Monte Carlo Simulation Studies of Polymer Systems

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Summary: Polymers molecules in solution or melt are more or less flexible and continuously change their shape and size. Thus, characteristic properties of the system fluctuate around statistical mean values which are dependent on the concentration of the solution, on the quality of the solvent used, and on the specific structure of the molecules, e.g. linear or star-branched. The most direct approach to these quantities on a molecular level are computer simulations. Due to restrictions of computer power fully atomistic simulations of macromolecules are presently still at the beginning but several arguments justify the use of simplified models. The most efficient way dealing with polymer systems are Monte Carlo simulations based on lattice chains, at least as long as static properties are of interest only. In the present paper a short introduction to the field is given and selected examples are presented in order to demonstrate the usefulness of these methods.

Introduction

The two classical methods of science are experimental investigations and development of theories. With the availability of fast computers simulation methods appeared as a third pillar of science: Model calculation is a powerful mediator between the two classical methods which provides a better understanding of molecules on a molecular scale. In addition, the outcome of numerical calculations mostly exceeds the spectrum and resolution of experimental investigations which allows to check existing theories in detail and to give guidelines for new theories. For example, the second osmotic virial coefficient A_2 can be extracted from the slope in a diagram π/c vs. c, with π: osmotic pressure and c: concentration. Exact enumeration of (overlapping) pairs of model chains[1] yield the excluded volume u which is directly related to A_2 by $A_2 = u \cdot N_A /(2M^2) \sim u / N^2$. Theory[2] predicts a scaling law behavior of A_2 (or u / N^2) with respect to the molecular weight M (or chain-length N), the exponent reading ca. –0.2 in case of an athermal (i.e. good) solvent. Actually, experimental[3] and numerical[4] data fairly well obey this law showing that the model used in the numeric calculations obviously makes sense. Now, the simulations in addition yield distance dependent

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qualities like the pair distribution function[5] which predicts a rather good compatibility of chains even in close vicinity. This is in contradiction to simple theoretical approach based on gaussian chains[6] but further distance dependent qualities give an explanation of this behavior[7-9]; the details are beyond the scope of this paper but the example nicely shows the common proceeding: direct or indirect verification of the model with the aid of experimental results and going into depth in order to obtain a realistic picture on a molecular scale simultaneously testing and/or developing theories on this level.

In the following a short introduction to the field is given (for further reading, e.g. see[10]) and selected topics of our own work (original as well as literature data) are presented in order to exemplify the benefit of Monte Carlo simulation studies based on simplified models of polymers.

Simulation of Polymer Systems

Quantum mechanical calculations from first principles may be used for the evaluation of the energy of configurations as a function of the position of atoms and thus for the determination of the configuration of minimum energy. This is an important task for the development of catalysts etc. Approximations are minimal but with increasing chain length the calculations become enormously exhaustive making these methods unsuitable for large molecules, at least in the moment. Molecular dynamics is based on the numerical integration of the equations of motion. The trajectory of the system in phase space is deterministically calculated and the interesting quantities are obtained as time averages (typically over pico to nanoseconds). Monte Carlo simulations on the other hand explore the phase space in a stochastic manner. Therefore, an ensemble average is obtained from a large number of randomly taken snapshots of the system. As unphysical movements are allowed, Monte Carlo techniques are less suitable for the calculation of dynamic properties, but the exploration of phase space is extremely efficient. Thus, as long as static properties are of interest only, they are the methods of choice.

The details of the calculation are dependent on the concentration regime which should be simulated. For the limiting case of an infinitely diluted solution intermolecular interactions between the dissolved molecules may be neglected and the situation is characterized by a single chain surrounded by (implicit) solvent. For finite concentrations a manybody system is used applying periodic boundaries. The limiting slope of concentration dependence in the range of highly diluted solutions may be

calculated from isolated pairs of molecules as mentioned above.

Clearly, we would like to portray nature as perfectly as possible, for example by an atomistic simulation using appropriate force fields. The total potential energy in such calculations is the sum of terms regarding bond length, bond angles, torsional angles as well as nonbonded interactions like van der Waals interactions. Comparing the benzene and the polystyrene system in Figure 1, the differences are quite obvious: The benzene molecule is fairly small compared to the box-size and a simulation run will give useful results. The styrene oligomers, however, extend over the whole box (being of equal size as is case of benzene) and the chains interact with their own periodic images which clearly will distort the results. Thus, a much larger box is necessary in this latter case and when proceeding from an oligomer to a polymer the number of essential terms will exceed nowaday's possibilities if all the details are regarded in full.

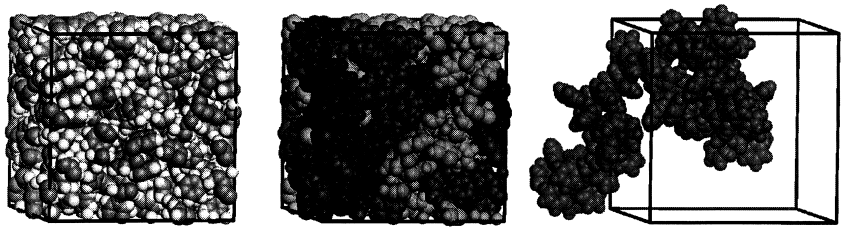


Figure 1. Snapshots of benzene at 298K (left diagram) and of some sort of melt of 60-mers of styrene at 400K as calculated with Materials Studio (Accelrys Inc.). In case of benzene different gray scales are used for the atoms C and H; in the middle and right diagram, the three oligomers are differently colored. Molecules or atoms, respectively, in the central box (original or periodic images) are shown in the left and middle box; in the right box only one of the three chains (disregarding periodic boundaries) is depicted.

Therefore, we have to make some simplification of the model, either by treating groups of atoms (for example CH_3-, CH_2- etc.) as a single unit (united atoms model) or by combining groups of monomers to single segments (coarse grained chains). This procedure only slightly diminishes the gap between the length scale of bonds and global size but it significantly reduces the number of energy terms which have to be calculated. The procedure makes sense for several reasons, the two most important being: (1) chain molecules have a very large number of internal degrees of freedom and therefore a practically indefinite number of possible configurations making the details of interaction of minor importance for general properties; (2) the chain length (or the number of segments of the model chain) serves as an independent parameter which allows the

calculation of a wide range of universal features depending on this parameter. Clearly, as chemical details get lost it is not possible to calculate particular properties of *specific* polymers. Nevertheless a large number of *universal* features may be calculated, e.g. scaling laws with respect to chain length.

To conclude, for this type of calculations a real macromolecule is substituted by a model chain consisting of segments, e.g. some sort of pearl necklace with hard beads in order to comply with the excluded volume effect surrounded by soft shells which define the radius of interaction. In this way the energy calculation may be traced back to counting contacts; the choice of the energy associated with a specific contact is characteristic of the solvent quality and allows the realization of different sorts of monomers. By locating the segments in some lattice we end up at the most efficient model of polymers for Monte Carlo simulations. In any case, each contact between segments of a self-avoiding configuration is attributed an energy $\varphi \cdot kT$ and the total energy E_i of configuration i equals $E_i = C_i \cdot \varphi \cdot kT$ (C_i..number of contacts, k..Boltzmann constant, T.. temperature). The energy parameter φ characterizes the gain or loss of energy accompanied by forming a contact between two segments (not adjacent along the chain) which previously were surrounded by solvent molecules; thus positive φ values characterize an exothermal solution (contacts avoided) and negative ones an endothermal solution (contacts forced) while $\varphi = 0$ represents an athermal system, portraying a polymer in a good solvent. The theta solution, on the contrary, is defined by (pseudo)ideal behavior expressed by $A_2 = 0$ and/or a direct proportionality between mean square dimensions and chain length.

The most simple approach to a model chain is a self avoiding walk grown step by step: bond vectors are chosen at random and the segments are added one after the other; if a double occupancy occurs before the desired chain length is reached it is rejected (because of the excluded volume effect) and a new trial is performed starting with a "monomer". As the statistical weight of each accepted configuration is given by its Boltzmann factor, $e^{-E_i/kT} \equiv e^{-C_i \cdot \varphi}$, in case of endothermal solutions (characterized by negative energy parameters) a few chains with a rather large Boltzmann factor may determine the properties of the whole ensemble. This problem (which is common to all static methods building chains from scratch) may be overcome by resorting to dynamic methods realized by the famous Metropolis-Rosenbluth algorithm[11]: Starting with an arbitrary configuration further configurations are drawn from an equilibrium distribution

by transforming a configuration into another one according to some transition probability deduced from two basic principals, ergodicity and detailed balance; omitting details we arrive at the rule: If the energy of the new configuration is smaller than or equal to the energy of the old one the new configuration is accepted, if not, it is accepted with the probability given by the Boltzmann factor of the energy-difference only. Thus, instead of weighting chains which have been chosen with equal probability, the configurations are selected according to their correct probability; as a consequence, all chains in the ensemble have the same statistical weight and the ensemble average is obtained from the (unweighted) sum. Clearly, a certain number of relaxation trials have to be performed in order to reach equilibrium before data sampling is started.

Both methods clearly have advantages and disadvantages. Static methods generate statistically independent chains making an error analysis straightforward. However, they are subject to the problem of a weighted average and apart from very special problems step-by-step methods are not suited for manybody systems.

In dynamic methods a system is transferred into a new system by some relaxation mechanism. Thus, the data are highly correlated which has to be considered in the error analysis via autocorrelation times or block averages which makes things more complicated. Averages, however, are simple averages and – which is most important – dynamic methods are appropriate for manybody systems as well (actually the Metropolis Rosenbluth algorithm was developed for a manybody system).

Relaxation mechanisms are clearly dependent on the specific model used. In the cubic lattice microrelaxations may be performed, like L-Flips or U-Flips or end-group rotations.[12] Alternatively or in addition, reptation may be used which means that the chain is moved along its own contour by removing one segment on the one end and adding a new segment at the other.[13] All these moves need empty sites and therefore are restricted to volume fractions $\phi < \approx 0.8$. For $\phi = 1$ (which might be regarded as a useful model of a polymer melt) other relaxation mechanisms[14] must be used which are based on reactions between segments of the chain, for example metathesis or substitution or dimerization followed by cleavage (the latter two also working intramolecular). These pseudokinetic relaxations are highly efficient. Starting from a system completely ordered in form of rigid rods the typical spaghetti like structure is obtained after a few relaxation trials per segment.

Examples

1) *Mean square dimensions as a function of volume fraction*

By use of a mixture of microrelaxations and pseudokinetic relaxations we were able to investigate the whole range of concentrations with extremely high precision. A lot of quantities characteristic of size, shape, microstructure etc. have been obtained.[15] As an example in Figure 2(a) the mean square radius of gyration $\langle s^2 \rangle$ vs. volume fraction ϕ is shown for athermal conditions, theta conditions and (for comparison) for ideal chains represented by so called non reversal random walks (chains whose segments may freely intersect; only backfolding of succeeding bonds is forbidden). In case of high dilution, the chains are much more expanded in a good solvent than in a theta solution (where the effect of the excluded volume is exactly compensated by an increased number of contacts between segments). In the athermal solution the intramolecular excluded volume effect (which is responsible for the expansion of the coils) with increasing concentration enters into competition with the intermolecular excluded volume effect – exercised by the surrounding chains – which leads to a compression of the coils. At $\phi = 1$ no solvent is left and the compensation of both effects should be perfect. Therefore, due to Flory,[16] in the melt the dimensions should coincide with those in an (infinitely diluted) theta-solution. Actually theta-dimensions are already obtained for $\phi \approx 0.7$ which is often used as an argument that this situation already represents a polymer melt. For $\phi = 1$, however, the dimensions are definitely smaller due to specific packing effects. The effect, however, is small and surely not easy to verify experimentally. The same holds true for theta conditions: As no solvent is left at $\phi = 1$ the curve coincides with the athermal one in this region; for small concentrations the dimensions slightly increase due to favorable intermolecular contacts between different chains. Anyway, theta-chains are larger than ideal chains because their segments have to avoid each other on a local scale, although both clearly obey the same scaling law (mean square dimensions are directly proportional to molecular mass or chain-length, respectively) according to the definition of theta conditions.

It should be noted that the initial slope of concentration dependence of any property may be calculated from pair data if the pair distribution function is known as well as the property of interest as a function of the distance between two coils.[7] This completely different approach predicts the results of a direct simulation with perfect precision (see Figure 2(b,c) and[17] which may be regarded as a mutual confirmation of both methods.

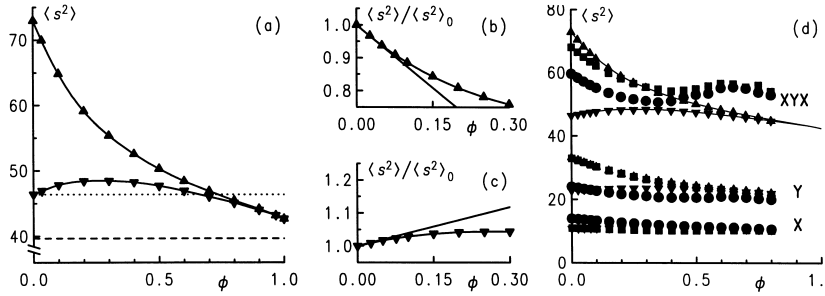


Figure 2. (a) Mean square radius of gyration $\langle s^2 \rangle$ vs. volume fraction ϕ for athermal (▲) and theta conditions (▼) taken from ref.[15]; ideal chains for comparison (dashes). (b,c) $\langle s^2 \rangle$ in multiples of $\langle s^2 \rangle_0$ of isolated chains; the straight lines result from pair data[17]. (d) $\langle s^2 \rangle$ of the whole chain (XYX), the middle block (Y) and the outer block (X) for triblocks ABA[17] (■) and BAB (●) as well as athermal (▲) and theta (▼) homopolymers.

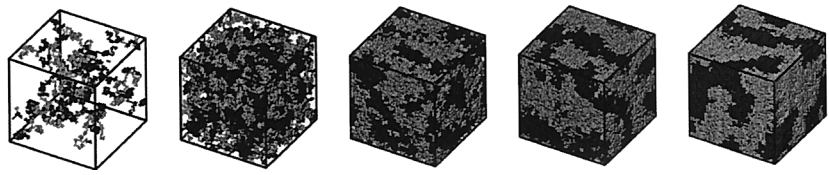
2) *Polymer blends*

Another example is the simulation of polymer blends. Here we have two sorts of polymers with repulsive interaction between their segments. By use of the pseudokinetic relaxation mechanism the simulation can be done without additional solvent because no empty sites are necessary for relaxation. For any initial distribution of chains over the system demixing occurs and an interface develops which remains fairly in place during the whole simulation (strictly speaking, two independent interfaces are developed because of the periodic boundaries used). This type of simulations aims at a characterization of the interface[18] as well as at the separate evaluation of chain properties in the interface[19] and in the bulk phase.[20]

3) Copolymers in selective solvents

Further highly interesting systems are copolymers in selective solvents, e.g. see ref.[17] and references cited therein. In Figure 2(d) the concentration dependence of the mean square radius of gyration of blockcopolymers of type ABA[17] and BAB[21] (the number of segments reading 40-80-40) is shown. The A and the B segments are repulsive for each other and the solvent is a good one for the A and a bad one (actually a theta solvent) for the B segments. Not unexpectedly, the average size of single triblocks is in between the values of the homopolymers. With increasing concentration the dimensions decrease but then they increase again and become similar for both systems as the effect of the solvent levels off making the situation symmetric at $\phi = 1$. (Microrelaxations and reptation were used exclusively in this investigation in order to avoid polydispersity, so the curves have to finish at $\phi = 0.8$). The increase of dimensions of the triblocks at

higher concentrations is a very interesting effect which becomes still more interesting when taking a look at the mean square dimensions of the individual blocks which act like the blocks of the homopolymers. Therefore, the increase of the dimensions of the whole chain obviously is caused by orientation effects: the blocks tend to separate. If the blocks would not be linked together demixing would occur as in case of polymer blends. However, the blocks are connected so that only microphase separation is possible. This can be shown by the concentration dependence of several parameters, but the most impressive way is to visualize snapshots of configurations as shown for the BAB system in Figure 3 (visualization by use of POV-ray, http://www.povray.org): With increasing concentration dark and pale regions develop which are well separated and some sort of lamellar phases can be seen. The behavior of the ABA system is quite similar (see[17]).



$\phi = 0.025$ $\phi = 0.20$ $\phi = 0.5$ $\phi = 0.65$ $\phi = 0.80$

Figure 3. Visualization of snapshots of BAB triblock copolymers the volume fraction indicated in the figure; A segments are marked gray, B segments black.

4) *Size and shape of linear and star-branched polymers*

As a last example we focus on the size and shape of linear and star-branched polymers. These simulations were done in the tetrahedral lattice which allows the generation of star branched chains with up to 12 arms by extending the hard core to the neighbors of the central segment.[22] The relaxation mechanisms was a mixture of microrelaxations[23] and the highly efficient pivot algorithm.[24] Theoretical approaches usually refer to infinite chain-length while numeric data always are subject to short-chain effects. In order to obtain reliable results by extrapolation chain length should be as large as possible; thus chains and stars with up to ca. 8000 segments have been produced.

Flory[25] postulated a power law dependence of mean square dimensions of athermal chains with respect to the number of bonds N, i.e. $\langle s^2 \rangle \sim N^{6/5}$. Thus, the ratio $\langle s^2 \rangle / N^{1.2}$ taken from Monte Carlo simulations and exact enumeration[26] depicted in Figure 4(a) should be a constant and independent of N. Actually, there exists a plateau for a certain range of small chain length in which the law appears to be verified and the absence of short-chain effects is pretended. Passing to longer chains, however, a deviation from the

plateau value is seen which increases with increasing chain length. Obviously, the predicted exponent 1.2 cannot be fully correct. Nowadays a slightly smaller theoretical value 1.176 is generally accepted for the limit of infinitely long chains and the functional form of the short chain correction (the leading term is linear in $N^{-0.46} \approx N^{-0.5}$) is known.[27] As can be seen in Figure 4(b) Monte Carlo data confirm that law, however, for the determination of intercept and slope (yielding the leading "short" chain correction term) rather long chains are necessary. The data shown in Figure 4 refer to linear chains, but mean square dimensions of star shaped chains obey exactly the same form of chain length dependence.[28]

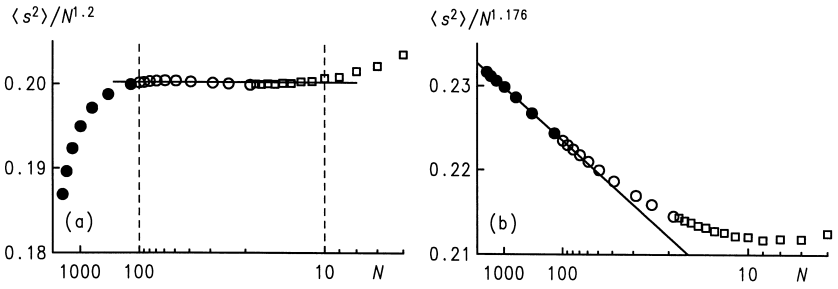


Figure 4. $\langle s^2 \rangle / N^{2\nu}$ vs. $1/\sqrt{N}$ with $2\nu = 6/5 = 1.2$ (left) and $2\nu = 1.176$ (right). Full circles are taken from ref. 28, squares from ref. 26, open circles are original data[21].

The squared radius of a stars usually is compared to the squared radius of a linear chain with the same overall number of segments. Interestingly, for athermal systems these so called g values obey the Zimm-Stockmayer[29] law which was evaluated for ideal stars while g values of theta stars are larger. These results are in full accordance with experimental investigations.[30] Thus it makes sense to discuss the instantaneous shape of chains and stars (a problem which is not experimentally solvable yet) on the basis of simulation data. The extention of an equivalent sphere whose radius is characterized by the radius of gyration gives an impression of the size of the molecule. In order to consider a nonsymmetrical behavior individual chains may be replaced by an equivalent ellipsoid instead of an equivalent sphere using a procedure introduced by Šolc and Stockmayer.[31] Based on the components of the squared radius of gyration along the principal axes of this ellipsoid several quantities characterizing the shape of configurations may be defined which show that individual configurations of linear chains are rather asymmetrical in shape; the asymmetry decreases with an increase of the number of arms, stars with an infinite number of arms finally being perfectly

symmetric.[28] Furthermore, an unambiguous correlation between shape and size is observed: symmetric coils are always compressed while asymmetrical chains are of extended size.[32]

Conclusions

Although programs are available which are suitable for simulations on a more or less fully atomistic scale (which clearly are highly valuable if proper used) at least for dense systems one has to be extremely careful in correctly setting up the system; when the size of the simulation box is made large compared to the size of the molecules (a necessary prerequisite) a treatment of dense systems consisting of long polymers currently seems out of reach. Nevertheless useful investigations may be performed by use of simplified models as long as universal features are of interest.

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