volume interaction (in polymer modeling and simulation)

Short-range repulsive interaction, which prevents two or more atoms, *particles,* or *chain segments* from overlapping significantly.

Note 1: The excluded volume interaction between two segments is often mediated by the solvent and depends on the thermodynamic state of the system (e.g., temperature and pressure).

Note 2: Within the *Edwards Hamiltonian*, this interaction may be modeled using a *delta-function pseudopotential* with a positive prefactor.

Note 3: The *Weeks–Chandler–Andersen potential* is a model of excluded volume interactions between spherical particles, typically used in combination with a *bead-spring model*.

Note 4: In simulations of *lattice models*, the excluded volume interaction among the segments may be implemented by preventing multiple occupancies of the lattice sites.

Note 5: A flexible macromolecule subject to such interactions can be described as a *self-avoiding random-walk chain*, with *scaling* laws for the end-to-end distance or the radius of gyration [18] distinct from those of a *freely-jointed chain*.

2.2.19 Expanded Lennard-Jones potential

Generalization of the *Lennard-Jones potential*, providing an empirical representation of the interaction energy between spherical *particles* with an impenetrable core of finite radius.

Note 1: Its mathematical expression is:

$$V_{\mathrm{ELJ}}(r) = \begin{cases} \infty, & r \le \Delta_{ij} \\ 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r-\Delta_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r-\Delta_{ij}}\right)^{6}\right], & r > \Delta_{ij} \end{cases}$$

where r is the distance between the *particles*' centers, Δ_{ij} is the core diameter for two particles of type i and j, and ε_{ij} and σ_{ij} are an interaction energy and distance analogous to those of the Lennard-Jones potential. The standard Lennard-Jones potential is recovered when $\Delta_{ij} = 0$. Assuming that each particle has a diameter Δ_{ii}, the diameter for cross-interactions is typically obtained by the *combination rule*: $\Delta_{ij} = (\Delta_{ii} + \Delta_{jj})/2$.

Note 2: It may be used as a simple alternative to a *Hamaker potential*, within a *coarse-grained model* of spherical nanoparticles.

2.2.20 Explicit solvent model

Description of a molecular system, in which the solvent or more generally the environment of the solute is represented by a *particle*-based model.

Note: Within a *concurrent multiscale model*, the interactions within the solvent and between the solvent and the solute may be represented more approximately than within the solute. For example, within a *QC/MM model*, a *force field* instead of the *ab initio* or *semiempirical model* is used for the solute.

2.2.21 Finitely extensible non-linear elastic (FENE) potential

Model that describes the stretching energy of a bond between two *particles* or of a *chain segments*, characterized by a finite maximum extensibility.

Note 1: Its mathematical expression is:

$$V_{\mathrm{FENE}}(r) = -\frac{kr_{\max}^2}{2}\ln\left[1-\left(\frac{r}{r_{\max}}\right)^2\right]$$

where r is the length of the bond, $r_{\max}$ is its maximum length, and k is its force constant. The FENE potential behaves like a *harmonic potential* (i.e., it is quadratic in r) when $r \ll r_{\max}$, and it diverges to infinity when $r \to r_{\max}$.

Note 2: It has a minimum at $r = 0$, but it can be used in conjunction with a *Lennard-Jones potential* or *Weeks–Chandler–Andersen potential* to represent other interactions, including those between particles that are directly bonded. The result is a potential with a non-zero equilibrium bond length.

Note 3: It may be used within a *coarse-grained*, *bead-spring model*. Depending on the situation, the main purpose of the finite extensibility may be to guarantee the preservation of inter-chain *entanglements*, or to prevent unphysically large stretching of the bonds in *non-equilibrium molecular dynamics* simulations.

2.2.22 Force field

Mathematical or numerical representation of the potential energy of a molecular system as a function of the coordinates of its constituting atoms or *particles*, from which conservative forces may be calculated by differentiation with respect to the particle coordinates, enabling its simulation by *molecular mechanics*, *molecular dynamics,* or *Monte Carlo* methods.

Note 1: No direct reference is made to the electron distribution within the system.

Note 2: A force field may consist of several additive terms, which are usually referred to as "potentials", as in *harmonic potential* and *Lennard-Jones potential*.

Note 3: The specification of a force field requires: (a) a classification of the atoms or particles according to types (e.g., in an *atomistic model* there may be tens of different carbon atom types, depending on their hybridization state, their polarity, etc.), (b) the functions that describe the individual contributions to the potential energy associated with both bonded (stretching, bending, torsion, etc.) and *non-bonded interactions*, and (c) the full set of parameters appearing in these functions. The parameters depend on the particle types. In *reactive force fields* and *machine learning potentials*, all the atoms of a given element belong to the same type.

Note 4: The functions that describe the individual contributions to the potential energy may be analytical or numerical (e.g., tabulated data or spline functions in some *coarse-grained models* and in *machine learning potentials*).

2.2.23 Freely jointed chain

random-walk chain

random-flight chain

Chain model consisting of infinitely thin rectilinear segments, each of which can take all orientations in space with equal probability, independently of its neighbors.

Note 1: In a freely jointed chain, two or more links can occupy the same volume simultaneously. This holds also for the *particles* within a *bead-spring model* chain, when the interactions among them are neglected.

Note 2: For a freely jointed chain containing a large enough number of links m, each of length b, the mean-square end-to-end distance [18] is given by the equation:

$$\langle r_0^2 \rangle = mb^2$$

and the distribution of end-to-end distances corresponds to that of an equivalent *Gaussian chain*.

Note 3: The lengths of the individual segments are fixed, but the chain may contain segments of different lengths. In this case, the length b should be interpreted as a root-mean-square length.[8, page 10].

Note 4: Adapted from reference [18].

2.2.24 Gaussian chain

Model of a disordered macromolecule in which the vector connecting any pair of *particles*, or the end-to-end vector of a *chain segment*, follows a Gaussian distribution.

Note 1: Mathematically, if $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$ denote the coordinates of two particles, the probability density of finding them separated by a vector $\boldsymbol{R}_{ij} = \boldsymbol{R}_j - \boldsymbol{R}_i$ is, in the three-dimensional (3D) case:

$$P_{3D}(\boldsymbol{R}_{ij}) = \left(\frac{3}{2\pi\langle R_{ij}^2\rangle}\right)^{3/2} \exp\left\{-\frac{3\boldsymbol{R}_{ij}\cdot\boldsymbol{R}_{ij}}{2\langle R_{ij}^2\rangle}\right\}.$$

where $\langle R_{ij}^2 \rangle$ is the mean-square value of their distance. Assuming an isotropic distribution of the vector's orientation, the probability density of finding the segments at a distance $R_{ij} = |\boldsymbol{R}_j - \boldsymbol{R}_i|$ is, in the three-dimensional case:

$$p_{3D}(R_{ij}) = 4\pi R_{ij}^2 \left(\frac{3}{2\pi\langle R_{ij}^2\rangle}\right)^{3/2} \exp\left\{-\frac{3R_{ij}^2}{2\langle R_{ij}^2\rangle}\right\}.$$

Note 2: A Gaussian chain can be described by *bead-spring model* without *excluded volume interactions*, in which the force constant of the harmonic spring connecting neighboring segments is:

$$K = \frac{3k_{\mathrm{B}}T}{b^2}$$

where $b^2 = \left\langle R_{i,i+1}^2 \right\rangle$ is the mean-square bond length, k_{B} is Boltzmann's constant, and T is the thermodynamic temperature.

Note 3: All models of linear chains in which the *long-range intramolecular interactions* between the segments are zero or negligible, such as the *bead-rod model*, the *freely jointed chain* and the freely rotating chain [18], lead to a Gaussian chain when the separation between the segments is larger than the chain's Kuhn length [18]. In this case $\left\langle R_{ij}^2 \right\rangle \sim |j - i|$, where the scaling symbol "~" indicates the omission of a proportionality constant with the dimension of length squared. This is a consequence of the Central Limit Theorem of statistics.

Note 4: The Gaussian chain model does not account for the finite extensibility of polymer chains, and it becomes invalid when they are stretched (e.g., by an external force) to the point where their end-to-end distance [18] approaches their contour length [18].

Note 5: A Gaussian chain model may be used a basis for a *mean-field theory* of polymers with excluded volume interactions, polymers at interfaces and block copolymers undergoing microphase separation, within a *polymer self-consistent field theory*. A Gaussian model, in which some segments representing cross-links are multiply connected to other segments, is also the basis for statistical theories of polymer networks.

2.2.25 Gay–Berne (GB) potential

Coarse-grained model for the interaction among anisotropic *particles* with the shape of an ellipsoid, which experience both attractive and repulsive pairwise interactions depending on their center-to-center distance and relative orientation.

Note 1: Its mathematical form is an anisotropic generalization of the *expanded Lennard-Jones potential*. Alternatively, a *Hamaker potential* may also be used to model the interaction among anisotropic particles.

Note 2: It can be used to model ellipsoidal particles that may be prolate, when they have a rod-like shape, or prolate, when they have a disk-like shape. In addition, they may have uniaxial symmetry ($D_{\infty\mathrm{h}}$ point group) or a lower biaxial symmetry ($D_{2\mathrm{h}}$ point group).

Note 3: In addition to three center-of-mass coordinates, each GB particle has two or three orientation coordinates (in three dimensions, respectively, for the uniaxial and biaxial symmetry cases).

Note 4: It has been modified and generalized by several authors. Thus, it is a "family of models", rather than a single model. It is typically employed for molecular or polymeric systems that may display liquid-crystalline order [15, page 246].

2.2.26 Hamaker potential

Model for the interaction between two rigid bodies, where the distance and angular dependence of the interaction are obtained by integrating a pairwise interparticle potential over the volume of the bodies, assuming a constant density of *particles* within them.

Note 1: Examples of rigid bodies whose interaction can be described by this model are spherical or ellipsoidal nanoparticles, cylindrical rods, and solid walls (a half-space). A Hamaker potential for spherical particles may be used as an alternative to the *expanded Lennard-Jones potential*. A Hamaker potential for ellipsoidal particles may be used as an alternative to the *Gay–Berne potential*.

Note 2: As an example, the Hamaker potential for the interaction between one particle and a flat solid wall occupying the half-space $z \leq 0$, also consisting of particles interacting with the former by a *Lennard-Jones potential*, is the following function of the particle z coordinate (equal to the particle-wall distance, when $z > 0$):

$$V_{\text{wall}}(z) = \frac{2\,\pi\rho\varepsilon\sigma^3}{3}\left[\frac{2}{15}\left(\frac{\sigma}{z}\right)^9 - \left(\frac{\sigma}{z}\right)^3\right]$$

where ε and σ are the parameters of the underlying Lennard-Jones potential, and ρ is the number density of particles within the wall.

2.2.27 Harmonic potential

Model of a contribution to the potential energy based on a quadratic dependence from some *internal coordinate* or *degree of freedom*.

Note 1: It is frequently used to approximate the dependence of the potential energy of a bond on its length r:

$$V_{\text{H}}(r) = \frac{\kappa}{2}(r - r_0)^2$$

where κ is the force constant and r_0 is the equilibrium bond length. An analogous expression may be used also for other types of internal coordinates, such as bond angle θ:

$$V_{\text{H}}(\theta) = \frac{\kappa}{2}\left(\theta - \theta_0\right)^2$$

Note 2: In *force field*-based simulations, the total potential energy of a system usually includes both harmonic and anharmonic terms. In these cases, the overall *potential energy surface* will be anharmonic.

Note 3: In an *ab initio model* or a *semiempirical model*, a harmonic potential usually indicates an approximation to the full potential energy surface of a system, valid for small displacements of the atoms from one if its *stationary points*.

2.2.28 Hydrodynamic interaction

In a solution or dispersion, the perturbation of the flow of the solvent or dispersing medium around a solute molecule, a *chain segment* of a dissolved macromolecule or dispersed entity, caused by the presence of the other solute molecules, segments, or dispersed entities.

Note 1: Hydrodynamic forces between solute *particles* are non-conservative, because they cannot be obtained by differentiation of a potential, and they are associated with solute-solvent friction and energy dissipation. It is long-range interaction, because in three dimensions, it decays approximately as $1/r$, as described by the Oseen tensor.

Note 2: In simulations based on an *implicit solvent model*, its effect may be included by methods such as *Brownian Dynamics*, *lattice Boltzmann*, and *multiparticle collision dynamics*.

Source: IUPAC recommendation [18], entry 3.4.25

2.2.29 Implicit solvent model

Description of a molecular system, in which the solvent or the environment of the solute is replaced by a continuum and by modified effective interactions among the solute *particles*.

Note 1: In a simulation of the dynamics of a system described with such models, the equations of motion of the solute atoms/particles may be modified in order to account for the effect of the solute-solvent collisions. The solvent's shear viscosity may be used to estimate the effect of solute-solvent collisions on the motion of the solute. See for example *Brownian Dynamics* simulations.

Note 2: The electrostatic part of the solvation free energy may be described by a *reaction field* model. It depends on the solvent relative permittivity and ion concentrations.

Note 3: The non-electrostatic component of the solute-solvent interaction may be modeled using the *solvent-excluded area* or the *solvent-accessible area*.

2.2.30 Incompressibility constraint

In a heterogeneous multi-component system, a mathematical relationship that enforces the sum of the volume fractions of the components to be everywhere equal to one.

Note 1: It is typically adopted in *polymer self-consistent field theory* and *polymer density functional theory* calculations on heterogeneous polymer systems. Under this constraint, the overall volume of the mixture is equal to the sum of the volumes of the separate components.

Note 2: A system is always incompressible when it is based on a *lattice model* of the polymer, including the solvent as a possible component.

2.2.31 **Lattice model** (in modeling and simulations of polymers)

Coarse-grained description of a system in which the *particles* (polymer *chain segments* or solvent molecules) are allowed to occupy a discrete set of coordinates, corresponding to the nodes of a lattice.

Note 3: In the simplest lattice models, which were originated by the Flory–Huggins theory [9 page 69; 13 page 140; 14 page 55] of polymer solutions and blends, the bond length and the diameter of all the particles coincide with the nearest-neighbor spacing on a simple cubic lattice.

Note 4: *Excluded volume* interactions can be enforced by preventing multiple occupation of the same lattice site.

Note 5: *Short-range* interactions typically operate only between particles on nearest-neighbor sites.

Note 6: Some lattice models may include more complicated lattices, fluctuating bonds lengths, and/or multiple occupancy of the sites, to model soft segments.

2.2.32 **Lennard-Jones (LJ) potential**

Model that describes the non-bonded interaction between two *particles*, using an inverse twelfth power to represent the repulsion at close distance and an inverse sixth power to represent the attraction at longer distance.

Note 1: It is isotropic as it depends only on the inter-particle distance r. One of its possible forms is:

$$V_{\mathrm{LJ}}(r) = \frac{A}{r^{12}} - \frac{C}{r^{6}}$$

where A and C are positive parameters. The same interaction potential may be written in terms of the interaction energy ε and an effective diameter σ [note that $V_{\mathrm{LJ}}(\sigma) = 0$]:

$$V_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

or alternatively in terms of the interaction energy ε and the equilibrium, minimum-energy distance $r_{\mathrm{min}} = 2^{\frac{1}{6}}\sigma$ [note that $V_{\mathrm{LJ}}(r_{\mathrm{min}}) = -\varepsilon$]:

$$V_{\mathrm{LJ}}(r) = \varepsilon\left[\left(\frac{r_{\mathrm{min}}}{r}\right)^{12} - 2\left(\frac{r_{\mathrm{min}}}{r}\right)^{6}\right].$$

Note 2: As in any *force field*, the parameters of the LJ potential generally depend on the particle types. The parameters for the interaction between unlike particles are often assigned on the basis of those for identical particles, using suitable *combination rules*.

Note 3: It is an example of *short-range potential*. It is often truncated at a *cut-off* distance. The *Weeks-Chandler-Andersen potential* is an important example of truncated LJ potential, where the cut-off is equal to the equilibrium distance r_{min}.

2.2.33 Long-range intramolecular interaction

Interaction between *chain segments*, widely separated in sequence along a chain, that occasionally approach one another during molecular flexing.

Note 1: This type of interaction is related to the *excluded volume of a segment*. In a good solvent, such interactions are on average repulsive and produce an expansion of a chain's average size, in comparison to that in the theta state [18].

Note 2: This definition is distinct from that of *long-range potential*, where the "range" does not refer to a separation along the chain's contour, but to an interparticle distance in space.

Note 3: This definition is complementary to that of *short-range intramolecular interaction*.

Source: IUPAC recommendation [18], entry 1.6

2.2.34 Long-range potential

Non-bonded contribution $u(r)$ to the potential energy of a system, whose dependence on inter-*particle* distance r decays sufficiently slowly to produce a divergence of the integral $U = \int_c^\infty u(r) r^{D-1} \mathrm{d}r$, where D is the spatial dimensionality of the system and c is a non-zero distance of the order of the particles' size.

Note 1: In the common situation of a three-dimensional system ($D = 3$), the *Coulomb potential* for charge-charge interactions, but also those charge-dipole and dipole-dipole interactions, are long-range, since they decay as r^{-1}, r^{-2}, and r^{-3}, respectively.

Note 2: This definition is distinct from that of the *long-range intramolecular interaction* [18], where the "range" does not refer to the interparticle Cartesian distance r, but to a separation along the contour of a polymer chain.

Note 3: This definition is complementary to that of *short-range potential*.

2.2.35 Machine learning (ML) potential

Data-driven representation of the *potential energy surface* for a system of *particles*, based on machine learning interpolation of the energies of a large number of *configurations* that have been calculated at a higher level of theory.

Note 1: ML potentials are typically applied to *atomistic models*, starting from a large database of calculations with an *ab initio model*.

Note 2: They can be considered to be sophisticated *force fields*, wherein the atoms are not assigned some pre-defined types, but they are classified exclusively according to the element type (i.e., by their atomic number). As for any other force field, the potential energy should be a differentiable function of the particles' coordinates, to allow calculation of the forces on them.

Note 3: In ML potentials, the total potential energy of a system if often approximated as the sum of the energies of its atoms.[25] Nonetheless, they are *many-body potentials* because the energy of each atom is a multi-dimensional function of its coordinates and those of all the atoms that are within a certain *cut-off* distance from it.

Note 4: They are *reactive force fields* because they do not involve any assumption about the connectivity of the atoms, thus allowing the formation and breaking of chemical bonds and changes in *topology*.

Note 5: A ML potential should satisfy certain symmetries, such as invariance to translation and rotation, or to a permutation of the order of the atoms. These properties can be enforced by converting the atomic coordinates to a suitable, large number of *collective coordinates* that are then fed to a ML model. One of the most popular ML techniques is artificial neural networks (NN). In this case, one may also encounter or use the term "NN potential".[25]

Note 6: ML techniques are not limited to interpolation procedures and are extensively applied to *data-driven analysis* of simulation data.

2.2.36 Many-body potential

Contribution to the potential energy of a system that depends on the coordinates of three or more *particles*.

Note 1: A *reactive force field* is always based on many-body potentials, because the propensity of two atoms to form a chemical bond is not a simple function of their distance but depends on the location of other neighboring atoms, due to saturation of their valence [16]. *Machine leaning potentials* are another important example.

Note 2: In simulations based on a non-reactive *force field*, the term is often applied to the non-bonding contributions to the energy, even though also bond bending and bond torsion potentials depend on the coordinates of three or four particles. The electrostatic energy within a *polarizable model* is an example of many-body potential,

because the interaction between two particles depends on fluctuating charges or multipole moments, which depend on the overall charge distribution of the system.

Note 3: A non-reactive, non-polarizable force field describes all non-bonding interactions using *two-body potentials*, but it may contain many-body contributions to the energy to describe bond bending (the energy depends on the positions of three neighboring atoms) and bond torsion (the energy depends on the positions of four neighboring atoms).

2.2.37 Mesoscale model

Representation of a molecular system characterized by space scales well above the size of the atoms and time scales well above that of atomic motions, but where thermal fluctuations and the heterogeneous nature of matter prevents a description based on a static macroscopic continuum.

Note 1: In a polymer system, a mesoscale model often involves *soft-core potentials* among the constituent *particles* and non-conservative forces and memory effects in the description of their dynamics.

Note 2: For polymers or soft-matter systems, the mesoscale may be tentatively identified with space resolutions which are comprised between 1 nm and 1 μm, and times between 1 ns and 1 ms. Above these time and length scales, the properties of the systems (mechanical, electromagnetic, etc.) can usually be described using the macroscopic continuum assumption. Below these time and length scales, an *atomistic model* is usually required.

Note 3: The *Brownian dynamics* of a nano- or micro-size particle suspended in a fluid can be taken as a prototypical mesoscale phenomenon. The *hydrodynamic interaction* is an example of a non-conservative force acting between such mesoscale particles. In combination with a polymer *coarse-grained model*, such as the *bead-spring model*, these lead to the Rouse theory [18] for polymer dynamics and its generalizations.

Note 4: *Polymer self-consistent theory* and *polymer density functional theory* are also mesoscale models for the structure and thermodynamics of heterogeneous polymeric materials.

2.2.38 Minimum image convention

Variant of the method of *periodic boundary conditions* in which each *particle* interacts uniquely with the closest image of each other particle in the system.

Note: The use of this convention is equivalent to assuming that the interaction *cut-off* between particles is comparable to size of the *simulation cell*, e.g., it is approximately equal to half of the cell length when this is cubic.

2.2.39 Morse potential

Model that describes the stretching energy of breakable bonds, characterized by a finite bond dissociation energy.

Note 1: Its mathematical form is:

$$V_{\mathrm{M}}(r) = D_{\mathrm{e}}[1 - \mathrm{e}^{-a(r-r_0)}]^2$$

where r is the interparticle distance (instantaneous bond length), D_{e} is the bond dissociation energy, r_0 is the equilibrium bond length, and a is a parameter that, together with the dissociation energy, determines the effective force constant k of the bond (second derivative of the potential energy at the minimum): $k = 2a^2 D_{\mathrm{e}}$.

Note 2: It may be used to describe bond breaking and formation within a *coarse-grained model*, or within an *atomistic model* with a *reactive force field*. It is used in vibrational spectroscopy to describe features that depend on the anharmonicity of the bonds that cannot be described by *harmonic potentials*.

Note 3: A bond described by a Morse potential may be considered broken when its length reaches a certain *cut-off*, typically a multiple of the equilibrium distance. A new bond may also form when the distance between two atoms becomes smaller than the cutoff, provided that they have free valencies.

Note 4: Adapted from ref. [20].

2.2.40 Multiscale model (MSM)

Any representation of a system that combines different levels of description, e.g., *continuum*, *coarse-grained*, *atomistic*, or *ab initio* models.

Note: The combination of different levels may occur by a *concurrent multiscale model* or a *sequential multiscale model*.

2.2.41 Periodic boundary conditions (PBC)

A *boundary condition* method that generates an infinite representation of a finite molecular system by replicating it periodically in space.

Note 1: The replicas, or images, of the finite system are related to it by the application of a set of symmetry operations that ensures space is filled consistently. The symmetry operations are typically translations, but rotations are also sometimes employed.

Note 2: The original molecular system is often denoted the primary image, and the space that encloses it the *simulation cell* or unit cell.

Note 3: This approximation is most often used in three-dimensions to represent not only crystals but also amorphous system such as glasses, liquids, and solutions. However, it can also be applied in one-dimension (fibers, wires, linear polymer chains), and in two-dimensions (membranes, slabs, surfaces).

Note 4: To describe an amorphous system, the size of the simulation cell should be significantly larger than any relevant *correlation length* describing the short-range order within it.

Note 5: The use of periodic boundary conditions may introduce *finite size effects*, when the lengths of the simulation cell are smaller than a certain value depending on the nature of the system.

2.2.42 Polarizable model

Electrostatic model in which the charge distribution of the *particles* is susceptible to fluctuate and undergo polarization [20], due to their mutual interactions or to external electric fields.

Note 1: A polarizable *force field* includes *many-body potentials* to describe the interactions among atomic charges or atomic multipole moments. These quantities depend on the *configuration* of the system and may be obtained by minimization of the electrostatic energy or by solution of some effective equations of motion, coupled to those for the particle positions and velocities.

Note 2: An *ab initio model* is intrinsically polarizable, to an extent that depends on the quality of the *basis set* and the electronic structure method (e.g., *density functional theory* or *Hartree–Fock theory*).

2.2.43 Quantum chemical/molecular mechanical (QC/MM) model

quantum mechanical/molecular mechanical (QM/MM) model

Concurrent multiscale model in which a small part of the system is treated explicitly by quantum chemical electronic structure techniques such as *density functional theory* or *Hartree–Fock theory*, whereas the rest of the system is represented by a molecular mechanics *force field*.

Note: The acronym QC/MM is to be preferred, as it describes more precisely the numerical methods that are used in these approaches.

2.2.44 Reaction field

Electric field resulting from the induced polarization of a medium surrounding a molecule, within a *continuum solvation model*.

Note 1: The polarization may be represented by a continuous charge distribution at the *solvent-accessible surface* or *solvent-excluded surface*.

Note 2: In a molecular simulation with *force fields*, its inclusion reduces the strength and range of the interactions among charged particles, allowing their truncation and therefore bypassing the evaluation of the "reciprocal space" part of the *Ewald summation*.

Note 3: Adapted from ref. [20].

2.2.45 Reactive force field

Atomistic model of a molecular system based on a *force field*, such that its chemical structure or *topology* may change over the course of a simulation as a result of the breaking, formation or rearrangement of chemical bonds.

Note 1: The atoms types, hybridization states, bond orders, and the charge distribution are not pre-assigned, but computed on-the-fly from the instantaneous *configuration* of the system.

Note 2: A reactive force field is a type of *many-body potential*.

Note 3: *Machine learning potentials* are typically built from large databases of structures that include systems with different topologies, reactive fragments, transition states for chemical reactions, etc.. In this case, they can also be considered reactive force fields.

2.2.46 Rotational isomeric state model (RIS)

Macromolecular chain model based on *rotational isomeric states*, possibly extended including additional *conformations*.

Note 1: It describes the effect of *short-range intramolecular interactions* on the properties of macromolecular chains. Statistical weights are assigned to allowed rotational isomeric state*s* based on the rotational potential energy about each type of skeletal bond.

Note 2: Bond lengths and angles are assumed constant.

Note 3: Considering also low energy conformations that do not correspond to potential energy minima may significantly increase the accuracy of calculations based on the model.

Note 4: It should not be confused with the *reference interaction site model (RISM)*.

2.2.47 Screened Coulomb potential

Model for the effective electrostatic interaction between two charged, point-like *particles*, when these are surrounded by a homogeneous medium containing further mobile charges.

Note 1: Its mathematical expression is:

$$V_{\mathrm{DH}}(r) = \kappa \frac{q_1 q_2}{r} \exp\left[-\frac{r}{\lambda_{\mathrm{DH}}}\right]$$

where r is the inter-particle distance, q_i and q_j are the particles' electric charges, κ is a constant inversely proportional to the permittivity of the surrounding medium, and λ_{DH} is the screening length. According to the Debye–Hückel (DH) theory of electrolyte solutions, λ_{DH} decreases with the solution's ionic concentration, being inversely proportional to the square root of the ionic strength [16].

Note 2: It is an example of *short-range potential*, for any finite value of λ_{DH}, unlike the *Coulomb potential* which is recovered in the limit $\lambda_{DH} \to \infty$.

Note 3: The screening length λ_{DH} can also be considered a *correlation length* for electrostatic interactions.

2.2.48 Self-avoiding random-walk chain

Freely jointed chain subject to the condition that the *chain segments* cannot intersect one another.

Note 1: Segments are considered to have a finite volume and cannot overlap significantly with each other. In the case of a *lattice model*, the sites of the lattice cannot be occupied by more than one segment.

Note 2: The model may be used to describe a macromolecule with *long-range intramolecular interactions*, mainly resulting from *excluded volume interactions* among its segments.

Source: IUPAC recommendation [18], entry 1.39.

2.2.49 Semiempirical model

Quantum mechanical description of a molecular system, based on an approximate solution of the Schrödinger equation for its valence electrons, exploiting computational simplifications arising from the neglect of certain electron-electron interactions and the usage of empirical parameters, characteristic of each element.

Note 1: Such models can be justified by introducing systematic approximations either within *Hartree–Fock theory* or *density functional theory*.

Note 2: The empirical parameters for the elements may be derived from experimental information (e.g., gas-phase spectroscopic properties), or from suitable calculations with an *ab initio model* on atoms, molecules, and compounds.

2.2.50 Sequential multiscale model

hierarchical multiscale model

Multiscale model wherein information about a system is transferred from a higher level, higher resolution description to a lower level, lower resolution one (*mapping*), and vice versa (*reverse mapping*).

Note 1: The information being exchanged may include, for example, the *particles'* coordinates, their motions, and their interactions.

Note 2: Examples are simulations in which some parameters such as a *coarse-grained model* are derived from simulations of an *atomistic model*, or the particle coordinates from the coarse-grained simulations are used to reconstruct a detailed atomistic model.

2.2.51 Short-range intramolecular interaction

Steric or other interaction involving atoms or groups or both situated within a few skeletal bonds of each other along a chain.

Note 1: The interacting atoms or groups are typically separated by fewer than 10 consecutive skeletal bonds in a chain.

Note 2: This definition is distinct from that of *short-range potential*, where the "range" refers to an interparticle distance in space, instead of a contour along a chain.

Note 3: This definitions is complementary to that of *long-range intramolecular interaction*.

Source: IUPAC recommendation [18], entry 1.5.

2.2.52 Short-range potential

Non-bonded contribution $u(r)$ to the potential energy of a system, whose dependence on inter-*particle* distance r decays sufficiently fast to ensure convergence of the integral $U = \int_c^\infty u(r) r^{D-1} dr$, where D is the spatial dimensionality of the system and c is a non-zero distance of the order of the particles' size.

Note 1: This definition is distinct from that of *short-range intramolecular interaction*, where the "range" refers to a separation along the contour of a polymer chain, instead of a distance in space.

Note 2: This definition is complementary to that of *long-range potential*.

2.2.53 Simulation cell

simulation box

Domain of space whose content identifies the molecular system to be simulated.

Note 1: In a system with *periodic boundary conditions*, it contains the primary image of the system. An infinite system is obtained from it by applying appropriate translations to its contents.

Note 2: In simulations of crystalline polymers and materials, the simulation cell may contain several crystallographic unit cells [16], to allow deviations in the *particles*' coordinates from the idealized crystallographic symmetry, due for example to defects or to thermal fluctuations.

Note 3: The cell is usually three-dimensional, but may be also be one- or two-dimensional in wire and surface problems, respectively.

2.2.54 Soft-core potential

Function that describes weakly repulsive interactions in which the potential energy and forces among two *particles* have a finite value for every distance and relative orientation.

Note 1: They typically occur within *mesoscale models* or very *coarse-grained models*, such as *dissipative particle dynamics*. In this case, each soft particle may represent several statistical *chain segments* or even a whole polymer chain.

Note 2: They may also be used to perform a rough initial equilibration of an amorphous polymer system that might initially contain unrealistically strong inter-particle overlaps. Hard-core potentials may be included after the elimination of such strong overlaps, using if necessary also a *reverse mapping* strategy to introduce a higher resolution description.

Note 3: Examples for spherically symmetric interactions are:

$$V_{ij}(r) = \begin{cases} \frac{A_{ij}}{2r_c}(r - r_c)^2, & r < r_c \\ 0, & r \geq r_c \end{cases}$$

often used to derive the conservative component of the pairwise force in dissipative particle dynamics, or:

$$V_{ij}(r) = \begin{cases} B_{ij}\left[1 + \cos\left(\frac{\pi r}{r_c}\right)\right], & r < r_c \\ 0, & r \geq r_c \end{cases}.$$

where in both equations r_c is a *cut-off* distance and A_{ij} and B_{ij} are two parameters, that should be positive if the interaction is repulsive.

2.2.55 Solvent model

environment model

Representation of the interaction between a macromolecule or a set of molecules (solute) and those surrounding them (solvent, environment).

Note 1: The model may include both thermodynamic or energetic effects, such as solvation contributions to the energy of the system, and dynamical effects, such as solute-solvent collisions represented by the stochastic forces in *Brownian dynamics* simulations.

Note 2: The aim of a separation of a system into solute and solvent is often to allow computational savings, by treating the latter at a lower level than the former, within a *concurrent multiscale model*. For example, in an *implicit solvent model*, the solvent is described by a *continuum model* neglecting all molecular details.

2.2.56 Solvent-accessible surface (SAS)

Surface traced by the center of a sphere representing a solvent molecule, as it rolls on a solute molecule, described as the union of the Van der Waals spheres of the atoms within it.

Note 1: It represents a possible estimate of the "molecular surface" or rather of the solute-solvent interface. By construction, it encloses the *solvent-excluded surface*.

Note 2: It depends on the effective solvent-sphere radius, which for a water molecule has a standard value of 0.14 nm, at room temperature and atmospheric pressure.

Note 3: It can be used within an *implicit solvent model* to separate the solute and the solvent regions.

2.2.57 Solvent-excluded surface (SES)

Internal boundary of the union of all possible spheres representing the solvent molecule, that do not overlap with the solute molecule, described as the union of the Van der Waals spheres of the atoms within it.

Note 1: It represents a possible estimate of the "molecular surface" or rather of the solvent-solute interface. By construction, it is enclosed within the *solvent-accessible surface*.

Note 2: It depends on the effective solvent-sphere radius, which for a water molecule has a standard value of 0.14 nm, at room temperature and atmospheric pressure.

Note 3: It can be used within an *implicit solvent model* to separate the solute and the solvent regions.

2.2.58 Surface area (SA) model

Estimate of the non-polar contribution to the solvation Gibbs energy of a macromolecular solute, assumed to have a linear dependence on the area of the solute's surface exposed to the solvent, within an *implicit solvent model*.

Note: There are different ways to define and compute a "molecular surface". Examples are the *solvent-accessible surface* and the *solvent-excluded surface*.

2.2.59 Two-body potential

Contribution to the potential energy of a system that depends on the *degrees of freedom* of exactly two *particles*.

Note: It is often used to describe a non-bonding contribution to the potential energy of a system, within a non-reactive *force field*. Compare it with the definition of *many-body potential*.

2.2.60 United atom (UA) model

Type of *coarse-grained model*, in which one atom and the hydrogens directly attached to it are grouped into a single *particle*.

Note: A UA model is nearly an *atomistic model*. In fact, a small fraction of hydrogen atoms may be retained for accuracy. The hydrogens attached to electronegative atoms, e.g., O and N, are generally retained to preserve the ability of certain functional groups to participate in directional hydrogen-bonding interactions.

2.2.61 Unperturbed chain

Chain molecule subject hypothetically only to *short-range intramolecular interactions* or also to *long-range intramolecular interactions* under conditions where their attractive and repulsive components cancel on average and can thus be neglected.

Note 1: An unperturbed chain adopts an ensemble of macroconformations that can be assimilated to a random walk, maximizing its entropy. The mean-square end-to-end distance or the mean-square radius of gyration [18] of the random coil conformations of an unperturbed linear chain increase linearly with molar mass (see note to *scaling*). Non-linear chains, such as branched or star shaped polymers, give rise to more complex behaviors.

Note 2: Experimentally, the chains of a polymer adopt an unperturbed conformation in the bulk amorphous phase or at the theta state [18] of a given polymer/solvent pair.

Note 3: Adapted from ref. [18].

2.2.62 Weeks–Chandler–Andersen (WCA) potential

Function adopted to represent purely repulsive interactions, derived from the *Lennard-Jones potential* by applying a *cut-off* at the equilibrium distance r_{min} and a vertical shift to the energy, to make the interaction energy and forces go to zero continuously at r_{min}.

Note 1: In mathematical terms:

$$V_{\mathrm{WCA}}(r) = \begin{cases} V_{\mathrm{LJ}}(r) - V_{\mathrm{LJ}}(r_{\mathrm{min}}), & r < r_{\mathrm{min}} \\ 0, & r \geq r_{\mathrm{min}} \end{cases}$$

where $V_{\mathrm{LJ}}(r)$ is the original LJ potential at a distance r.

Note 2: The WCA potential is often used in combination with a *bead-spring model*, to represent the *excluded volume interaction* among the *chain segments* within a polymer solution or melt.

2.2.63 Worm-like chain

Kratky–Porod chain

Infinitely thin linear chain model of finite continuous curvature, with the change of the direction of curvature at any point being random.

Note 1: The model can be used to describe chains of different degrees of flexibility, from *freely jointed chains* to rigid rods, and is particularly useful for representing stiff, single-strand, and multi-strand chains.

Note 2: Adapted from reference [18].

2.3 METHODS

2.3.1 Ab initio molecular dynamics (AIMD)

first-principles molecular dynamics (FPMD)

Any *molecular dynamics* simulation method in which the forces on the atomic nuclei are derived at regular intervals from an *ab initio model* of the system's electronic structure.

Note 1: It includes *Car–Parrinello molecular dynamics* and *Born–Oppenheimer molecular dynamics* as special cases.[6, page 1]

Note 2: *Density functional theory* and *Hartree-Fock theory* represent two electronic structure methods that are commonly used in this context.

Note 3: A simulation based on a *semiempirical model* may be considered an approximation to an AIMD simulation, as it also provides a concurrent description of the system's electronic structure and dynamics.

2.3.2 **Barostat** (in polymer modeling and simulation)

Computational procedure that allows changes in the density of the system alongside the motion of the individual *particles*, in response to differences between the instantaneous pressure of the system and the target pressure of its implicit environment.

Note 1: In combination with a *thermostat*, it is typically used to simulate systems in the *NPT ensemble*.

Note 2: The instantaneous pressure of a system is related to the instantaneous stress tensor $\boldsymbol{\sigma}$ as follows:

$$P = -\frac{1}{3}\mathrm{Tr}(\boldsymbol{\sigma}) = -\frac{\sigma_{xx} + \sigma_{yy} + \sigma_{yy}}{3}$$

where Tr() indicates the trace of a square matrix and $\boldsymbol{\sigma}$ is calculated from the system's temperature and the *virial*.

Note 3: The instantaneous pressure of a system always fluctuates in time, even when this is coupled to a barostat and is at equilibrium. Only the mean value of the pressure is expected to converge and become equal to the pressure of the environment, for a sufficiently long simulation time (much longer than the *correlation time* of the system's density).

Note 4: In simulations with *periodic boundary conditions*, where the number of particles is fixed, the density of the system is determined by the size of the *simulation cell*. In the simplest case, the pressure is controlled by isotropic rescaling of the three axes of the cell. It is possible to devise algorithms and carry out simulations with an anisoptropic barostat (or "stress-stat"), which allows changes in the shape of the simulation box as

well as changes in its volume, in response to differences between individual components of the instantaneous stress tensor of the system and of the environment.

2.3.3 Basis set

Set of one-electron functions employed for the expansion of the orbitals entering the electronic wave function and/or of the electron density of a system, when seeking an approximate solution of the Schrödinger equation by an *ab initio model* or *semiempirical model*.

Note 1: In a molecular quantum chemical context, the most common examples of basis sets are those based on localized, atomic-orbital-like functions (e.g., Gaussian functions or linear combinations of Gaussians). Other choices are possible, for example delocalized functions (e.g., plane waves, often used in *Car-Parrinello molecular dynamics* simulations), or a grid of points ("real-space" or "numerical" basis sets).[4] pp 208-211.

Note 2: Sometimes, for reasons of computational efficiency, an auxiliary basis set is introduced to expand the products of pairs of one-electron basis functions. Such products occur, for example, in the expression for the electron density.

Note 3: The present definition is more general than that in [20], which includes only a special class of Gaussian basis sets.

2.3.4 Born–Oppenheimer molecular dynamics (BOMD)

The *Ab initio molecular dynamics* method based on the Born–Oppenheimer approximation [20], in which the forces on the nuclei are obtained from an approximate solution of the time-independent electronic Schrödinger equation at the current nuclear positions, excluding transitions between *potential energy surfaces* representing the system's ground and excited states.

2.3.5 Brownian dynamics

Method for the simulation of the high-friction or over-damped limit of *Langevin dynamics*, which means that *particles* obey the Langevin equation but with the acceleration term neglected.

Note 1: The pertinent equation for a particle i is commonly expressed in terms of its diffusion coefficient, D_i, and is:

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = \frac{D_i}{k_\mathrm{B}T} F_i(x_i) + R_i(t)$$

where x_i is the particle's position at time t, $F_i(x_i)$ is the net force on the particle at the same time, k_B is the Boltzmann constant, T is the thermodynamic temperature, and $R_i(t)$ is a stochastic term, which is modeled as a stationary random Gaussian process with a zero mean and a variance given by:

$$\langle R_i(t) R_j(t') \rangle = 2D_i \delta_{ij} \delta(t - t').$$

Note 2: The method can be used in combination with an *implicit solvent model*, which takes into account the effect of the solvent on the mutual forces among the solute particles, possibly including also their *hydrodynamic interaction*.

2.3.6 Car–Parrinello molecular dynamics (CPMD)

Ab initio molecular dynamics method in which the electronic structure of the system and the forces on the nuclei deriving from it are obtained from the dynamics of a fictitious system, thus describing concurrently the time dependence of the nuclear and the electronic degrees of freedom.

Note 1: The CPMD scheme approximates the *Born–Oppenheimer molecular dynamics*, when certain simulation parameters (e.g., timestep and the fictitious mass of the electronic system) are chosen appropriately.

Note 2: The original implementation of the method, by R. Car and M. Parrinello in 1985, was based on a combination of *density functional theory*, *effective core potentials*, and plane-wave *basis sets*.[6] Since then, several related methods have been proposed and implemented.

2.3.7 Configurational bias Monte Carlo move

Monte Carlo move in which the change in *configuration* of a chain molecule is made by removing a section of two or more *chain segments* from one end of a chain and then "regrowing" the chain from the same end, using *importance sampling* to select the position of the segments as they are appended one at a time to the chain.

Note 1: The bias created by importance sampling is removed by the computation of *Rosenbluth weights* for the attachment of each segment.

Note 2: Compare with the *reptation move*, where the section removed from one end of a linear polymer chain is regrown from the other end. Note that, unlike reptation moves, configurational bias Monte Carlo moves are not restricted to linear chains and may be applied, for example, to branched polymers.

2.3.8 Continuum configurational bias Monte Carlo move

Subset of *configurational bias Monte Carlo moves* in which the position of the next *particle* is drawn by sampling the possible particle positions from a continuous distribution.

2.3.9 Density functional theory (DFT)

Method for the calculation of the ground-state energy and other properties of a molecular system using the electron density function [20] as the basic variable, bypassing the explicit evaluation of an electronic wavefunction.

Note 1: The theoretical possibility of computing the ground-state energy of a molecular system from the knowledge of its electron density, and of obtaining the correct electron density by variational minimization of the associated energy, is guaranteed by theorems first proved by Hohenberg and Kohn in 1964 [4, page 615].

Note 2: Most applications of DFT are based on a computational scheme first proposed by Kohn and Sham in 1965 [4, page 235]. The method employs a reference independent-particle model, forming a Slater determinant [20] and building the electron density function from a set of one-electron functions (Kohn-Sham spin-orbitals). The spin-orbitals are obtained by solution of a one-electron Schrödinger equation, containing an exchange-correlation potential to account for the effects of the antisymmetry principle [20] and of electron correlation [20]. Practical implementations of Kohn-Sham DFT are similar to those of the *Hartree–Fock theory* and differ mainly in the choice of the approximation to the (unknown) exchange-correlation potential.

Note 3: It is a quantum mechanical method, loosely related to *polymer density functional theory*, which is rooted in statistical mechanics of classical systems.

Note 4: Density functional theory can be extended to allow an evaluation of some excited electronic states of a molecular system, by including its interaction with time-dependent electromagnetic fields. This extension is known as time-dependent density functional theory.

2.3.10 Dissipative particle dynamics (DPD)

Simulation method that may be derived from the classical *molecular dynamics* method by including pairwise friction and random forces acting between spatially neighboring *particles*, in addition to the conservative forces derived from a *force field*.

Note 1: The dissipative forces are proportional to the longitudinal, and sometimes also to the transverse, components of the relative velocities of the two particles. The random forces include a proportionality factor, related to the dissipative forces and the temperature through a fluctuation-dissipation relation. Both are strictly pairwise and, like the conservative forces, satisfy Newton's third law.

Note 2: The method is often applied to rather coarse-grained, *mesoscale models* of soft matter systems. In this context, the conservative forces between particles originate from a *soft-core potential* and are usually taken to be strictly repulsive and linear, becoming zero at a *cut-off* distance identical to that for the application of the dissipative and random forces.

Note 3: It is usually used in the context of *Brownian dynamics*. In the case of low friction, it can also be used as hydrodynamics conserving local Langevin *thermostat*.

2.3.11 Double re-bridging Monte Carlo move

double-bridging Monte Carlo move

Monte Carlo move in which the change in *configuration* of two chain molecules is made by removing one or more *chain segments* from the interiors of both chain molecules, and then reconnecting one of the two remaining segments of the first chain molecule to one of the two remaining segments of the second chain molecule, and also reconnecting the other remaining segment of the first chain molecule to the other remaining segment of the second chain molecules, using in aggregate the same total number of *particles*.

Note: There is very low probability of finding pairs of segments, such that the two chains generated by this move have exactly the same length as the original ones. To overcome this problem, moves introducing some polydispersity may be allowed.

2.3.12 Dynamical density functional theory (DDFT) (in polymer modeling and simulations)

Computational procedure to describe the time-evolution of the density profile of each component in a multi-component polymer system, subject to driving forces derived from Gibbs or Helmholtz energy functionals that depend on the various density profiles.

Note 1: For a system at equilibrium, the density profiles are independent of time and correspond to a possible solution of the equations of *polymer density functional theory*.

Note 2: The theory is loosely related to time-dependent *density functional theory* that can be used to calculate electronic excitations in molecular systems.

2.3.13 End-bridging Monte Carlo move

Monte Carlo move in which the change in *configuration* of two chain molecules is effected by removing one or more *chain segments* from the interior of the first chain molecule and then reconnecting one of the two remaining segments of the first chain molecule to the end of the second chain molecule, using the same number of *particles*.

2.3.14 End-rotation Monte Carlo move

Monte Carlo move in which the rotational state of the penultimate bond at the end of a polymer chain or chain branch is altered.

2.3.15 Equilibration run

Simulation whose purpose is to allow the system to evolve to an ensemble of *configurations* that is representative of its thermodynamic equilibrium state and is independent of the initial configuration used to set up the simulation.

Note 1: In the context of simulations of polymer melts and other amorphous systems, the criteria for equilibration should include both the stability of *block averages* of relevant thermodynamic or structural properties (e.g., the energy and its components, density, chain radii of gyration [18], *radial distribution functions*), and the relative

magnitude of the chains' root-mean-square displacements and radii of gyration (the former should be much larger than the latter).

Note 2: An equilibration run may adopt a different set of methods than the subsequent *production run*. For example, a system might be equilibrated by a *Monte Carlo* scheme, before simulating its equilibrium properties by *molecular dynamics*.

2.3.16 Ewald summation

Method for the evaluation of *long-range interactions* in an infinite crystal or a system with *periodic boundary conditions*, in which the potential energy and forces are obtained as a sum of "direct space" and "reciprocal space" contributions.

Note: The typical application is the calculation of the electrostatic energy of a set of point charges q_i with coordinates r_i $(i = 1,...,N)$. Let us assume for simplicity that the charges, e.g., in a crystal, are distributed within a cubic unit cell whose side has length L. In this case, the electrostatic energy is:

$$U = \sum_{i=1}^{N} q_i V(\boldsymbol{r}_i)$$

where the electrostatic potential at point, $V(\boldsymbol{r}_i)$, is calculated from a "direct space" summation over $\boldsymbol{n} = (i_x,i_y,i_z)L$ $(i_\alpha = 0, \pm 1, \pm 2,...)$ and a "reciprocal space" summation over $\boldsymbol{k} = 2\pi/(i_x,i_y,i_z)L$:

$$V(\boldsymbol{r}_i) = \sum_{\boldsymbol{n}}{}' \sum_{j=1}^{N} q_j \frac{f_\alpha(\boldsymbol{r}_j - \boldsymbol{r}_i + \boldsymbol{n})}{|\boldsymbol{r}_j - \boldsymbol{r}_i + \boldsymbol{n}|} + \sum_{\boldsymbol{k}}{}' \sum_{j=1}^{N} q_j g_\alpha(k) \mathrm{e}^{i\boldsymbol{k}\cdot(\boldsymbol{r}_j - \boldsymbol{r}_i)} \quad .$$

The functions f_α and g_α depend on a common parameter α and determine the relative weights and the convergence properties of the direct and reciprocal space summations. The primes over the two summations indicate the exclusion of $\boldsymbol{n} = \boldsymbol{0}$ (when $j = i$) and of $\boldsymbol{k} = \boldsymbol{0}$.

2.3.17 Extended continuum configurational bias Monte Carlo move

Type of *rebridging* or *end-bridging Monte Carlo move* in which interior *chain segments* are re-inserted in the polymer chain one at a time, using *importance sampling* to select the trial segment positions from a sample of possible positions drawn from a continuous distribution and *Rosenbluth weights* to remove the associated bias.

2.3.18 Force bias Monte Carlo

Monte Carlo method in which forces on the *particles* in the current *configuration* are used in the generation of a new trial configuration, rather than generating configurations at random.

Note: As in any biased Monte Carlo scheme, a new configuration must be accepted with a criterion that is different from ordinary *Metropolis Monte Carlo*, in order to ensure the validity of the *detailed balance* principle.

2.3.19 Geometry optimization

Computational procedure that searches for a *stationary point* on a system's *potential energy surface.*

Note 1: The more common searched for stationary points are minima and first-order saddle points (transition states). In the first case, it is sometimes referred to as "geometry minimization".

Note 2: A global geometry optimization aims at the identification of a system's *global minimum*.

Note 3: It may be carried out with *constraints* or *restraints* on the system's degrees of freedom, for example, to scan a section of the potential energy surfaces as a function of one or more parameters or to take into account additional information from experiments.

2.3.20 Gibbs ensemble Monte Carlo

Monte Carlo method for the simulation of the equilibrium between two fluid phases, whereby a conventional simulation of two separate systems is combined with random attempts to transfer one molecule from one system to the other, using a criterion similar to *Metropolis Monte Carlo* to accept or reject such a move.

Note 1: Between the transfer moves, the simulations of the two separate systems may be performed either by *molecular dynamics* or by Monte Carlo, typically in the *NPT ensemble* with the same temperature and pressure for both systems.

Note 2: The transfer moves may involve all or just a subset of molecules. For example, to describe the swelling equilibrium of a polymer network by a solvent, only the solvent molecules would be exchanged between the two systems.

Note 3: The method has some similarities with simulations in the *μVT ensemble*, where molecules are created or deleted within a single system, to simulate the exchange with an implicit reservoir of *particles* at a constant chemical potential. In that case, the total number of molecules within the system is not conserved.

2.3.21 Hartree–Fock (HF) theory

Numerical approach in which the electronic wavefunction for a molecular system is approximated as a fixed linear combination of Slater determinants [20] of variable one-electron spin-orbitals.

Note 1: The forms of the spin-orbitals are found by applying the variational principle to obtain the wavefunction with the lowest electronic energy. There are obtained by numerical methods based on a *self-consistent field* approach.

Note 2: The most common type of Hartree–Fock wavefunction consists of a single Slater determinant. In cases where there are more than one, the coefficients of the determinants in the expansion are determined by constraints on the wavefunction, normally the value of its spin multiplicity.

Note 3: It is a *mean-field theory* as it neglects electron-electron correlations [4, page 124] in the evaluation of the system's wavefunction and energy. Many post-Hartree–Fock methods exist, which recover some of the correlation energy [14] arising from this omission. Alternatively, electron correlation effects can also be included by *density functional theory*.

2.3.22 Kinetic Monte Carlo

dynamic Monte Carlo

Monte Carlo method whose purpose is to simulate the evolution of a system in time, subject to stochastic transition processes among its possible states.

Note 1: The possible states of the system correspond to distinct local minima on a *potential energy surface*, or to all states in a lattice model. These states, and the allowed transitions between them, must be defined or known ahead of the simulation.

Note 2: The selection of possible transitions and their probabilities are based on physically meaningful transitions and rates between states, thereby providing a connection to physical time. The average rate of the transition between two neighboring states depends on the energy barrier separating them, according to transition state theory [5, page 356; 21].

Note 3: The time resolution is limited by the scale at which no two transition events occur simultaneously. The increment in time associated with a particular transition event is determined stochastically, as given by Fichthorn and Weinberg [26].

Note 4: A subset of kinetic Monte Carlo simulations incorporates purely local transitions (e.g., single-*particle* moves, bond moves) that are not necessarily connected to physical time. Formal criteria for associating such moves with specific measurable processes must be followed to recover physical time.

Note 5: When *Metropolis Monte Carlo* sampling is used for the transition probabilities between any two states i and j with energies E_i and E_j, a dynamical interpretation implies that the height of the energy barrier, $E^{\ddagger}$, above that of the higher energy state, $\Delta_{ij}=E^{\ddagger}-\max[E_i, E_j]$ is the same for all allowed transitions.

Note 6: For off-lattice models, comparable results may be obtained also by *temperature-accelerated dynamics*.

2.3.23 Importance sampling

Method used in statistics to improve the *Monte Carlo* evaluation of a multi-dimensional integral, by evaluating the integrand function preferentially at state points that make the largest contributions to the integral.

Note: It is a variance reduction technique. Its goal is to accelerate the convergence rate of a stochastic modeling procedure, enhancing its computational efficiency.

2.3.24 Langevin dynamics

Method for simulating dynamics of *particles* that implicitly takes into account their collisions with the environment, by including stochastic and friction forces within the *molecular dynamics* equations.

Note 1: The pertinent equation for a particle i is the Langevin equation:

$$m_i \frac{\mathrm{d}^2 x_i}{\mathrm{d}t^2} = F_i(x_i) - \zeta_i \frac{\mathrm{d}x_i}{\mathrm{d}t} + R_i(t)$$

in which m_i, x_i, and ζ_i are the particle's mass, position, and friction constant, $F_i(x_i)$ is the force on the particle due to a *force field* or an external potential, and $R_i(t)$is a stochastic fluctuating force, which is modeled as a stationary random Gaussian process with a zero mean and a variance given by:

$$\langle R_i(t) R_j(t') \rangle = 2\zeta_i k_\mathrm{B} T \delta_{ij} \delta(t - t')$$

where k_B is Boltzmann's constant and T is the thermodynamic temperature.

Note 2: The method is commonly used for modeling the Brownian motion of solutes, particles, or polymer *chain segments* within a fluid medium. *Brownian dynamics* is obtained when the second derivative term in the Langevin equation can be neglected.

Note 3: The Langevin equation is also often expressed in terms of either the collision frequency, γ_i, or the diffusion coefficient, D_i, instead of the friction constant. These are related to the friction constant by the equation $\zeta_i = m_i \gamma_i$, and by the Einstein relation, $D_i \zeta_i = k_\mathrm{B} T$, respectively. The Einstein relation and the previous equation linking the stochastic forces to the friction constants are consequences of the fluctuation-dissipation theorem for a system obeying the principle of *detailed balance*.

Note 4: For small values of the friction constants ζ_i, the Langevin equation can be used to perform molecular dynamics simulations with a local *thermostat*, in the *NVT ensemble*.

2.3.25 Lattice Boltzmann (LB)

Mesoscale model simulation method based on the solution of a fully discretized version on the Boltzmann equation, yielding a time-dependent probability distribution of *particle* positions and momenta within a fluid.

Note 1: The Boltzmann equation was originally derived within the kinetic theory of gases, but its discretized version may be applied also to dense systems such as ordinary liquids, or multi-phase systems such as emulsions and fluids in porous media.

Note 2: In the LB method, space is discretized into a regular array of lattice sites, time is discretized, and velocities are chosen such that one time step will connect only nearby lattice sites. Free streaming along the lattice links alternates with local on-site collisions. Care must be taken to restore isotropy and Galilean invariance in the hydrodynamic limit (i.e., at large length and time scales).

Note 3: The LB method may be used in combination with a higher-resolution method, within a *concurrent multiscale model*. One example is the use of an *atomistic model* or a *coarse-grained model* for a macromolecule in solution, while applying the LB method to treat the flow of the surrounding solvent, which is associated with the *hydrodynamic interaction*.

2.3.26 **Mapping** (in polymer modeling and simulation)

Procedure within a *multiscale model*, whereby a high-resolution representation of a system is replaced by a lower-resolution one with an decrease in the number of *particles*, but ensuring that the interactions or selected observables computed from lower-resolution model match as closely as possible those of the original model.

Note 1: During mapping, there is generally a loss of information as the coordinates of a particle of the lower-resolution model (e.g., a *coarse-grained model*) are calculated from those of two or more particles of the higher-resolution one (e.g., an *atomistic model*).

Note 2: The potential energy terms describing the interactions among the coarse-grained particles may be defined *a priori*, or they may be derived from those of the higher-resolution model by a range of criteria (e.g., iterative Boltzmann inversion, force matching, relative entropy, etc.).

Note 3: Due to loss of information about the *configuration* of the system during mapping, the potentials describing the interactions between the low-resolution units have an entropic component (i.e., they are *potentials of mean force*) and they thus they depend on the thermodynamic state of the system (e.g., on temperature, pressure, presence and composition of a solvent, etc.).

2.3.27 Metropolis Monte Carlo

Monte Carlo method in which the probability that a new *configuration* in a *Markov chain* is accepted (q_{acc}), after being generated as a trial configuration by one of several possible *Monte Carlo moves*, is given the Metropolis acceptance criterion:

$$q_{\mathrm{acc}} = \min\left\{1, \frac{p_{\mathrm{trial}}}{p_{\mathrm{curr}}}\right\}$$

where p_{trial} is the Boltzmann factor for the new configuration, and p_{curr} is the Boltzmann factor for the current configuration. If the new configuration is rejected, with probability $q_{\mathrm{rej}} = 1 - q_{\mathrm{acc}}$, the current configuration is re-counted again in the calculations of thermodynamic averages.

Note 1: The min{} function appearing in Metropolis criterion implies that a trial configuration is always accepted if its Boltzmann factor is greater than that of the current configuration, otherwise it may be accepted with a probability given by the ratio $p_{\mathrm{trial}}/p_{\mathrm{curr}}$.

Note 2: In the common case of the *NVT ensemble*, the ratio of the Boltzmann factors is:

$$\frac{p_{\mathrm{trial}}}{p_{\mathrm{curr}}} = \exp\left[-(V_{\mathrm{trial}} - V_{\mathrm{curr}})/k_{\mathrm{B}}T\right]$$

where V_{trial} and V_{curr} are the potential energies in the new and the current configurations, k_{B} is Boltzmann's constant, and T is the thermodynamic temperature.

Note 3: It is an example of *importance sampling*, in which *configuration space* is sampled non-uniformly so that configurations having greater probability are sampled more often.

Note 4: The Metropolis acceptance criterion ensures the validity of the *detailed balance* principle, when the probability of generating a trial configuration from the current one is identical to the probability of generating the current configuration from the trial one. In biased Monte Carlo simulations, the two probabilities are not the same and one must use a non-Metropolis acceptance criterion to preserve the detailed balance principle.

2.3.28 Molecular dynamics (MD)

classical molecular dynamics

Computer simulation method for the study of physical movements of *particles*, whose *trajectories* over a given period of time are obtained by the numerical solution of equations derived from Newton's, Lagrange's, or Hamilton's classical equations of motion.

Note 1: The system does not need to be molecular, in a strict chemical sense. The term "molecular dynamics" is commonly used also in the simulation of ionic or metallic systems.

Note 2: The particles whose motion are simulated are individual atoms in *atomistic models*, larger units such as whole polymer *chain segments* in *coarse-grained models*.

Note 3: Examples of modifications of Newton's equations of motion include the introduction of terms representing the interaction of the system with the environment, both under equilibrium (see *ensemble*, *barostat,* and *thermostat*) and non-equilibrium conditions (e.g., an imposed mechanical deformation or thermodynamic gradient in *non-equilibrium molecular dynamics*).

Note 4: It may or may not involve a concurrent quantum mechanical description of the electronic structure of the system, in order to derive the potential energy and the forces acting of the atomic nuclei (see *ab initio molecular dynamics*).

2.3.29 Molecular mechanics (MM)

Family of computational methods, based on the approximate evaluation of the potential energy of a molecular system by means of a *force field*.

Note: The term is often reserved for *geometry optimization* methods that locate minima and saddle points on the *potential energy surface* of a system and characterize them by a *vibrational normal mode analysis*, in which temperature and thermal motions do not play a role. This feature distinguishes MM from simulations based on *molecular dynamics* and *Monte Carlo* methods.

2.3.30 Monte Carlo (MC) (in polymer modeling and simulation)

Family of methods for sampling the behavior of a system containing many interacting *particles*, allowing simulation and analysis of event sequences using random numbers to generate possible outcomes in an iterative process.

Note 1: Even within the restricted area of particle-based simulations of polymers and other materials, there are actually several MC methods. While originally elaborated for the study of equilibrium multi-particle systems like liquids, they were subsequently applied also to studies of the dynamics of macromolecular systems, chemical reactions, and phase transitions.[1, page 147; 2, page 23; 5, page 1]

Note 2: Observables A are calculated as mean values over a statistically significant number N of *configurations*, as follows:

$$\langle A \rangle = \frac{1}{N} \sum_{i=1}^{N} A(\{\boldsymbol{r}_i\})$$

where $A(\{\boldsymbol{r}_i\})$ is the value of the observable when the system is in configuration $\{\boldsymbol{r}_i\}$. Estimates of the statistical uncertainties over these mean values, eliminating the effect of correlations among successive configurations, may be obtained by a method involving *block averages*.

Note 3: An efficient search for the most probable configurations to be entered into the above expression is provided by the *Metropolis Monte Carlo* algorithm, based on the construction of a *Markov chain* of configurations.

Note 4: MC methods can be used to simulate both *atomistic*, *coarse-grained,* and *lattice models* of polymers and other complex fluids. The latter may not amenable to simulations with other methods, such as *molecular dynamics*.

Note 5: More generally, it is a family of methods for the evaluation of multi-dimensional integrals by means of a random sample [16], with applications in statistical data analysis, nuclear and particle physics, economics, biology, etc.

2.3.31 Monte Carlo cycle

A set of consecutive *Monte Carlo moves*, usually taken to be proportional to number to the number of *particles* or of *degrees of freedom* in the simulation.

2.3.32 Monte Carlo move

Algorithm that leads to a change in the *configuration* of a system involving an element of randomness.

2.3.33 Multiparticle collision dynamics

stochastic rotation dynamics

Mesoscale model simulation method, in which the solute *particles* interact with a fluid background (solvent) represented by other particles that obey the ideal gas law, undergoing mutual, multi-particle collisions at regular intervals in time. The background particles act a *thermostat* for the solute particles and couple their motion to the possible macroscopic flow of the solvent, thus accounting for the *hydrodynamic interaction*.

Note: It is an example of *concurrent multiscale model*, as it adopts different resolutions in the description of the solute and solvent.

2.3.34 Non-equilibrium molecular dynamics (NEMD)

Molecular dynamics simulations of systems that are not in thermodynamic equilibrium, due, for example, to the presence of flows, imposed thermodynamic gradients, or evolution through a series of essentially irreversible processes as a result of being far from equilibrium.

Note 1: They can be categorized as either steady state or non-steady simulations. The former typically invoke a change in the equations of motion and in the *boundary conditions*, such that a non-equilibrium steady state is generated and maintained. The latter follows the evolution of the system toward equilibrium after some well-

defined perturbation, for example, through nucleation and growth of a new phase as the result of a sudden change in temperature or some other parameter.

Note 2: Shear flow can be introduced by relative shifts of the periodic images of the *simulation cell* (Lees–Edwards boundary conditions, see ref. [1], page 361) or by deformation and periodic remapping of the simulation cell. A deformation and periodic remapping scheme can also be used to simulate steady state elongational flow (ref. [1], page 365).

2.3.35 NPT ensemble

isothermal-isobaric ensemble

Statistical collection of points in *phase space* describing a system with a constant number of *particles* N, in thermodynamic equilibrium with an environment at constant pressure P and constant temperature T.

Note 1: In thermodynamics, it corresponds to a closed system that can exchange energy with the environment, both as heat and mechanical work. The system's energy E and volume V fluctuate.

Note 2: Several algorithms are available in *molecular dynamics* simulations, in order to include exchange of energy between the system and the environment though a *thermostat* and a *barostat*.

Note 3: In *Monte Carlo* simulations, *configurations* consistent with the NPT ensemble are obtained by including trial moves in which the system's volume may change, depending on the difference between the pressure (or the stress) within the system and that assigned to its environment.

Note 4: If the system and the simulation method satisfy the condition of *ergodicity*, a representative ensemble may be generated by a single simulation of sufficient length. Otherwise, it is necessary to carry out several independent simulations, starting from different initial conditions.

2.3.36 NVE ensemble

microcanonical ensemble

Statistical collection of points in *phase space* describing a system with a constant number of *particles* N, constant volume V, and constant energy E.

Note 1: In thermodynamics, it corresponds to an isolated system. The system's temperature T and pressure P fluctuate, by an extent that depends on its specific heat and compressibility, respectively.

Note 2: In classical *molecular dynamics* simulations, it is generated by integration of Newton's equations of motion for the particles. Depending on the boundary conditions, in addition to the energy, such a simulation may preserve also the total linear momentum and angular momentum of the system.

2.3.37 NVT ensemble

canonical ensemble

Statistical collection of points in *phase space* describing a system with a constant number of *particles* N and a constant volume V, in thermodynamic equilibrium with an environment at a constant temperature T.

Note 1: In thermodynamics, it corresponds to a closed system, which can exchange energy with the environment in the form of heat. The energy E and pressure P fluctuate. In a system with *periodic boundary conditions*, the volume corresponds to that of the *simulation cell*.

Note 2: Several algorithms are available in *molecular dynamics* simulations, in order to include exchange of energy (heat) between the system and the environment through a *thermostat*.

Note 3: In *Monte Carlo* simulations, consistent NVT *configurations* are obtained by application of the *Metropolis Monte Carlo* algorithm and its generalizations.

2.3.38 Particle-field method

Numerical approach to the approximate evaluation of the non-bonded interactions within a system of *particles*, in which average particle densities are first evaluated from their coordinates, and then these densities are used to evaluate their interactions, within a *mean-field theory*.

Note: When the density fields are described on a discrete grid of points, it may be classified as a *particle-mesh method*.

2.3.39 Particle-mesh method

Numerical approach to the evaluation of the *electrostatic interactions* for a system of *particles*, wherein the electrostatic potential produced by the particles' charge distribution is calculated on a discrete grid of points by Fourier transforms and then interpolated at the particle positions.

Note 1: There is in fact a family of such methods, which differ by a number of computational details. These methods are typically used to evaluate the *long-range potential* for particles whose distance is beyond a given *cut-off*. Interactions between particles at distances below the cut-off are calculated by a *particle-particle method*.

Note 2: It provides an efficient alternative to the evaluation of the "reciprocal space" contribution to the electrostatic energy in the *Ewald summation* method.

2.3.40 Particle-particle method

Numerical approach to the evaluation of the non-bonded interactions within a system of *particles* using a *force field*, involving a double summation over all distinct particle pairs.

Note 1: In finite systems, it provides a straightforward, formally exact calculation of the interactions among the particles.

Note 2: In infinite systems, such as those with periodic boundary conditions, it is typically applied to the evaluation of the interactions for inter-particle distances below a given *cut-off*. An example is the "real space" contribution to the energy of a system of charged particles. Beyond the cut-off, the interactions may be either neglected or, to better account for the *long-range potential*, calculated by the "reciprocal space" part of the *Ewald summation* method or by a *particle-mesh method*.

2.3.41 Pivot Monte Carlo move

Rotation Monte Carlo move in which the *conformation* of one bond in the backbone of the chain molecule is altered, so that one part of the chain "pivots" relative to the other.

2.3.42 Polymer density functional theory (PDFT)

Theoretical description of the equilibrium structure of a polymer system, according to which its Helmholtz energy F is a unique functional of the density fields for each species $\phi_A(\mathbf{r})$, $\phi_B(\mathbf{r})$, ... i.e., $F = F[\phi_A(\mathbf{r}), \phi_B(\mathbf{r}), ...]$, which is a minimum at an equilibrium state.

Note 1: The density fields are the local volume fractions of each species, and they are related by an *incompressibility constraint*. When there is no such constraint, the system's overall density is not fixed and the appropriate functional of the densities is the Gibbs energy.

Note 2: It is based on classical statistical mechanics and is loosely related with *density functional theory*, which is a quantum mechanical method allowing the evaluation of the ground-state energy of a system based on its electron density.

Note 3: The theory may be extended to systems away from equilibrium, with the densities evolving in time according to the equations of *dynamical density functional theory*.

Note 4: The method shares some features of *polymer self-consistent field theory*, but with an approximate treatment of the distribution of chain macroconformations.

2.3.43 Polymer reference interaction site model (PRISM)

Theory for the equilibrium *radial distribution functions* and thermodynamics of polymeric liquids, based on a generalization of the *reference interaction site model*, to take into account the conformational flexibility of the polymer chains.

Note 1: For long polymer chains, the sites are generally assumed to be equivalent. For example, considering a *united atom model* of molten polyethylene, a PRISM calculation would yield a single radial distribution function for all CH_2 groups, irrespective of their position along the chain.

Note 2: The intramolecular correlation functions may be either given as an input to a PRISM calculation, under the assumption that the ensemble of polymer macroconformations corresponds to that of an *unperturbed chain*, or obtained together with the intermolecular correlation functions, within a *self-consistent field* approach.

2.3.44 Polymer renormalization group theory

Method for the systematic evaluation of the large-scale statistical properties of polymer chains, based on the invariance of such properties to successive *scaling* transformations that eliminate the *degrees of freedom* describing smaller-scale features.

Note 1: A scaling transformation involves a hierarchical coarse-graining of a polymer chain, whereby m consecutive *chain segments* are grouped into a single segment, and the parameters defining the chain's structure are rescaled accordingly.[9, page 290; 12, page 113; 14, page 51] In particular, we have the following transformation of the number of chain segments (N), the segment length (b), and the parameter for *excluded volume interaction* (u):

$$N \rightarrow N/m, \qquad b \rightarrow m^p b, \qquad u \rightarrow m^q u,$$

where p and q are positive constants (scaling exponents). The physically acceptable solutions correspond to the choice of the scaling exponents that leave the large-scale properties of the chain, such as its mean-square end-to-end distance, invariant under a recursive application of the scaling transformation (fixed points).

Note 2: In addition to polymers, different versions of renormalization group theory have been developed and applied to the description of other scale-invariant, self-similar physical systems and phenomena, to which *mean-field theory* is not applicable due to strong fluctuation or correlation effects.[9, page 76] Its original applications, that predated that to polymers, include the description of critical phenomena, continuous phase transitions, strongly correlated systems, and elementary *particles*.

2.3.45 Polymer self-consistent field theory (PSCFT)

Method to calculate the *chain segment* densities and the probability distributions of the chain macroconformations within an inhomogeneous polymer system, relying on a *mean-field theory* to reduce a many-chain problem to that of a single chain within an effective field produced by the other chains.

Note 1: The effective field at a given point depends on the segment densities at that point and determines the probability distribution of the chain conformations. The method is a type of *self-consistent theory* because the probability distributions are used to compute updated values of the segment densities, until the input and output data are identical.

Note 2: The interaction between two segments depends on their chemical nature, but it is independent of whether they belong to the same or to different chains.

Note 3: The method is often applied with an *incompressibility condition*, implying that sum of the volume fractions of different types of segment is everywhere equal to unity.

Note 4: The probability distributions of the chain conformations are computed under the assumption that these behave as *Gaussian chains*, but are otherwise exact. This feature differentiates the method from *polymer density functional theory*, where the distributions are approximated.

Note 5: Within this formalism different monomers may be attracted to different regions of space due to the features of the effective potential field, leading for example to important applications the simulation of polymers at surfaces and the microphase-separated morphologies of block copolymers.

2.3.46 Production run

Simulation whose purpose is to collect data from a set of *phase space* points that are representative of the system at equilibrium in a given *ensemble* or, for a *non-equilibrium molecular dynamics* simulation, under a set of conditions corresponding to some well-defined perturbation.

2.3.47 Rebridging Monte Carlo move

Monte Carlo move in which the change in *configuration* of a chain molecule is made by removing a number of consecutive *chain segments* from the interior of the chain molecule, and then reconnecting the two remaining parts of the chain using the same number of segments, usually in a different configuration from the original.

2.3.48 Replica exchange

parallel tempering

Monte Carlo method in which multiple replicas of a systems are simulated simultaneously at a series of thermodynamic states. At certain intervals, an attempt is made to swap *configurations* belonging to two different thermodynamic states, using an acceptance criterion based on a generalization of the *Metropolis Monte Carlo* algorithm.

Note 1: Between swap attempts, the individual systems may evolve by a conventional Monte Carlo method, or by some other methods such as *molecular dynamics*.

Note 2: The difference between the thermodynamics parameters of successive states (e.g., their temperature) should be chosen small enough so that that swap attempts have a suitable acceptance rate.

Note 3: The thermodynamic state of one replica of the system is generally chosen to ensure that *configuration space* is adequately sampled in that state, i.e., there is *ergodicity*. For example, the temperature should be high enough to allow overcoming also large energetic barriers between different configurations.

2.3.49 **Reptation move**

slithering snake move

Monte Carlo move in which a change in *configuration* of a linear polymer chain is made by removing one or more consecutive *chain segments* from one end of the chain and appending them to the other end, so that the chain molecule appears to slide along the contour of its backbone.

Note 1: Compare it with the *configurational bias Monte Carlo move*, where a section is removed and regrown from the same end of a polymer chain.

Note 2: *Importance sampling* may be used to select the position of the segments as they are appended one at a time to the chain. The bias thus created is removed by the computation of *Rosenbluth weights* for the attachment of each segment.

2.3.50 **Reverse mapping** (in polymer modeling and simulation)

back-mapping

Procedure within a *multiscale model*, whereby a low-resolution representation of a system is replaced by a higher-resolution one, with an increase in the number of simulated *particles*.

Note 1: As suggested by the name, it is usually performed in order to return to a higher-resolution model (e.g., an *atomistic model*), which had been originally mapped onto the lower-resolution one (e.g., a *coarse-grained model*).

Note 2: It generally cannot be performed uniquely and exactly. The coordinates of the lower-resolution model must be supplemented with some additional information (e.g., statistical distributions for some high-resolution *internal*

coordinates such as bond lengths and angles, databases of probable chain *conformations*, etc.) in order to produce a viable starting model for a subsequent higher-resolution simulations, followed by a *geometry minimization* or *equilibration run* to relax the system. Machine learning techniques may be used to perform this task, starting from a large dataset of polymer *configurations*.

2.3.51 Reverse Monte Carlo (RMC)

Monte Carlo method whose purpose is to generate an ensemble of *configurations* that reproduce an a priori *distribution function*.

Note: In its original use, RMC refers to the method developed by McGreevy and Pusztai in 1988 [27], in which the a priori distribution is the experimentally measured structure factor *S(q)* from wide angle X-ray scattering, which is related to the *pair distribution function*.

2.3.52 Reference interaction site model (RISM)

Theory for the equilibrium structure and thermodynamics of molecular liquids, based on the solution of coupled integral equations for the intermolecular *pair distribution functions*, for all pairs of sites in the molecules.

Note 1: A site may correspond to an atom, a *united atom*, or a *coarse-grained particle*. These are assumed to interact by strictly pairwise, spherically symmetric potentials.

Note 2: Small molecules are usually assumed to be rigid. In this case, the intramolecular correlations between the sites are given as an input to a RISM calculation, based on the molecular geometry.

Note 3: It should not be confused with the *rotational isomeric state model (RIS)*.

2.3.53 Rosenbluth weight

Factor by which the probability of accepting a trial *configuration* of a chain molecule must be multiplied during a *Monte Carlo move* with *importance sampling*, in order to recover the correct Boltzmann distribution of configurations.

2.3.54 Rotation Monte Carlo move

Monte Carlo move in which the change in *configuration* of a chain molecule is made by altering the *rotational isomeric state* of one or more bonds in the backbone of the chain, drawn at random from a distribution of rotation states.

Note: A crankshaft move is a special type of rotational Monte Carlo move in which two neighboring bonds are rotated in a concerted way, so as to leave the chain macroconformation to the exterior of the rotated bonds unchanged.

2.3.55 Simulated annealing

Procedure by which a system is equilibrated at high temperatures and is then slowly cooled, allowing it to settle into arrangements characterized by minimum values of an objective function.

Note 1: The aim of simulated annealing is to identify the *global minimum* of an objective function. The procedure aims to prevent trapping in local minima of the objective function that are close to the starting structure of the search.

Note 2: The objective function may be the total energy of the system, a measure of the deviation in the computed system's properties from a set of experimental data, a combination of these quantities, or any other real-valued multivariate function to be minimized.

Note 3: The method is general and not restricted to *particle*-based simulations of molecular systems. In this case, the temperature is a simulation parameter that controls the accessibility of states characterized by high values of the objective function, and may be unrelated to the temperature of a real physical system.

Note 4: In particle-based models of molecular systems, structures can be explored using *molecular dynamics* or *Monte Carlo* approaches, using the previously accepted structure as the starting point. Structures in a given temperature window are accepted if they improve the objective function but also if they increase it, albeit with lower probability, depending on the ratio between the objective function and temperature. Hence barriers confining starting structures can be overcome. Local energy minimization protocols (e.g., by the steepest descent method) may also be employed alongside MC and MD.

2.3.56 Temperature-accelerated dynamics

Method for simulating the dynamics of systems characterized by large energetic barriers in which a *molecular dynamics* simulation is performed at an elevated temperature in order to sample relevant activated transitions more rapidly and then correcting for the temperature-induced bias in relative rates of transition by filtering out those transitions that would not occur at the original temperature.

Note 1: The method assumes applicability of transition state theory [21], in the harmonic approximation.

Note 2: The method requires a means for identifying when a transition has occurred in a molecular dynamics simulation.

Note 3: In contrast to *kinetic Monte Carlo*, prior knowledge of all relevant activated transitions is not required.

2.3.57 **Thermostat** (in polymer modeling and simulation)

Computational procedure adopted in *molecular dynamics* simulations, which allows changes in the total energy of the system during integration of the *particles*' equations of motion, in response to differences between the instantaneous temperature of the system and the target temperature of its implicit environment.

Note 1: It is typically used to simulate systems in the *NVT ensemble* or, in combination with a *barostat*, in the *NPT ensemble*. It is also used to allow the exchange of heat between the system and the environment in *non-equilibrium molecular dynamics* simulations.

Note 2: The instantaneous temperature of a system, derived from the mean-square velocities of its particles, always fluctuates in time, even when this is coupled to a thermostat and is at equilibrium.

Note 3: A thermostat is said to be local when it acts separately on small groups of particles, typically just one (see *Langevin dynamics*) or two (see *dissipative particle dynamics*). Otherwise, it is said to be global.

2.3.58 **Translation Monte Carlo move**

Monte Carlo move in which the change in *configuration* of a whole molecule or a part of it is made by displacing one or more *particles* by a length drawn at random from a distribution of lengths, and in a direction drawn at random from a distribution of directions.

2.3.59 **Umbrella sampling**

Technique in computational physics and chemistry used to improve sampling of a system through the application of suitable *restraints*, in situations where *ergodicity* is hindered by the form of the system's *potential energy surface*.

Note 1: It is a particular physical application of the more general *importance sampling* in statistics.

Note 2: The restrains force the system to explore an ensemble of *configurations* that may have very high energies. The bias thus introduced can be removed afterward to recover the statistical properties of the unbiased system.

2.3.60 **μVT ensemble**

grand-canonical ensemble

Statistical collection of points within a generalized *phase-space* describing a system with a variable number *particles* at a constant volume V, in thermodynamic equilibrium with an environment at a constant temperature T, whose particles are at constant chemical potential μ.

Note 1: In thermodynamics, it corresponds to an open system in contact with an infinite particle reservoir and a *thermostat*.

Note 2: In a multi-component system, each chemical species has a distinct chemical potential. The exchange of particles (usually whole molecules) between the system and the environment may occur for all or just a subset of the chemical species (e.g., for the solvent or small volatile molecules, but not for the polymer molecules).

Note 3: Since the particles within the reservoir are not simulated explicitly, the exchange of particles corresponds to the creation and deletion of new particles within the system. A simulation in the μVT ensemble may involve a *Monte Carlo* simulation, to add or delete molecules within the system at fixed time intervals according a stochastic algorithm, in combination with a *molecular dynamics* simulation to relax the system.

Note 4: A simulation in the μVT ensemble has some similarities with a *Gibbs ensemble Monte Carlo*, where phase equilibria are simulated by exchanging molecules between two parts of a composite system. In that case, the total number of molecules in the composite system is conserved.

2.4 DATA ANALYSIS

2.4.1 Autocorrelation function

Function describing the statistical correlation between the values of a fluctuating variable X at two different points in space or time.

Note 1: It is obtained when $X = Y$ in a *correlation function*.

Note 2: It usually decays to zero for large distances or times, but not necessarily in a monotonic way. A *correlation length* or *correlation time* may be extracted from it, to summarize the characteristics of this decay.

Note 3: Examples are the autocorrelation functions of the density (a *space correlation function*) and of the *particles*' velocities (a *time correlation function*).

2.4.2 Block average

Average of a fluctuating quantity over a contiguous subset of data points within a *trajectory*.

Note 1: Block averages (of the energy and its components, of the density or the pressure, etc.) may be used to monitor the state of a system during an *equilibration run*, highlighting possible systematic variations of these quantities by reducing the statistical noise in the original, non-averaged data.

Note 2: Block averages may also be used to estimate errors on averages of correlated data producing a simulation (for example, the radius of gyration [18] of a polymer chain at different times). The effect of the correlations can be systematically eliminated by a recursive method,[28] involving averages over blocks of exponentially increasing size, similar in spirit to the *polymer renormalization group theory*.

2.4.3 Correlation function

Function that describes how two fluctuating quantities, X and Y, are statistically correlated:

$$C_{XY}(s) = \langle X(p+s) \cdot Y(p) \rangle$$

where p and $p + s$ indicate two values of an independent variable separated by a displacement s, and the angular brackets indicate an average over the allowed values of p, over statistically independent realizations of the system, over different parts of the system, or a combination of these.

Note 1: Important special cases are the *autocorrelation functions* (when $X = Y$), *cross-correlation functions* (when $X \neq Y$), *time correlation functions* (when p and s represent time coordinates), and *space correlation functions* (when p and s represent space coordinates).

Note 2: The definition corresponds to a two-point correlation function, because it describes the correlation between two variables at two different times or two different points in space (p and $p + s$), but it may also be generalized to the correlation between three or more variables.

Note 3: The averaging over all possible values of the independent variable p is meaningful when the system is at equilibrium or in a time-independent steady state (for time correlation function), or is spatially homogeneous (for space correlation functions). When this is not the case, a correlation function can still be computed but it depends also on p.

Note 4: The fluctuating variables are usually defined in such a way that their average values are zero. Thus, given two arbitrary fluctuating variables $\tilde{X}(p)$ and $\tilde{Y}(q)$, the variables that enter the evaluation of the correlation function are $X(p) = \tilde{X}(p) - \langle\tilde{X}\rangle$ and $Y(p) = \tilde{Y}(p) - \langle\tilde{Y}\rangle$. Since the correlation between variables typically vanishes when they are widely separated in space or time, we have:

$$\lim_{s\to\infty} C_{XY}(s) = \lim_{s\to\infty} \langle X(p+s)\cdot Y(p)\rangle = \langle X(p+s)\rangle \cdot \langle Y(p)\rangle = 0.$$

Note 5: Two variables are said to be correlated when $C_{XY}(s) > 0$, anticorrelated when $C_{XY}(s) < 0$, uncorrelated when $C_{XY}(s) = 0$, over a significant range of the s variable.

Note 6: A correlation function is typically normalized, either in such a way that $C_{XY}(0) = 1$, or $\int C_{XY}(s)ds = 1$, or by some other criterion that must be specified in each case.

2.4.4 Correlation length

Distance characterizing the decay or the range of a *space correlation function*.

Note 1: Similar to the *correlation time*, a correlation length may be specified and computed in different ways, depending also on the expected or observed behavior of the correlation function. A macromolecular system may be characterized by several correlation lengths, for example, describing the decay of short-range correlations within the backbone of a single chain, and that of long-range correlations associated with the large-scale structure of the chains (e.g., a phase-segregated morphology).

Note 2: A correlation length may be extracted also from a peak or some other feature of a suitable structure factor $S_{AB}(q)$, that can be measured in scattering experiments and is related to the Fourier transform of a *pair distribution function* or a *radial distribution function*. The conversion from a wavevector with modulus q_c [corresponding for example to a maximum of $S_{AB}(q)$] to the associated correlation length l_c is $l_c = 2\pi/q_c$.

Note 3: Diverging correlation lengths may occur under certain conditions, implying that the system has no characteristic length scale. For example, the correlation length extracted from the intramolecular radial

distribution function of a random coil polymer is infinite, implying that the correlations persist up to a distance comparable to the chain's root-mean-square radius of gyration [18].

2.4.5 Correlation time

Duration of an interval characterizing the decay of a *time correlation function*.

Note 1: It is possible to identify a correlation time with a relaxation time, describing the return to equilibrium of a system following an external perturbation, provided that the perturbation is small enough for the system to respond linearly.

Note 2: A correlation time may be associated with a specific molecular mechanism or mode of motion, depending on the variables entering the definition of the time correlation function. For example, if the variable is the end-to-end vector of a polymer chain, it quantifies the time required for the chain to undergo a significant reorientation through Brownian motion.

Note 3: A correlation time may be specified and computed in different ways, depending also on the expected or observed behavior of the associate time correlation function. These evaluations are not necessarily equivalent. The following notes provide some examples, without aiming at being exhaustive. The examples are based on analytical expressions, which do not include noise and may correspond more or less closely to correlation functions that are measured or computed numerically from simulation data.

Note 4: Consider a correlation function that decays as a simple exponential:

$$C_{XY}(t) = \exp\left(-\frac{t}{\tau}\right).$$

In this case, τ is the correlation time for the X and Y quantities that may be equivalently obtained by (a) recording the time necessary for the function to decay by a fraction $1/e$ of its starting value, (b) from a fit of the function, using τ as an adjustable parameter, or (c) by integration of the correlation function, since:

$$\tau = \int_0^\infty \exp\left(-\frac{t}{\tau}\right)dt.$$

Note 5: A more complex case is obtained when the correlation function derives from two or more phenomena occurring at very different rates, for example:

$$C_{XY}(t) = A\exp\left(-\frac{t}{\tau_1}\right) + (1-A)\exp\left(-\frac{t}{\tau_2}\right).$$

where A $(0 < A < 1)$ and $(1 - A)$ represent the relative importance of the two processes. In this case, criterion (a) from Note 3 has no general solution and requires a numerical or graphical analysis, criterion (b) leads to two distinct correlation times (τ_1 and τ_2), provided the fit is carried out with two exponential functions, criterion (c) leads to a weighted average of the two correlation times:

$$\tau^* = \int_0^\infty C_{XY}(t)dt = A\tau_1 + (1-A)\tau_2.$$

Note 6: A common situation in polymers, soft matter, and glassy systems is the one in which relaxation can be described by the Kohlrausch function:

$$C_{XY}(t) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]$$

which is also called "stretched exponential" when $\beta < 1$, "compressed exponential" when $\beta > 1$. In this case, criterion (a) from Note 3 gives the relaxation time τ, criterion (b) gives τ and the parameter β that can be related to the distribution of relaxation times within the system, criterion (c) gives an average relaxation time:

$$\tau^* = \int_0^\infty C_{XY}(t)dt = \frac{\tau}{\beta}\Gamma\left(\frac{1}{\beta}\right)$$

where Γ is the gamma function. Note that $\tau^* > \tau$ when $\beta < 1$, whereas $\tau^* < \tau$ when $\beta > 1$.

Note 7: A correlation time can be infinite, when *constraints*, *restraints,* or features of the *potential energy surface* on the system prevent a complete relaxation of certain variables or properties. This occurs, for example, for the autocorrelation functions of the end-to-end vectors of the chain strands within a cross-linked polymer network, or in glassy systems. A possible correlation function, combining the examples in Note 4 (with $\tau_2 \to \infty$) and Note 5, is:

$$C_{XY}(t) = A\exp\left[-\left(\frac{t}{\tau_1}\right)^\beta\right] + (1-A).$$

Note 8: In some cases, a correlation time may also be extracted from a growing function. An example is the diffusion time, which corresponds to the time required by a polymer chain to achieve a mean-square displacement equal to its mean-square radius of gyration $\langle s^2 \rangle$ [18]. Since, for a polymer chain with center-of-mass coordinate $\boldsymbol{R}(t)$ and an isotropic diffusivity D, the mean-square displacement is:

$$\langle [\boldsymbol{R}(t+t_0) - \boldsymbol{R}(t_0)] \cdot [\boldsymbol{R}(t+t_0) - \boldsymbol{R}(t_0)] \rangle = 6Dt$$

we have:

$$\tau_{\text{diff}} = \frac{\langle s^2 \rangle}{6D}.$$

2.4.6 Cross-correlation function

Function describing how two distinct fluctuating variables X and Y are statistically correlated over time or space.

Note: It is obtained when $X \neq Y$ in a *correlation function*. For example, X and Y could represent the displacements or the velocities of two different *chain segments* within a macromolecule.

2.4.7 Data-driven analysis

Any method based on information science to structure and interpret large data sets.

Note 1: This array of techniques overlap strongly with the field of chemometrics [23].

Note 2: Principal Component Analysis [23] is an important example of information science approach to the analysis of very large datasets produced by molecular simulations.

Note 3: Data driven analysis often leads to clustering of data based on mathematical or statistical criteria, where a direct interpretation of the variables or descriptors may be difficult. The challenge is always to connect these results to measurable physical quantities.

Note 4: The construction of *machine learning potentials* is another important application of information science to molecular simulations.

2.4.8 Finite size effect

Property modification resulting from simulated phase domains of finite size, as opposed to idealized infinite systems.

Note 1: Also, artefacts in a simulation resulting from the representation of a system with *periodic boundary conditions* using a small, possibly insufficient, number of independent atoms or molecules. In this case, the system is technically infinite, but there may nonetheless be some effects depending on the finite size of the *simulation cell*.

Note 2: Examples of this effect arise when modeling polymer crystals and their transformations (e.g., melting) imposing a simulation cell that is too small or polymer melts using a simulation cell smaller that the root-mean-square radius of gyration [18] of the *unperturbed chains*.

Note 3: Its importance may depend on the thermodynamic state of the system being investigated. In general, it becomes more important when a *correlation length* within the system increases and approaches the shortest length of the system or of the simulation cell. This may occur, for example, in the simulation of fluids close to the critical point of the vapor-liquid coexistence curve.

Note 4: Undesired finite size effects may sometimes be eliminated from a simulation by studying the *scaling* of the calculated properties with respect to some measure S of the system size (e.g., the number of *particles* or the volume, keeping the particle density constant), and using this information to extrapolate to the thermodynamic limit $S \rightarrow \infty$.

2.4.9 Mass-weighted coordinate

Hybrid variable involving the product of functions of mass and position variables.

Note 1: Common examples are mass-weighted Cartesian coordinates, ξ_i, which take the form:

$$\xi_i = \sqrt{m_i}\, x_i$$

where m_i and x_i are a *particle*'s mass and Cartesian coordinate, respectively.

Note 2: It is used because it is convenient in many theoretical derivations. For example, in mass-weighted Cartesian coordinates, the energy of a classical harmonic oscillator, with angular frequency ω, is:

$$E = \frac{1}{2}\left(\frac{\mathrm{d}\xi_i}{\mathrm{d}t}\right)^2 + \frac{1}{2}\omega^2\xi_i^2$$

Note 3: Likewise, the intrinsic *reaction coordinate* has been defined in terms of mass-weighted Cartesian coordinates as the minimum energy path between two adjacent minima on a *potential energy surface*.

2.4.10 Pair distribution function

Function, generally denoted as $g_{\mathrm{AB}}(\boldsymbol{r},\boldsymbol{q})$, giving the probability of finding a *particle* of type A at position $\boldsymbol{r}$ and another particle of type B at position $\boldsymbol{q}$, relative to a hypothetical ideal gas with the same particle densities.

Note 1: If the system is spatially homogeneous, or translationally invariant, it is a function only of the vector connecting the particles: $g_{\mathrm{AB}}(\boldsymbol{r},\boldsymbol{q}) = g_{\mathrm{AB}}(\boldsymbol{r}-\boldsymbol{q})$. If the system is also isotropic, it is a function only of the distance between the two particles: $g_{\mathrm{AB}}(\boldsymbol{r},\boldsymbol{q}) = g_{\mathrm{AB}}(|\boldsymbol{r}-\boldsymbol{q}|)$. In the latter case, the pair distribution function becomes a *radial distribution function*.

Note 2: It can be defined also as the *space correlation function* of the particle number densities [$\rho_{\mathrm{A}}(\boldsymbol{r})$ and $\rho_{\mathrm{B}}(\boldsymbol{q})$, respectively, for particles of types *A* and *B*], divided by the average particle densities at the same points in space:

$$g_{\mathrm{AB}}(\boldsymbol{r},\boldsymbol{q}) = \frac{\langle\rho_{\mathrm{A}}(\boldsymbol{r})\rho_{\mathrm{B}}(\boldsymbol{q})\rangle}{\langle\rho_{\mathrm{A}}(\boldsymbol{r})\rangle\,\langle\rho_{\mathrm{B}}(\boldsymbol{q})\rangle}.$$

2.4.11 Potential of mean force (PMF)

Free energy as a function of one or more *collective coordinates*, the negative gradient of which gives the average force acting on that *configuration* averaged over all other coordinates and momenta within a statistical distribution.

Note 1: The PMF along a pre-defined variable or *reaction coordinate*, R, can be calculated as the integral of a mean force $\langle F(r)\rangle$ over a *reaction path*:

$$w(R) = -\int_{R_0}^{R}\langle F(r)\rangle dr + w(R_0)$$

where $w(R_0)$ is the value of the PMF at a reference point R_0

Note 2: When there are two or more relevant collective coordinates, the PMF represents a multi-dimensional free energy surface, in analogy with the *potential energy surface*.

Note 3: Adapted from ref. [23].

2.4.12 Primitive path analysis

Method to determine the backbone of the *reptation* tube of a polymer chain, which is originally defined as the shortest path between the endpoints of a chain, and which preserves the *topology* associated with the *entanglements* with other chains or itself.

Note 1: The original concept of primitive path, by S. F. Edwards [10, page 188], is based on a description of the topological *constraints* on a chain as fixed obstacles representing average positions of other chains.

Note 2: Numerical methods account for the fact that the primitive path is to be calculated simultaneously for all chains in system. The minimization of the chain's contours may be based on purely geometrical or on energetic criteria.

Note 3: Different analysis methods give somewhat different paths, and thus different average lengths of the chain strands between the entanglements, but only by a constant factor within error bars.

2.4.13 Quasi-harmonic analysis

Method for determining the effective vibrational modes, and their associated frequencies, by analyzing the motions within a system simulated by *molecular dynamics*.

Note 1: This is most commonly done by finding the eigenvalues and eigenvectors of the mass-weighted covariance matrix of *particle* positions obtained from the simulation. The eigenvalues and eigenvectors are proportional to the inverse square of the frequencies and to the *normal mode* vectors, respectively.

Note 2: It is closely related and is similar to *relaxation normal mode analysis*, but it applies to systems whose fluctuations occur in the neighborhood of a minimum.

Note 3: Unlike a *vibrational normal mode analysis*, it does not require the precise location of a stationary point and the evaluation of the second derivative matrix of the potential energy, effectively incorporating the effect of temperature-dependent anharmonic motions.

2.4.14 Radial distribution function

Function, generally denoted as $g_{AB}(r)$, giving the probability of finding a *particle* of type A at a distance r from another particle of type B, relative to a hypothetical ideal gas with the same number densities of particles.

Note 1: It is symmetric with respect to the particle types, i.e., $g_{AB}(r) = g_{BA}(r)$.

Note 2: If ρ_A and ρ_B are the number densities of particles of type A and B, $dN_A = 4\pi r^2 \rho_A g_{AB}(r)dr$ is the average number of particles A within a spherical shell of radius r and thickness dr from a reference particle B, whereas $dN_B = 4\pi r^2 \rho_B g_{AB}(r)dr$ is the average number of particles B within a spherical shell of radius r and thickness dr from a reference particle A.

Note 3: In a disordered and isotropic bulk system (e.g., a liquid or an amorphous polymer), $g_{AB}(r)$ tends to 1 when $r \to \infty$, due to the vanishing of correlations in the positions of particles separated by large distance.

Note 4: The function $h_{AB}(r)=g_{AB}(r)-1$ is known as a radial correlation function. It is a special case of a *space correlation function*. Its Fourier transform $[\hat{h}_{AB}(k)]$ is closely related with the partial structure factor $S_{AB}(k)$, that under appropriate conditions can be measured by X-ray and neutron scattering experiments.

Note 5: For a model of an ideal random coil polymer, such as linear *freely-jointed chain* or an equivalent *Gaussian chain* with an effective bond length b, the intramolecular radial distribution function among the polymer segments decays according to the law:

$$g_{\text{ideal}}(r) = \frac{C}{b^2 r} \qquad \text{(in three dimensions, for } b < r < R_g\text{)}$$

where C is a constant with the dimensions of volume, and R_g is the chain's root-mean-square radius of gyration [18].

Note 5: The result in the previous note may be extended to real polymer chains in a good solvent, accounting for the effect of *excluded volume interactions* through the *scaling* exponent ν.[9,13] Using ν=3/(d+2), according to Flory's *mean-field theory* (where d is the space dimensionality, i.e., d = 3 in three dimensions), the intramolecular radial distribution function of the chain is approximately given by:

$$g_{\text{real}}(r) = \frac{C}{r^d}\left(\frac{r}{b}\right)^{1/\nu} = \frac{C}{b^{(d+2)/3}} r^{2(1-d)/3} \qquad \left(\text{in } d \text{ dimensions, for } b < r < R_g\right).$$

Note 6: The radial distribution function depends only on the distance r and therefore neglects the possible dependence of the particles' correlations on their positions and relative orientation. Therefore, it is most useful for spatially homogeneous and isotropic systems. The *pair distribution function* generalizes its definition to systems which might be spatially heterogeneous (e.g., due to an interface) and/or anisotropic (e.g. liquid crystalline or oriented).

2.4.15 Reaction coordinate

Collective coordinate that changes during the conversion of reacting entities into products and whose value measures the progress of the transformation.

Note 1: Possible examples for an elementary reaction can be a bond length or bond angle or a combination of bond lengths and/or bond angles; in certain cases, non-geometric parameters, such as the calculated bond order of some specified bond, may be applicable. In some cases, it may just be an arbitrary representation of the degree of advancement of a reaction, corresponding to a defined value of internal energy or free energy for the reacting system.

Note 2: A *configuration* of the system is identified with the reactants or the products of the reaction, depending on whether the value of the reaction coordinate is smaller or larger than a threshold value, corresponding to the transition state.

Note 3: It is normally chosen so as to follow the least demanding path from reactants to products on the *potential energy surface*, i.e., following the lines of steepest energy descent from the transition state to the reactants and to the products.

Note 4: For reactions which are not elementary but stepwise, it is the sequence of reaction coordinates for the successive individual reaction steps.

2.4.16 Reaction path

Sequence of points in the *configuration space* interconnecting the reactant and product energy minima on a *potential energy surface*.

Note 1: The points on a reaction path are characterized by different values of a *reaction coordinate*.

Note 2: Adapted from ref. [20].

2.4.17 Relaxation normal mode analysis

Method to extract the *correlation times* and the associated *normal modes* of a polymer at equilibrium, by diagonalization of the time-dependent correlation matrix (M_{kl}) between the *chain segments*:

$$M_{kl}(t) = \frac{\langle \boldsymbol{x}_k(t) \cdot \boldsymbol{x}_l(0) \rangle}{\langle x_k^2 \rangle^{1/2} \langle x_l^2 \rangle^{1/2}}$$

where $\boldsymbol{x}_k(t) = \boldsymbol{r}_k(t) - \boldsymbol{r}_{k-1}(t)$ is the vector connecting two consecutive segments at a time t, $\langle x_k^2 \rangle = \langle \boldsymbol{x}_k(0) \cdot \boldsymbol{x}_k(0) \rangle$, and the angular brackets indicate an average over time and over an ensemble of identical chains.

Note 1: The relaxation times describe the time-dependence of the eigenvalues of the correlation matrix.

Note 2: The analysis may be performed numerically, on data from a *molecular dynamics* or *Brownian dynamics* simulation, or analytically in some special cases. One important example is the Rouse theory [18] for the dynamics of polymer chains, which neglects the effect of *excluded volume interactions*, *entanglements*, and *hydrodynamic interactions*. For a *bead-spring model* of a linear chain containing N beads, the N-1 Rouse normal modes $\boldsymbol{X}_p(t)$ are then given by:

$$\boldsymbol{X}_p(t) = \frac{1}{N}\sum_{i=1}^{N} \boldsymbol{r}_i(t) \cos\left[\frac{\left(i-\frac{1}{2}\right)p\pi}{N}\right] \qquad (p=1,\ldots,N-1).$$

The Rouse normal modes are said to be orthogonal because their *cross-correlation functions* are zero:

$$\frac{\langle \boldsymbol{X}_p(t) \cdot \boldsymbol{X}_q(0)\rangle}{\langle \boldsymbol{X}_p(0) \cdot \boldsymbol{X}_q(0)\rangle} = \delta_{pq} \exp\left(-t/\tau_p\right)$$

and the corresponding relaxation times are approximately (for $p \ll N$) given by:

$$\tau_p(T) = f(T)\frac{N^2}{p^2}$$

where $f(T)$ is a prefactor accounting for the temperature dependence of the relaxation times.

2.4.18 Screening length

Characteristic distance for the decay of a *potential of mean force* or of a *space correlation function*, describing a reduction in the bare distance-dependent interaction between two *particles*.

Note 1: Examples of bare distance-dependent interactions are the *excluded volume interaction* and *hydrodynamic interaction*, with the corresponding distances being the excluded volume screening length, the electrostatic screening length, and the hydrodynamic screening length.

Note 2: An important example is the Debye–Hückel screening length, λ_{DH}, which converts the *Coulomb potential* into the *screened Coulomb potential* that acts between charges dissolved in an electrolyte medium.

2.4.19 Space correlation function

Correlation function whose independent variable is a spatial coordinate (in the general case of a multi-dimensional variable) or a length or distance (in the special case of a one-dimensional variable).

2.4.20 Time correlation function

Correlation function whose independent variable is time.

Note 1: An example is the correlation between the velocities of a *particle* [$\boldsymbol{v}(t)$] at two different times:

$$C_{vv}(t) = \langle \boldsymbol{v}(t_0 + t) \cdot \boldsymbol{v}(t_0) \rangle$$

where the dot indicates a scalar product, and the angular brackets may indicate an average over several time origins t_0, over an ensemble of identical particles, or both.

Note 2: The rate of decay of a correlation function may be summarized by a *correlation time*.

Note 3: The linear transport coefficients of a system (diffusion coefficients, viscosity, thermal and ionic conductivities, for example) can be obtained from the integral of relevant time *autocorrelation functions* $C_{XX}(t)$ of a time-dependent quantity X, using statistical mechanical relationships first derived by M. S. Green and R. Kubo [1, page 74; 7, page 503]. Their form for a generic transport coefficient γ is:

$$\gamma = L \int_0^\infty C_{XX}(t) dt$$

where L is a dimensional constant. For example, integration of the velocity autocorrelation function for an ensemble of particles yields their diffusivity.

2.4.21 Trajectory (in modeling and simulations of polymers)

A sequence of *configurations* or of *phase-space* points of a system or a part of it generated during a simulation.

Note 1: Additional data may be included such as the total energy and its components, the pressure and the stress, the atomic charges and multipole moments in a *polarizable model*, the *topology* in a *reactive force field* simulation, the change density and the orbitals in an *ab initio molecular dynamics* simulation. Metadata, such as information about the software and hardware used to generate the trajectory, may also be included.

Note 2: The order of the frames (configurations or phase space points) in it may or may not be significant. For example, in a *molecular dynamics* simulation, the frames are normally ordered by increasing time, while in *Monte Carlo* simulations, the order is less important, since these usually represent an *ensemble* of configurations of a system at equilibrium, without any reference to time.

2.4.22 Vibrational normal mode analysis

Method for determining the *normal modes*, and their associated frequencies, for a *stationary point* of a molecular system.

Note 1: This is done within the harmonic approximation by finding the eigenvalues and eigenvectors of the second derivative matrix (Hessian) of the potential energy with respect to the system's *mass-weighted coordinates* at a given *configuration*. The eigenvalues and eigenvectors are proportional to the square of the frequencies, and to the normal mode displacement vectors, respectively.

Note 2: Although they omit anharmonic contributions, the normal mode frequencies are often a good approximation to a system's vibrational frequencies that are observed in infrared and Raman spectroscopic experiments.

Note 3: The normal mode frequencies are useful for estimating the vibrational contributions to a system's free energy and other thermodynamic quantities.

Note 4: An isolated unconstrained non-linear molecule of N atoms has $3N - 6$ ($3N - 5$, in the case of a linear molecule) normal modes. When using Cartesian coordinates for the analysis, $3N$ normal modes are obtained. Three of these extra modes are translational modes and three (two for linear molecules) are rotational modes.

Note 5: The normal mode frequencies are either real and positive or imaginary, depending upon the curvature at the point on the *potential energy surface* at which they are calculated. At a minimum, all frequencies are real and positive, whereas at a n^{th}-order saddle point, n of the frequencies will be imaginary. The translational and rotational modes have a zero frequency.

Note 6: Compare with the *quasi-harmonic analysis*.

3 ALPHABETICAL LIST OF TERMS

Table 1 provides an alphabetical index of terms defined in this document.

Table 1. Alphabetical list of terms.

Term	Term number
μVT ensemble	2.3.60
Ab initio model	2.2.1
Ab initio molecular dynamics (AIMD)	2.3.1
Atomistic model	2.2.2
Autocorrelation function	2.4.1
Barostat (in polymer modeling and simulation)	2.3.2
Basis set	2.3.3
Bead-rod model	2.2.4
Bead-spring model	2.2.3
Block average	2.4.2
Bonded potential	2.2.5
Born–Oppenheimer molecular dynamics (BOMD)	2.3.4
Boundary condition (in polymer modeling and simulation)	2.2.6
Brownian dynamics	2.3.5
Buckingham potential	2.2.7
Car–Parrinello molecular dynamics (CPMD)	2.3.6
Chain segment	2.1.1
Coarse-grained (CG) model	2.2.8
Collective coordinate	2.1.2
Combination rule	2.2.9
Concurrent multiscale model	2.2.10
Configuration (in statistical mechanics)	2.1.4
Configuration (stereochemical)	2.1.3
Configuration space (in statistical mechanics)	2.1.5
Configurational bias Monte Carlo move	2.3.7

Conformation (stereochemical)	2.1.6
Conformer	2.1.7
Constraint	2.1.8
Continuum configurational bias Monte Carlo move	2.3.8
Continuum model	2.2.11
Correlation function	2.4.3
Correlation length	2.4.4
Correlation time	2.4.5
Coulomb potential	2.2.12
Cross-correlation function	2.4.6
Cut-off (in polymer modeling and simulation)	2.2.13
Data-driven analysis	2.4.7
Degree of freedom (in statistical mechanics)	2.1.9
Delta-function pseudopotential	2.2.14
Density functional theory (DFT)	2.3.9
Detailed balance	2.1.10
Dissipative particle dynamics (DPD)	2.3.10
Distribution function (in statistical mechanics)	2.1.11
Double re-bridging Monte Carlo move	2.3.11
Dynamical density functional theory (DDFT) (in polymer modeling and simulations)	2.3.12
Edwards Hamiltonian	2.2.15
Effective core potential (ECP)	2.2.16
Electrostatic model	2.2.17
End-bridging Monte Carlo move	2.3.13
End-rotation Monte Carlo move	2.3.14
Ensemble (in statistical mechanics)	2.1.12
Entanglement (in polymer science)	2.1.13
Equilibration run	2.3.15
Ergodicity (in statistical mechanics)	2.1.14
Ewald summation	2.3.16
Excluded volume interaction (in polymer modeling and simulation)	2.2.18

Excluded volume of a macromolecule	2.1.15
Excluded volume of a segment	2.1.16
Expanded Lennard-Jones potential	2.2.19
Explicit solvent model	2.2.20
Extended continuum configurational bias Monte Carlo move	2.3.17
Finite size effect	2.4.8
Finitely extensible non-linear elastic (FENE) potential	2.2.21
Force bias Monte Carlo	2.3.18
Force field	2.2.22
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Generalized coordinate	2.1.17
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Harmonic potential	2.2.27
Hartree–Fock (HF) theory	2.3.21
Holonomic constraint	2.1.19
Hydrodynamic interaction	2.2.28
Implicit solvent model	2.2.29
Importance sampling	2.3.23
Incompressibility constraint	2.2.30
Internal coordinate representation	2.1.20
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Langevin dynamics	2.3.24
Lattice Boltzmann (LB)	2.3.25
Lattice model (in modeling and simulations of polymers)	2.2.31
Lennard-Jones (LJ) potential	2.2.32
Long-range intramolecular interaction	2.2.33

Long-range potential	2.2.34
Machine learning (ML) potential	2.2.35
Many-body potential	2.2.36
Mapping (in polymer modeling and simulation)	2.3.26
Markov chain	2.1.21
Mass-weighted coordinate	2.4.9
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Minimum image convention	2.2.38
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4 ACRONYMS

Table 2 provides an alphabetical list of acronyms used in this document.

Table 2. List of acronyms.

Acronym	Term	Term number
AIMD	Ab initio molecular dynamics	2.3.1
BOMD	Born–Oppenheimer molecular dynamics	2.3.4
CPMD	Car–Parrinello molecular dynamics	2.3.6
DDFT	Dynamical density functional theory	2.3.12
DFT	Density functional theory	2.3.9
DPD	Dissipative particle dynamics	2.3.10
ECP	Effective core potential	2.2.16
FENE	Finitely extensible non-linear elastic	2.2.21
GB	Gay–Berne	2.2.25
GC	Coarse-grained	2.2.8
HF	Hartree–Fock	2.3.21
LB	Lattice Boltzmann	2.3.25
LJ	Lennard-Jones	2.2.32
MC	Monte Carlo	2.3.30
MD	Molecular dynamics	2.3.28
ML	Machine learning	2.2.35
MM	Molecular mechanics	2.3.29
MSM	Multiscale model	2.2.40
NEMD	Non-equilibrium molecular dynamics	2.3.34
PBC	Periodic boundary conditions	2.2.41
PDFT	Polymer density functional theory	2.3.42
PES	Potential energy surface	2.1.29
PMF	Potential of mean force	2.4.11
PRISM	Polymer reference interaction site model	2.3.43
PSCFT	Polymer self-consistent field theory	2.3.45

QC/MM	Quantum chemical/molecular mechanical	2.2.43
RIS	Rotational isomeric state model	2.2.46
RISM	Reference interaction site model	2.3.52
RMC	Reverse Monte Carlo	2.3.51
SA	Surface area	2.2.58
SAS	Solvent-accessible surface	2.2.56
SCF	Self-consistent field	2.1.35
SES	Solvent-excluded surface	2.2.57
UA	United atom	2.2.60
WCA	Weeks–Chandler–Andersen	2.2.62

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6 REFERENCES

[1] M. P. Allen, D. J. Tildesley. *Computer Simulation of Liquids*, 2nd Edition, Oxford University Press, Oxford, UK (2017).

[2] D. Frenkel, B. Smit. *Understanding Molecular Simulation. From Algorithms to Applications*, 3rd ed., Academic Press, New York, NY (2023).

[3] M. J. Field. *A Practical Introduction to the Simulation of Molecular Systems*, 2nd ed., Cambridge University Press, Cambridge, UK (2007).

[4] F. Jensen. *Introduction to Computational Chemistry*, 3rd ed., J. Wiley and Sons Ltd., Hoboken, NJ (2017).

[5] D. P. Landau, K. Binder. *A Guide to Monte Carlo Simulations in Statistical Physics*, 3rd ed., Cambridge University Press, Cambridge, UK (2009).

[6] D. Marx, J. Hutter. *Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods*, Cambridge University Press, Cambridge, UK (2009).

[7] M. Tuckerman. *Statistical Mechanics: Theory and Molecular Simulation*, Oxford University Press, Oxford, UK (2010).

[8] P. J. Flory. *Statistical Mechanics of Chains Molecules*, Interscience Publishers, New York, NY (1969).

[9] P. G. de Gennes. *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY (1979).

[10] M. Doi, S. F. Edwards. *The Theory of Polymer Dynamics*, Oxford University Press, Oxford, UK (1986).

[11] W. L. Mattice, U. W. Suter. *Conformational Theory of Large Molecules: The Rotational Isomeric State Model in Macromolecular Systems*, Wiley-Interscience, New York, NY (1994).

[12] A. Yu. Grosberg, A. R. Khokhlov. *Statistical Physics of Macromolecules*, American Institute of Physics, Woodbory, NY (1994).

[13] M. Rubinstein, R. H. Colby. *Polymer Physics*, Oxford University Press, Oxford, UK (2003).

[14] T. Kawakatsu. *Statistical Physics of Polymers*, Springer, Berlin, DE (2004).

[15] C. Zannoni. *Liquid Crystals and their Computer Simulations*, Cambridge University Press, Cambridge, UK (2022).

[16] A. D. McNaught, A. Wilkinson. *Compendium of Chemical Terminology – IUPAC Recommendations, 2nd ed. (Gold Book)*. Blackwell Scientific Publications, Oxford, UK (1997). https://doi.org/10.1351/goldbook.

[17] R. G. Jones, J. Kahovec, R. Stepto, E. S. Wilks, M. Hess, T. Kitayama, W. V. Metanomski. *Compendium of Polymer Terminology and Nomenclature – IUPAC Recommendations 2008 (Purple Book)*. RSC Publishing, Cambridge, UK (2008).

[18] R. Stepto, T. Chang, P. Kratochvíl, M. Hess, K. Horie, T. Sato, J. Vohlídal. "Definition of terms relating to individual macromolecules, macromolecular assemblies, polymer solutions, and amorphous bulk polymers (IUPAC Recommendations 2014)", *Pure Appl. Chem.* **87**, 71–120 (2015). https://doi.org/10.1515/ci-2015-0316

[19] R. G. Jones, C. K. Ober, P. Hodge, P. Kratochvíl, G. Moad, M. Vert. "Terminology for aggregation and self-assembly in polymer science (IUPAC Recommendations 2013)", *Pure Appl. Chem.* **85**, 463–492 (2013). http://doi.org/10.1351/PAC-REC-12-03-12

[20] V. I. Minkin. "Glossary of Terms used in Theoretical Organic Chemistry", *Pure Appl. Chem.* **71**, 1919–1981 (1999). http://doi.org/10.1351/pac199971101919

[21] K. J. Laidler. "A Glossary of Terms Used in Chemical Kinetics, Including Reaction Dynamics (IUPAC Recommendations 1996)", *Pure Appl. Chem.* ***68***, 149–192 (1996). http://doi.org/10.1351/pac199668010149

[22] G. P. Moss. "Basic terminology of stereochemistry (IUPAC Recommendations 1996)", *Pure Appl. Chem.* **68**, 2193–2222 (1996). http://doi.org/10.1351/pac199668122193

[23] C. L. Perrin, I. Agranat, A. Bagno, S. E. Braslavsky, P. A. Fernandes, J.-F. Gal, G. C. Lloyd-Jones, H. Mayr, J. R. Murdoch, N. S. Nudelman, L. Radom, Z. Rappoport, M.-F. Ruasse, H.-U. Siehl, Y. Takeuchi, T. T. Tidwell, E. Uggerud, I. H. Williams. "Glossary of terms used in physical organic chemistry (IUPAC Recommendations 2021)" *Pure Appl. Chem.* **94**, 353–534 (2022). https://doi.org/10.1515/pac-2018-1010.

[24] D. B. Hibbert. "Vocabulary of Concepts and Terms in Chemometrics (IUPAC Recommendations 2016)", *Pure Appl. Chem.* **88**, 407–443 (2016). https://doi.org/10.1515/pac-2015-0605.

[25] J. Behler. "Perspective: Machine learning potentials for atomistic simulations", *J. Chem. Phys.* **145,** 170901 (2016). https://doi.org/10.1063/1.4966192

[26] K. A. Fichthorn, W. H. Weinberg. "Theoretical foundations of dynamical Monte Carlo simulations", *J. Chem. Phys.* ***95***, 1090–1096 (1991). https://doi.org/10.1063/1.461138

[27] R. L. McGreevy, L. Pusztai. "Reverse Monte Carlo simulation: a new technique for the determination of disordered structures", *Mol. Sim.* ***1***, 359–367 (1998). https://doi.org/10.1080/08927028808080958

[28] H. Flyvbjerg, H. G. Petersen. “Error estimates on averages of correlated data”, *J. Chem. Phys.* **91**, 461–466 (1989) . https://doi.org/10.1063/1.457480