Edited by
Avraam I. Isayev

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Avraam I. Isayev

Encyclopedia of Polymer Blends

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**Preface**

The *Encyclopedia of Polymer Blends* includes scientific publications in various areas of blends. Polymer blends are mixtures of two or more polymers and/or copolymers. Polymer blending is used to develop new materials with synergistic properties that are not achievable with individual components, without the need to synthesize and scale up new macromolecules. Along with a classical description of polymer blends, articles in the encyclopedia will describe recently proposed theories and concepts that may not be accepted yet but reflect future development. Each article provides current points of view on the subject matter. These up-to-date reviews are very helpful for understanding the present status of science related to polymer blends.

The encyclopedia will be the source of existing knowledge related to polymer blends and will consist of five volumes. Volume 1 describes the fundamentals, including the basic principles of polymer blending, thermodynamics, miscible, immiscible, and compatible blends, kinetics, and composition and temperature dependence of phase separation. Volume 2 covers the principles, equipment, and machinery for polymer blend processing. Volume 3 deals with the structure of blended materials that governs their properties. Volume 4 describes various properties of polymer blends. Volume 5 discusses the blended materials and their industrial, automotive, aerospace, and other high technology applications. Individual articles in the encyclopedia describe the topics in terms of historical perspective, the state-of-the-art science, and technology and its future.

This encyclopedia is intended for use by academicians, scientists, engineers, researchers, and graduate students working on polymers and their blends.

Volume 1 is devoted to fundamental principles of polymer blends and is divided into eight chapters. These chapters cover the basic thermodynamic principles defining the miscible, immiscible, or compatible nature of amorphous, semi-crystalline and liquid crystalline polymer blends, and temperature and composition dependent phase separation in polymer blends. They are detailed below and build upon each other.

Chapter 1 is devoted to molecular simulation of polymer melts and blends, including methods, phase behavior, interfaces, and surfaces that are currently the
subject of active research. This chapter describes molecular models for polymers, Monte Carlo simulations, and wetting and phase diagrams in confined geometries, techniques that are commonly used to determine the phase behavior of oligomer melts and blends. It also describes molecular dynamics methods, including basic and non-equilibrium molecular dynamics and atomistic simulations of polymer melts and blends, reversible mapping between atomistic, coarse grained, and field models, and comparison with experiments and future challenges.

Chapter 2 is devoted to the thermodynamics of flexible and rigid rod polymer blends. The fundamentals of nematic phase, scalar orientational order parameter, free energy of rigid rod solutions, nematic–isotropic phase separations, entropy- and energy-driven nematic ordering are introduced. Then, the phase separations of mixtures of flexible polymers and rigid rod-like molecules and low molecular weight liquid crystalline molecules in a thermal equilibrium state are discussed. Recent theoretical models to describe phase behavior, combining Flory–Huggins theory of isotropic mixing for polymer blends, Onsager theory, and the Maier–Saupe model of a nematic phase are presented. Based on time-dependent Landau–Ginzburg equations, the thermal instabilities of the phase separations and morphologies with the interplay between orientation and concentration fluctuations are described. Through recent theoretical and experimental studies, the phase separation dynamics of inhomogeneous mixtures consisting of conserved and nonconserved order parameters are considered.

Chapter 3 provides a brief review of recent developments in areas of amorphous polymer blends. Differential mixing, chain dynamics, and glass transition properties for individual polymer components in miscible binary blends, as well as new methods to experimentally acquire such information, are considered. Miscible blend dynamics and length scales of mixing of amorphous polymer blends are discussed. Amorphous biopolymer blends involving polymers obtained from renewable feedstocks is also briefly reviewed.

Chapter 4 considers the phase field modeling of polymer crystallization and phase separation in crystalline polymer blends. In particular, recent advances in establishing thermodynamic phase diagrams of binary crystalline polymer blends and concomitant dynamics of solid–liquid phase transformation coupled with liquid–liquid phase separation driven by thermal-quenching are described. A general free energy description of the phase field theory of the crystal solidification of pure substances is introduced with emphasis on the formation of a single crystal and spherulitic growth. Then, the approach is extended to crystallization of semicrystalline polymers and their blends by coupling with Flory–Huggins theory of liquid–liquid demixing. Various phase diagrams obtained by solving the combined Flory–Huggins and phase field free energy equations are compared with measured phase diagrams. This combined free energy is further utilized in the framework of the time-dependent Ginzburg–Landau (TDGL-Model C) dynamics pertaining to the concentration and crystal order parameters to elucidate the competition between the pattern formation and dynamics of liquid–liquid phase separation and solid–liquid phase transition. Effects of thermal, molecular orientation, and concentration field on the crystalline morphology development are discussed.
Chapter 5 is devoted to miscibility criterion in polymer blends and its determination, including experimental and theoretical considerations. A general and theoretical background to the experimental determination of miscibility based on thermodynamics, glass transition, and phase equilibria is given. Scattering and microscopy techniques and spectroscopic techniques, including infrared and Raman spectroscopy, to determine dynamics above and below the glass transition relaxations are described.

Chapter 6 deals with theoretical and experimental developments in the physical aging of polymer blends. In particular, aging data for polymer blends are reviewed and compared to the relevant homopolymer data. The past and present phenomenological, empirical and molecular models of aging are discussed. Enthalpic, volume, and mechanical relaxation, positron annihilation lifetime spectroscopy and other spectroscopic and scattering techniques are also considered. Then, specific examples on aging of blends are presented in systems where the effects of intermolecular interactions are important. Finally, complex behaviors of aging of phase separated blends are considered.

Chapter 7 provides a review of recent developments in the theory and modeling of nanoparticle-filled polymer blends. The influence of nanoparticles on the dynamics of phase separation in binary polymer blends, depending on the nanoparticle size, shape anisotropy, and surface treatment, is discussed. Theoretical methods of description of the phase diagrams in polymer/nanoparticle blends are considered, with special emphasis on the discussion of mesoscale field-based models (extended Flory–Huggins lattice theory) allowing one to calculate various hybrid particle/polymer structures. Finally, experimental and theoretical data on the influence of particles, their loading, and composite morphology on specific material properties, including the modulus of elasticity and electrical conductivity, are presented.

Chapter 8 details the modeling of the self-assembly of ternary blends encompassing photosensitive chemical reactions that create defect-free, hierarchically ordered materials. Starting with a brief review of literature, this chapter provides a description of theoretical models and then shows how one can control the evolution of such systems by varying the reaction rate coefficients in a specified manner. A further discussion on the formation of defect-free structures in the binary and ternary systems via a combination of stationary and moving light sources is given. Then, description is provided on the use of a photomask to control the structure formation within thin films of ternary blends.

Each chapter provides a summary and outlook for future development in blends followed by a list of abbreviations and symbols and then references.

There are many people who contributed to the completion of this volume. I wish to express my profound appreciation to the contributors of the various chapters for being patient with my requests for revisions and corrections. I would also like to thank Dr. Gustavo Carri, Dr. Valeriy Ginzburg, Dr. Dmitry Golovaty, Dr. Hendrik Heinz, Dr. Alamhir Karim, Dr. Thein Kyu, Dr. Akihiko Matsuyama, Dr. Sindee Simon and Dr. Victor Yashin for providing excellent reviews of various chapters. Their inquisitive reviews were very helpful in improving the quality of this volume.
Preface

I am thankful to Wiley-VCH Publishers for undertaking this project and for their patience, understanding, and cooperation with the authors at all stages of preparation. Finally, the support and patience of my family and the families of all the chapter authors contributed to the completion of this volume.

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1 Molecular Simulation of Polymer Melts and Blends: Methods, Phase Behavior, Interfaces, and Surfaces

Peter Virnau, Kurt Binder, Hendrik Heinz, Torsten Kreer, and Marcus Müller

1.1 Introduction

Understanding thermodynamic properties, including also the phase behavior of polymer solutions, polymer melts, and blends, has been a long-standing challenge [1–7]. Initially, the theoretical description was based on the lattice model introduced by Flory and Huggins [1–7]. In this model, a flexible macromolecule is represented by a (self-avoiding) random walk on a (typically simple cubic) lattice, such that each bead of the polymer takes one node of the lattice, and a bond between neighboring beads of the chain molecule takes a link of the lattice. For a binary polymer blend (A,B), two types of chains occur on the lattice (and possibly also “free volume” or vacant sites, which we denote as V). The model (normally) does not take into account any disparity in size and shape of the (effective) monomeric units of the two partners of a polymer mixture. Between (nearest neighbor) pairs AA, AB, and BB of effective monomers, pairwise interaction energies, $e_{AA}$, $e_{AB}$ and $e_{BB}$, are assumed. Thus, this model disregards all chemical detail (as would be embodied in the atomistic modeling [8–10], where different torsional potentials and bond-angle potentials of the two constituents can describe different chain stiffness).

Despite the simplicity of this lattice model, it is still a formidable problem of statistical mechanics, and its “numerically exact” treatment already requires large-scale Monte Carlo simulations [11–13]. Consequently, the standard approach has been [1–7] to treat this Flory–Huggins lattice model in mean-field approximation, which leads to the following expression for the excess free energy density of mixing [4]:

$$\frac{\Delta F}{k_B T} = \frac{\phi_A \ln \phi_A}{N_A} + \frac{\phi_B \ln \phi_B}{N_B} + \phi_V \ln \phi_V + \chi_{AB} \phi_A \phi_B + \frac{1}{2} \chi_{AA} \phi_A^2 + \frac{1}{2} \chi_{BB} \phi_B^2.$$  (1.1)

Here $\phi_A$, $\phi_B$ and $\phi_V = 1 - \phi_A - \phi_B$ are the volume fractions of monomers of type A, B and of vacant sites, respectively. Every lattice site has to be taken by either...
an A monomer, a B monomer, or a vacancy, and for simplicity the (fixed) lattice spacing is taken as our unit of length. \(N_A\) and \(N_B\) are chain lengths of the two types of polymers (we disregard possible generalizations that take polydispersity into account [5]). Thus, the first three terms on the right-hand side of Eq. (1.1) represent the entropy of mixing terms, while the last three terms represent the enthalpic contributions \(\chi_{AB}, \chi_{AA}\) and \(\chi_{BB}\) are the phenomenological counterparts of the pairwise interaction energies \(\varepsilon_{AB}, \varepsilon_{AA}\) and \(\varepsilon_{BB}\), respectively. Note that in the entropic terms the (translational) entropy of a polymer is reduced by a factor \(1/N\) in comparison to a corresponding monomer because of chain connectivity. In deriving this simple expression for the entropy, the fact that polymer chains on the lattice cannot intersect either themselves or other chains has not been explicitly taken care of: the excluded volume constraint is only taken into account via the constraint that a lattice site can be taken by at most one monomer, but only the average occupation probabilities \(\phi_A, \phi_B\) and not the local concentrations \(c^A_i, c^B_i\) of a lattice site \(i\) enter: while \(c^A_i = 1\) or 0 and \(c^B_i = 1\) or 0, \(\phi_A = \langle c^A_i \rangle_T, \phi_B = \langle c^B_i \rangle_T\). By \(\langle Q \rangle_T\) we denote a thermal average of an observable \(Q\) in the sense of statistical mechanics at a given temperature, \(T\), that is:

\[
\langle Q \rangle_T = \frac{1}{Z} \sum_C Q(C) \exp\left[\frac{-E(C)}{k_BT}\right]
\]

\[
Z = \sum_C \exp\left[\frac{-E(C)}{k_BT}\right], \quad F = -k_BT \ln Z
\]

where the sums are extended over all configurations \(C\) (“microstates”) of the considered statistical system, \(E(C)\) is the corresponding energy function (the “Hamiltonian” of the system [4,9,10]), and \(Z\) its partition function.

From these definitions it should be clear that in the exact expression for the enthalpy one should expect terms of the type:

\[
\chi_{AB} \left( \frac{1}{2q} \right) \sum_{\text{j[-n.n. of i]}} \left( \langle c^A_i c^B_j \rangle_T + \langle c^B_j c^A_i \rangle_T \right)
\]

where \(q\) is the number of nearest neighbors of a site \(i\) on the lattice, rather than \(\chi_{AB} \phi_A \phi_B\). The latter expression results, of course, if this correlation function is factorized, \(\langle c^B_j c^A_i \rangle_T \approx \langle c^B_j \rangle \langle c^A_i \rangle = \phi_B \phi_A\). This neglect of correlations in the occupancy of lattice sites would become accurate in the limit \(q \to \infty\), but turns out to be rather inaccurate for the simple cubic lattice, which has \(q = 6\) only. Moreover, as far as unmixing of a polymer blend is concerned, only interchain contacts and not intrachain contacts contribute (strongly attractive intrachain interactions can cause contraction or even collapse of the random coil configurations).

We shall not discuss Eq. (1.1) further for the general case, but rather focus on the two most important special cases, namely incompressible blends and incompressible polymer solutions. Taking \(\phi_v = 0\) one can reduce Eq. (1.1) to a simpler expression [1-4], where \(\phi_A = \phi, \phi_B = 1-\phi\):

\[
\frac{\Delta F}{k_BT} = \frac{\phi \ln \phi}{N_A} + \frac{(1-\phi) \ln (1-\phi)}{N_B} + \chi \phi (1-\phi)
\]
where in the mean-field approximation the Flory–Huggins parameter $\chi$ is related to the pairwise energies by:

$$\chi = q \left[ \varepsilon_{AB} - \left( \varepsilon_{AA} + \varepsilon_{BB} \right) / 2 / k_B T \right]$$

(1.5)

As an example for the predictions that follow from Eqs. (1.4) and (1.5), we note that the stability limit (“spinodal curve”) of the homogenous phase is given by the vanishing of the second derivative of $\Delta F$ with respect to $\phi$:

$$\partial^2 (\Delta F / k_B T) / \partial \phi^2 = 0$$

(1.6)

which yields the equation:

$$\chi = \chi_\phi (\phi) = \left\{ \left[ \phi N_A \right]^{-1} + (1-\phi) N_B \right\} / 2$$

(1.7)

Equation (1.7) describes the spinodal curve in the plane of variables ($\chi, \phi$). The maximum of the spinodal curve for such a binary incompressible mixture yields the critical point, that is:

$$\phi^{\text{crit}} = \left( \sqrt{N_A / N_B + 1} \right)^{-1}, \quad \chi^{\text{crit}} = 2 \left( N_A^{-1/2} + N_B^{-1/2} \right)^{-2}$$

(1.8)

For the simplest case of a symmetric mixture ($N_A = N_B = N$), this reduces to $\phi^{\text{crit}} = 1/2$, and $\chi^{\text{crit}} = 2/N$.

The case of an incompressible polymer solution results if we interpret B as a solvent molecule in Eq. (1.4) by putting $N_B = 1$ [or alternatively put $\phi_B = 0$ in Eq. (1.1) and reinterpret $V$ as solvent molecule]. However, while for polymer mixtures in the state of dense melts incompressibility is often a reasonable first approximation, for polymer solutions in some cases such an assumption is inadequate, for example, if one uses supercritical carbon dioxide as a solvent for the polymers [7, 14].

When one tries to account for real polymer systems in terms of models of the type of Eqs. (1.1)–(1.8), the situation is rather unsatisfactory; however, when one fits data on the coexistence curve or on $(\partial^2 (\Delta F / k_B T) / \partial \phi^2)_T$, the latter quantity being experimentally accessible via small angle scattering, one finds that one typically needs an effective $\chi$ parameter that does not simply scale proportional to inverse temperature, as Eq. (1.5) suggests. Moreover, there seems to be a pronounced $\phi$-dependence of $\chi$, in particular for $\phi \to 1$. Near $\phi = \phi^{\text{crit}}$, on the other hand, there are critical fluctuations (which have been intensely studied by Monte Carlo simulations [11–13, 15] and also in careful experiments of polymer blends [16–18] and polymer solutions [19]). Sometimes in the literature a dependence of the $\chi$ parameter on pressure [18] or even chain length is reported, too. Thus, there is broad consensus that the Flory–Huggins theory and its closely related extensions [20] are too crude as models to provide predictive descriptions of real polymer solutions and blends. A more promising approach is the lattice cluster approach of Freed and coworkers [21–23], where effective monomers block several sites on the lattice and have complicated shapes to somehow “mimic” the local chemical structure. However, this approach requires rather cumbersome numerical calculations, and is still of a mean-field character, as
far as critical phenomena are concerned. We shall not address this approach further in this chapter.

A very popular approach to describe polymer chains in the continuum is the Gaussian thread model [24–26], and if one treats interactions among monomers in a mean-field-like fashion this leads to the so-called “self-consistent field theory” [27–33] of polymers. This theory is an extension of the Flory-Huggins theory to spatially inhomogeneous systems (like polymer interfaces or microphases-separated copolymer systems), with respect to the description of the phase diagrams of polymer solutions and blends. However, it still lacks chemical detail and is on a mean-field level; hence we shall not dwell on it further here.

An alternative approach that combines the Gaussian thread model of polymers with liquid-state theory is known as the polymer reference interaction site model (PRISM) approach [34–38]. This approach has the merit that phenomena such as the de Gennes [3] correlation hole phenomena and its consequences are incorporated in the theoretical description, and also one can go beyond the Gaussian model for the description of intramolecular correlations of a polymer chain, adding chemical detail (at the price of a rather cumbersome numerical solution of the resulting integral equations) [37, 38]. An extension to describe the structure of colloid–polymer mixtures has also become feasible [39, 40]. On the other hand, we note that this approach shares with other approaches based on liquid state theories the difficulty that the hierarchy of exact equations for correlation functions needs to be decoupled via the so-called “closure approximation” [34–38]. The appropriate choice of this closure approximation has been a formidable problem [34–36]. A further inevitable consequence of such descriptions is the problem that the critical behavior near the critical points of polymer solutions and polymer blends is always of mean-field character.

There have been many other attempts to base the description of polymer solutions, melts, and blends on liquid-state theory (e.g., [41–44]) and we shall not mention all of them. Perhaps the most widely used and successful approaches are based on Wertheim’s [45, 46] perturbation theory devised to deal with the equation of state of associating fluids. Theories based on this approach, where attractive interactions between different monomers or monomers and solvent particles are treated in first order thermodynamic perturbation theory, often appear under acronyms like TPT1 or SAFT (statistical associating fluid theory). Comparisons with computer simulations [7, 47, 48] have shown that TPT1-MSA [49, 50] (here MSA stands for a closure approximation known [51] as “mean spherical approximation”) yields rather reasonable results on phase coexistence, but typically a large overestimation of the two-phase region occurs, and the critical behavior is described as mean-field like; so the correct Ising-type criticality [11–15] cannot be described as expected. The latter comment applies to the many variants of SAFT (e.g., [52–56]) as well. However, as a caveat, apart from this shortcoming and other systematic errors resulting from the fact that thermodynamic perturbation theory [57] becomes generally inadequate at low temperatures and errors from the closure approximations [51] occur, we mention that some variants of such theories invoke additional uncontrolled approximations that may lead to further
uncontrolled errors. For example, the now rather popular perturbed chain (PC)-
SAFT approach [56] relies on an expansion of isotherms as sixth-order polynomials
of the monomer density and this may give rise to completely spurious gas–gas and
liquid–liquid phase equilibria [58, 59] in the equation of state of a homopolymer, in
addition to the standard liquid–gas two-phase region, which is the only physically
meaningful phase separation of typical homopolymers at high temperatures.

A general conclusion that can be drawn from this short survey on the many
attempts to develop analytical theories to describe the phase behavior of polymer
melts, polymer solutions, and polymer blends is that this is a formidable problem,
which is far from a fully satisfactory solution. To gauge the accuracy of any such
approaches in a particular case one needs a comparison with computer simulations
that can be based on exactly the same coarse-grained model on which the analytical
theory is based. In fact, none of the approaches described above can fully take into
account all details of chemical bonding and local chemical structure of such
multicomponent polymer systems and, hence, when the theory based on a simplified
model is directly compared to experiment, agreement between theory and experi­
ment may be fortuitous (cancellation of errors made by use of both an inadequate
model and an inaccurate theory). Similarly, if disagreement between theory and
experiment occurs, one does not know whether this should be attributed to the
inadequacy of the model, the lack of accuracy of the theoretical treatment of the
model, or both. Only the simulation can yield “numerically exact” results (apart from
statistical errors, which can be controlled, at least in principle) on exactly the same
model, which forms the basis of the analytical theory. It is precisely this reason that
has made computer simulation methods so popular in recent decades [58–64].

Consequently, we focus here on computer simulations exclusively. The outline of
the remainder of this chapter is as follows: Section 1.2 presents on overview of
polymer models (from lattice models to atomistic descriptions) and will also describe
the most important aspects of Monte Carlo simulations of these models. As an
example, recent work on simple short alkanes and solutions of alkanes in super­
critical carbon dioxide [47, 48] will be presented, to clarify to what extent a comparison
of Monte Carlo results on phase behavior and experimental data is sensible, and
which experimental input into the models is indispensable to make them predictive.

In Section 1.3 we continue the discussion of Monte Carlo simulations of polymer
blends and polymer solutions, but with the emphasis on interfaces that result in the
context of phase separation: interfaces between coexisting phases in the bulk (liquid–
liquid interfaces in a blend, liquid–vapor-type interfaces in a solution) and at solid
external walls. It will be shown how all the surface free energies entering Young’s
formula for the contact angle of droplets can be determined, and how one can
estimate the location of wetting transitions. Coarse-grained models are the focus of
this section.

Section 1.4 discusses the basic aspects of molecular dynamics simulation of
polymer melts and blends with both coarse-grained and chemically detailed models.
While the first part of this section emphasizes the basic aspects of the technique,
Section 1.4.2 emphasizes non-equilibrium aspects such as the response to shear
deformation, and the special techniques necessary to simulate such phenomena
(non-equilibrium molecular dynamics, NEMD). Since shear deformations create heat, the proper thermostating of the system in the context of a NEMD simulation needs to be carefully considered, and this will be explained in this section. Of course, the processing of polymer solutions, melts, and blends in their molten state is always an indispensable step prior to the production of (typically solid) polymeric materials, and hence addressing such problems by the theoretical modeling is clearly adequate and necessary.

While most sections in this chapter emphasize coarse-grained models, it must be stressed that such models can elucidate qualitative trends, but a quantitative prediction of properties of specific polymeric materials is not achieved. The latter task is attempted by molecular dynamics simulations of chemically realistic atomistic models (Section 1.5). Although the feasibility of this “brute force” approach is limited due to excessive demands of computer resources to equilibrate melts of macro-molecules with high molecular weights, and there are also uncertainties about the force fields, nevertheless various encouraging results have been obtained, and some examples of them will be reviewed in this section. The “mapping” between atomistic and coarse-grained models will be discussed briefly.

Finally, Section 1.6 gives a short summary of the state of the art and outlook on closely related problems that were not covered in this chapter.

1.2
Molecular Models for Polymers and Monte Carlo Simulations

1.2.1
Modeling Polymers in Molecular Simulations

If generic properties of polymers need to be determined, it is often sufficient to rely on lattice models. For comparison with experiments of particular melts and blends, more sophisticated off-lattice models are typically applied. These models are described by force fields that determine the interactions between atoms or groups of atoms, and the quality of the modeling is essential for the predictive quality of the simulations. Force field parameters can be derived from direct comparison with experimental data, from quantum mechanical calculations, or both. In the first part of this section, we present generic polymer models that are commonly used in molecular simulations without focussing on any particular substance. Emphasis is placed on lattice and simple off-lattice models that will also be discussed in the next three sections. Section 1.5 is dedicated to chemically realistic descriptions.

The first model that took into account excluded volume effects was the self-avoiding-walk (SAW), which was introduced about 60 years ago [65, 66]. Each monomer occupies a lattice site on a simple cubic lattice. The bond length between adjacent monomers is fixed by the lattice constant and the bond angles are restricted by the geometry of the lattice. This model is well-suited to describe generic polymers in dilute, good solvent conditions and exhibits the correct scaling behavior
\( R_g^2 \propto N^{2\nu} \), \( \nu \approx 0.588 \). Variations of this model, like the interacting SAW (iSAW), allow for interactions between non-adjacent beads and can even undergo a phase transition to a globular state, reproducing the generic behavior of a single chain under bad solvent conditions. A particularly popular extension of the iSAW to two types of beads is even able to describe generic properties of proteins. In the HP (hydrophobic–polar) model \([67]\), non-adjacent hydrophobic beads attract each other, whereas interactions between hydrophobic and polar beads and between two polar beads are restricted to excluded volume. These simple conditions suffice to form a hydrophobic core as observed in crystal structures of proteins. Likewise, polymer blends can be readily implemented in such simple models if we allow for a second type of chains and specified interactions between monomers of like and unlike species. Polymers on a simple cubic lattice exhibit two major disadvantages. On the one hand, both bond length and bond angles are fixed and, on the other hand, Monte Carlo simulations on the simple cubic lattice are often plagued with ergodicity problems \([68]\). The bond fluctuation model \([69]\) was introduced to address these issues while preserving the computational efficiency of lattice models. Again, the basic idea is simple: instead of occupying a simple lattice site, a monomer now occupies a whole lattice cell. Neighboring beads are only allowed to move such that the bond does not stretch or compress too much. Specifically, bond vectors are chosen to prevent overlaps of adjacent monomers and intersection of bonds during simulation. Note that, due to this additional flexibility, the bond fluctuation model already resembles to some extent a coarse-grained continuum model.

A simple and very popular example of a coarse-grained off-lattice model is given by the bead-spring chain of Kremer and Grest \([70, 71]\). In this model monomers interact via a Lennard-Jones potential:

\[
V_{ij}(r) = \begin{cases} 
4\varepsilon \left[ \frac{\sigma}{r} \right]^{12} - \left[ \frac{\sigma}{r} \right]^{6} + \text{const.}, & \text{if } r < r_c \\
0, & \text{else}
\end{cases}
\]  

(1.9)

To increase computational efficiency the Lennard-Jones potential usually is cut and shifted at either twice the minimum value, or 2.5\( \sigma \). The constant in Eq. (1.9) is chosen such that \( V_{ij} \) is continuous at \( r = r_c \). The value of \( \varepsilon \) sets the scale of energy (and temperature \( T \), which is often normalized as \( T^* = k_B T / \varepsilon \)), and the size \( \sigma \) of effective monomers sets the scale of length. In addition, adjacent beads interact with the so-called FENE potential:

\[
V_{\text{FENE}}(r) = -\text{const.} \cdot \varepsilon \cdot \ln \left[ 1 - \left( \frac{r}{r_{\text{max}}} \right)^2 \right]
\]  

(1.10)

Constants in Eq. (1.10) are chosen such that the most favorable distance between bonded monomers is slightly smaller than the distance between non-bonded monomers to prevent crystallization. Alternatively, a harmonic potential can be used for bonded monomers instead of Eqs. (1.9, 1.10). As indicated for lattice models, polymer blends can be implemented by adjusting the interaction strength \( \varepsilon \) for monomers of
type A and B and between A and B. By mapping $\varepsilon$ and $\sigma$ to experimental energy and length scales, simulations of this model can be compared with experiments of specific polymers. In these scenarios, single Lennard-Jones beads typically represent groups of carbon atoms [47].

The next steps towards a more chemically detailed description are so-called united atom models. In this class hydrogen atoms are grouped together with the heavier atoms to which they are attached. These potentials typically contain both bond bending and torsional terms. Fully atomistic models, which frequently are used in simulations of biopolymers [72], consider hydrogen as a separate particle and often contain electrostatic terms as well. Section 1.5 presents a few selected examples of atomistic polymer models in comparison with experiments.

At the end of this introductory section we emphasize that the model should be adequate for the problem in question. Adding additional parameters to describe the system in a chemically realistic manner increases the computational cost and does not necessarily lead to better agreement with experiments. This should be considered, especially because on today’s computers fully atomistic molecular dynamics simulations are typically limited to box sizes of a few nanometers and 10s or 100s of nanoseconds of simulated time.

1.2.2

Basics of Monte Carlo Simulations

Classical molecular simulations are dominated by two classes of algorithms: Monte Carlo and molecular dynamics [62, 63]. Monte Carlo generally aims at generating independent configurations of a statistical system that contributes to the Boltzmann-weighted statistical average of an observable. This information can also be obtained from molecular dynamics simulations in which a starting configuration is evolved according to Newton’s equations of motion. In addition, molecular dynamics generates information about the dynamical evolution of a system. In the following, we give a short overview and present a selection of several techniques important for studying polymer blends and melts. After a brief introduction to basic Monte Carlo algorithms we focus on grand-canonical simulations, which are commonly used to determine phase diagrams of polymer melts and blends. Molecular dynamics simulations are introduced in Section 1.4.

Monte Carlo simulations are, as indicated by the name, based on the idea of evolving a system by drawing random numbers. Unfortunately, statistically meaningful configurations are typically confined to a small volume of phase space. To evolve a system within this volume we apply importance sampling, that is, we only sample states that actually contribute to statistical averages.

To derive the relevant equations we consider our system to be in a particular state $i$. This state is in equilibrium with its environment if the probability flows in and out of this state are equal:

$$\sum_j P(i) a_i^o j = \sum_j P(j) a_j^o i \quad \forall j$$

(1.11)
where $P(i)$ is the probability of residing in state $i$, which is typically given by the Boltzmann distribution;

$\omega_{ij}$ is the probability of jumping from $i$ to $j$ as given by the algorithm;

$a_{ij}$ is the probability of selecting or placing a particular particle for the move.

The system is in equilibrium if Eq. (1.11) applies to all states. Equation (1.11) is always fulfilled if the stricter condition:

$$P(i)a_{ij}\omega_{ij} = P(j)a_{ji}\omega_{ji} \quad \forall i, j$$

(1.12)
is met, which is known as detailed-balance. Several ways to fulfill detailed-balance are conceivable. The Metropolis criterion [83] was historically the first implementation of detailed balance, and remains by far the most popular choice today:

$$\omega_{ij} = \min \left( 1, \frac{a_{ij}P(j)}{a_{ji}P(i)} \right).$$

(1.13)

For example, consider a local Monte Carlo scheme for a Lennard-Jones liquid in the NVT (constant particle number, volume, and temperature) ensemble: We choose one particle at random, and move it a fixed distance away from the previous position in an arbitrary direction. For the reverse move (from $j$ to $i$) $a_{ij} = a_i$; the two prefactors cancel out. $P_i \propto \exp[-\beta E(i)]$ according to the canonical Boltzmann distribution. Equation (1.13) indicates that the move is always accepted if the energy of the system is lowered by the displacement. If the energy increases, the move is accepted with probability $\exp(-\beta \Delta E)$, that is, we draw a random number between 0 and 1 and accept the move if the random number is smaller than $\exp(-\beta \Delta E)$.

Apart from local displacements, a wide variety of Monte Carlo moves can already be formulated using Eq. (1.13). For instance, an end-monomer can be cut from a polymer chain and reattached at the other end. In this case the movement of the chain resembles a slithering snake, from which the name of the algorithm is derived [73, 74]. In dilute systems, a monomer can be selected at random, around which one side of the polymer is rotated by an arbitrary angle (or an angle allowed by the lattice geometry). This so-called pivot algorithm is currently the most efficient way to simulate single chains in good solvent conditions [75, 76]. For globular states, various end- [77] and internal-rebridging [78, 79] algorithms have been developed in which the chain is cut and reconnected internally. A version that cuts and rebridges two chains in a melt also exists [80]. From this list it becomes immediately clear that Monte Carlo moves do not have to mimic physically feasible moves of a real polymer chain. This characteristic is oftentimes advantageous as it allows for a fast and efficient sampling of configuration space. On the downside, information about the physical evolution of the system is lost.

### 1.2.3 Determination of Phase Behavior

In the following, we focus on a set of techniques commonly used to determine the phase behavior of oligomer melts [47, 48] and blends [81] to give an example of how
MC techniques are applied in practice. The methodology is rather general and in principle can be applied to any molecular liquid [82] or spin system. It also has advantages over techniques like Gibbs ensemble Monte Carlo [83] because it can be combined with finite-size scaling in the vicinity of the critical point. In addition, the method yields interfacial properties. Our presentation follows Reference [47]. Simulations are typically performed in the grand canonical $\mu VT$ ensemble with periodic boundary conditions, that is, we fix the chemical volume and temperature but allow for particle insertions or deletions. For a simple Lennard-Jones liquid, Eq. (1.13) becomes:

$$w_i = \min \left(1, \frac{V}{n+1} \exp \left(-\beta \Delta E + \beta \mu \right) \right)$$  \hspace{1cm} (1.14)

for insertion from $n$ particles to $n+1$ particles in the system, and:

$$w_{\bar{i}} = \min \left(1, \frac{1}{V} \exp \left(+\beta \Delta E - \beta \mu \right) \right)$$  \hspace{1cm} (1.15)

for deletion attempts from $n$ to $n-1$; $V$ denotes the volume of the simulation box. The simulation of polymer melts is slightly more involved because insertions of whole chains are typically rejected in a melt due to overlaps. To attenuate this problem, more advanced schemes like configurational bias Monte Carlo [85–88] need to be implemented. Again, the basic idea is simple: the first particle is inserted at random. Subsequent particles of the chain are inserted after the surrounding area is scanned for favorable vacancies. The bias, however, has to be considered when final acceptance probabilities are calculated. This algorithm, combined with local updates schemes introduced above, works very well for oligomers. Melts containing larger chains remain challenging and the efficiency of the grand canonical insertion attempt still limits the applicability of the whole approach.

In a typical simulation run, a joint histogram of particle number and energy is accumulated. The system is at coexistence when an unweighted simulation spends an equal amount of time in the coexisting phases. If we plot the probability distribution as a function of particles in the melt, we obtain a double-peaked distribution at coexistence and the areas below the two peaks are equal [88, 90]. Coexistence densities can be calculated by determining the average particle numbers in the gas and the liquid peak and dividing the respective numbers by the volume of the simulation box.

In practice, it is difficult to estimate the coexistence chemical potential ahead of time. However, if two distributions at $\mu$, $T$ and $\mu'$, $T'$ overlap sufficiently, it is possible to extrapolate data from $\mu$, $T$ to $\mu'$, $T'$ and avoid a second simulation [91]. The probability of a certain configuration $c$ at $\mu'$, $T'$ is given by:

$$P_{\mu',T'}(c) = \frac{Z'}{Z} P_{\mu,T}(c) \exp \left(-\beta'\Delta E + (\mu' - \mu) n \right)$$  \hspace{1cm} (1.16)

where $P_{\mu',T'}(n_0)$ is the sum over all configurations $c_i$ at $n_0$.

$$\sum_{\{c_i\}_n=n_0} P_{\mu,T}(c_i) \propto \sum_{\{c_i\}_n} \delta (n-n_0)$$

can be determined from the original data set. After a suitable normalization, the grand canonical partition sums $Z$ and $Z'$
disappear and we obtain:

\[ P_{\mu', T'}(n_0) = \frac{\sum_{\{\alpha\}} \delta(n-n_0) \ e^{-(\beta'-\beta)E_i + (\mu'-\mu)\mu_0}}{\sum_{\{\alpha\}} \ e^{-(\beta'-\beta)E_i + (\mu'-\mu)\mu_0}} \]  

(1.17)

From a statistical mechanics viewpoint, molecular systems share several properties with Ising spin systems if density fluctuations are substituted with spin flips. Polymer melts and blends without long-range interactions typically belong to the 3d-Ising universality class [92, 93], and critical points can be determined with techniques that were originally derived for spin systems [94]. To this extent we can calculate second- or fourth-order cumulants [94]:

\[ U_2 = \frac{\langle M^2 \rangle}{\langle |M| \rangle^2}, \quad U_4 = \frac{\langle M^4 \rangle}{\langle M^2 \rangle^2} \]  

(1.18)

which become system size independent and cross at the critical point (Figure 1.1). \( M \) denotes the order parameter of the transition. For liquid–vapor phase coexistence it is given by:

\[ M \equiv \varrho - \langle \varrho \rangle \]  

(1.19)

In practice, we perform several simulations close to the critical point for different simulation box volumes and determine the coexistence chemical potential as indicated above. These simulations can be extrapolated to different temperatures close to \( T_c \) to obtain \( U_K(V, T)(K = 2, 4) \). The critical point is the intersection point of the cumulants. The computation of cumulants is closely related to finite-size effects [95–97] that haunted computer simulations in the early days but are now under firm control: In a macroscopic system the correlation length diverges at the

![Figure 1.1](image-url)  

**Figure 1.1** Second- and fourth-order cumulants for a LJ + FENE pentamer in comparison to the corresponding values for the 3d Ising distribution at criticality (horizontal straight lines). Each line has been extracted from a single simulation by extrapolating the data set to several temperatures. Adapted from Reference [47].
critical point. In a system of finite size, the correlation length can at most be equal to half of the linear dimension of the simulation box, which has to be considered in the vicinity of $T_c$. Definition (1.19) is sufficient for most purposes. Note, however, that an exact mapping of fluid criticality to Ising criticality has to consider field-mixing effects [92] and $M$ becomes a linear combination of density and energy. Owing to higher order effects and corrections to scaling the values of $U_4$ and $U_2$ at the intersection points of the curves in Figure 1.1 deviate slightly from the asymptotic values obtained for the 3d Ising model (dotted horizontal lines). Note, however, that the intersections of both $U_2$ and $U_4$ occur at about the same temperature, which can be determined with good accuracy.

Away from the critical point, that is, at low temperatures, both phases are separated by a free energy barrier that corresponds to a region of low probability. This barrier cannot be overcome by thermal fluctuations. Several sophisticated schemes have been devised to address this issue. Multicanonical methods [98] modify the Hamiltonian in order to sample a range of densities uniformly. To this end, a weight function $w[n]$ is added to the original Hamiltonian. The simulated distribution $P_{\text{sim}}(n) = P(n) \exp(-w[n])$ becomes flat for the choice of $w(n) \approx \ln P(n)$. Unfortunately, $P(n)$ is a priori unknown, but can be estimated by extrapolating an overlapping data set [91]. A sequence of simulations and extrapolations typically starts close to the critical point where barriers between both peaks are small and no weighting is required for the first run. The weight function $w(n)$ can also be self-adjusted during simulation [99–102]. Note, that some of these schemes violate detailed balance and bear the risk of systematic errors. However, they are well-suited to generate an educated guess for the probability distribution, which can be used in a weighted simulation with fixed weights. A detailed discussion of methods to overcome free energy barriers can be found in Reference [103].

In the following we focus on a scheme that is based on umbrella sampling [104] and circumvents most of these problems. In successive umbrella sampling [105] the relevant range of states is subdivided into small windows that are sampled consecutively. This allows us to simulate without a weight function or to generate a weight function on the fly from previous windows by means of extrapolation. In the simplest implementation, we start with an empty box and allow the system to change only between 0 and 1 particle. A histogram $H(n)$ monitors how often each state is visited ($n$ denotes the number of particles in the simulation box). After a predetermined number of insertion/deletion Monte Carlo moves, the ratio $H(1)/H(0)$ is determined, and we move the window to the right (to allow 1 and 2 particles). This procedure is repeated until all relevant states have been sampled. Then, the (unnormalized) probability distribution can be estimated recursively:

$$\frac{P(n)}{P(0)} = \frac{H(1)}{H(0)} \cdot \frac{H(2)}{H(1)} \cdots \frac{H(n)}{H(n-1)}$$

or:

$$\ln \frac{P(n)}{P(0)} = \ln \frac{H(1)}{H(0)} + \ln \frac{H(2)}{H(1)} + \cdots + \ln \frac{H(n)}{H(n-1)}$$