

Deviations from chain ideality:
Are they detectable in simulations and
neutron scattering of polyisobutylene?

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*To my daughter,
Henriette Jacobia*

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1 | Résumé de la thèse

Introduction

Selon l'hypothèse d'idéalité de Flory, les chaînes de polymères flexibles à l'état fondu se présentent sous la forme de marches aléatoires à trois dimensions, aussi appelées pelotes gaussiennes. Cette hypothèse suppose que toute information relative à la conformation locale (c.-à-d., les angles de liaison ou angles de torsion) subit une décroissance exponentielle le long de la chaîne principale et, par conséquent, n'a aucune influence sur la conformation à grande échelle. De plus, il est avancé que l'écrantage du volume exclu par les chaînes voisines compense tout effet de gonflement. Des expériences de diffusion neutronique (DN) effectuées il y a une trentaine d'années confirment que les polymères adoptent bien des configurations gaussiennes. S'ensuit l'un des piliers de la théorie des polymères : En solution "suffisamment dense" tout polymère flexible peut être décrit comme une marche aléatoire à trois dimensions, indépendamment de sa structure chimique, et ce, après un rééchelonnage adéquat.

Les progrès réalisés dans les domaines des techniques de simulation et de la puissance informatique ont rendu possible l'étude de chaînes très longues. Ceci a permis d'observer de plus près la structure des chaînes de polymère à l'état fondu et révélé une déviation par rapport à la chaîne idéale. Cette déviation est faible, par conséquent un soin extrême est nécessaire pour la distinguer du bruit.

Jusqu'à présent, la déviation par rapport à la structure gaussienne a uniquement été étudiée dans le cas de modèles à gros grains, par simulation et calcul analytique. La présente thèse cherche à vérifier si ces déviations peuvent également être mesurées à l'aide de simulations atomistiques réalistes et d'expériences de DN modernes.

Modèle de simulation

Nous avons choisi d'étudier le polyisobutylène (PIB) pour plusieurs raisons ; il a été largement étudié et caractérisé par le biais de théories et d'expériences et il fait figure de candidat idéal en ce qui concerne l'analyse de sa structure à l'aide de la technique de DN. En outre, le choix du PIB est historiquement pertinent, car Flory a publié des données relatives à ce polymère pour démontrer son hypothèse d'idéalité.

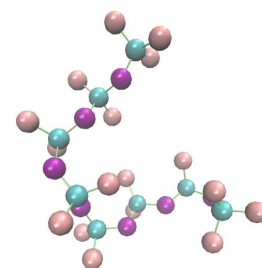


Figure 1.1: Une chaîne PIB simple représentée sous forme d'atomes unifiés. Les groupes de méthyle sont illustrés sous forme de billes orange, les groupes de méthylène sont violets et les atomes quaternaires C sont turquoise. La taille des billes n'a pas été mise à l'échelle.





Nous avons simulé le PIB à l'aide d'un modèle existant dans lequel les atomes d'hydrogène ne sont pas représentés explicitement, mais regroupés avec leurs atomes de carbone respectifs afin de former des amas d'atomes unifiés (AU). Une molécule PIB représentée sous forme d'AU est illustrée dans la figure 1.1. Même simplifiée, la structure monomère des atomes unifiés est complexe et les simulations prennent du temps. Il est nécessaire de rassembler de nombreuses données relatives aux chaînes longues, afin d'observer les déviations ; cependant, le temps nécessaire aux simulations de chaînes longues augmente significativement pour les modèles de polymères plus complexes. Les modèles à gros grains, tels les modèles à billes et ressorts (BR), manquent d'informations chimiques et, par conséquent, il est plus aisé d'équilibrer et d'acquérir un nombre raisonnable de configurations de chaînes indépendantes.

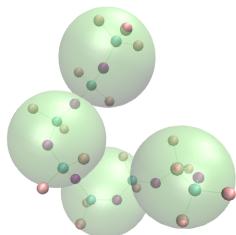


Figure 1.2: Les grandes sphères vertes représentent le modèle à gros grains, dans lequel nous avons introduit les informations atomistiques du PIB.

Nous avons commencé par simuler un modèle BR, doté d'une rigidité similaire à celle du PIB ; Nous avons développé des algorithmes pour ajouter progressivement des informations atomistiques, selon un modèle à « grains fins » (cf. figure 1.2). Cette méthode nous a permis d'engendrer un grand nombre de configurations de chaînes.

Déviations de l'hypothèse d'idéalité

Ainsi que nous l'avons expliqué précédemment, de récentes études ont démontré l'existence d'une déviation de la structure des chaîne de polymère par rapport à la pelote gaussienne. Les interactions de très courte portée, résultant de l'incompressibilité du fondu, peuvent agir entre monomères distants le long du contour ce qui entraîne un gonflement de la chaîne. L'effet de ces interactions peut être observé dans le cadre de la fonction de corrélation d'orientation des liaisons ainsi que du facteur de forme.

Fonction de corrélation d'orientation des liaisons

La fonction de corrélation d'orientation des liaisons mesure la façon dont les informations sur la conformation locale décroissent le long de la chaîne principale. En cas d'absence d'interactions de longue portée le long du contour, la fonction de corrélation doit diminuer de façon exponentielle. La figure 1.3 illustre un comportement en loi de puissance, dans la dernière partie de la fonction de corrélation. L'exposant de la loi de puissance équivaut à $-\frac{3}{2}$, conformément à la non-idéalité prévue. Le ralentissement de la décroissance des informations résulte des interactions entre monomères distants le long du contour. Afin d'exclure les effets de bout de chaîne, il est essentiel d'étudier des polymères de longueur suffisante ; de plus, il est nécessaire de calculer la moyenne de la fonction de corrélation d'orientation des liaisons en se basant sur un grand nombre de configurations de chaîne, afin de pouvoir détecter un signal clair.



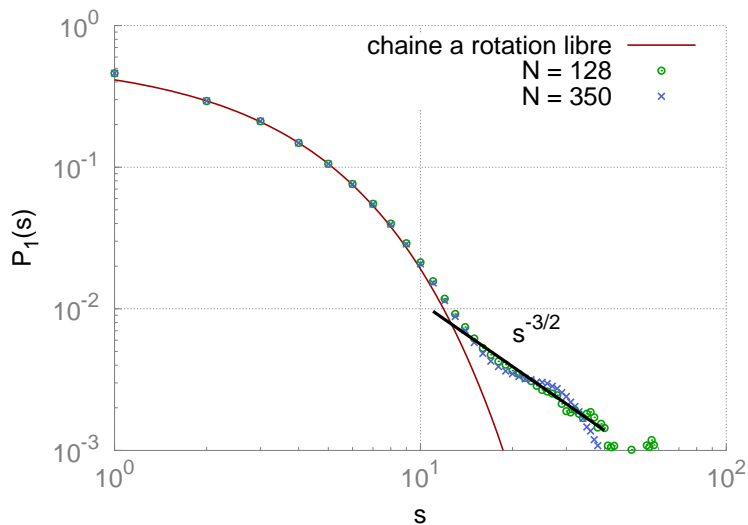


Figure 1.3: Fonction de corrélation d'orientation des liaisons. s représente le nombre de liaisons séparant les segments ; la ligne rouge représente la décroissance exponentielle des chaînes idéales et la ligne noire indique la loi de puissance.

Facteur de forme

Il est absolument nécessaire de comparer nos simulations avec des données expérimentales. Pour ce faire, nos collaborateurs à Knoxville, aux États-Unis (Tennessee), ont rassemblé des données résultant de la diffusion des neutrons aux petits angles (DNPA) sur un PIB. Jusqu'à présent, les données DNPA soumises aux méthodes d'analyse usuelles ne se sont pas avérées concluantes. Les simulations offrent l'occasion incomparable non seulement d'analyser les données en espace réel, mais également d'utiliser les mêmes configurations de chaîne pour calculer le facteur de forme. Nous sommes en mesure de calculer le facteur de structure d'après les simulations ; cependant, il se peut que le modèle AU, adapté aux simulations, ait un facteur de structure différent. En ajoutant des atomes d'hydrogène explicites au modèle AU, le facteur de structure simulé peut être directement comparé aux données résultant de l'expérience. Cela nous aidera à mieux comprendre comment la diffusion est affectée par les effets de non-idéalité. Nous espérons que le passage de l'espace réel à l'espace réciproque permettra de démontrer la non-idéalité des chaînes polymères.





2 | Introduction

A cornerstone of modern polymer physics is Flory’s famous “ideality hypothesis” which states that a chain in a melt behaves as if all intra-chain excluded volume interactions were absent [1–3]. It is generally accepted that any local conformational information (i.e. bond angles or torsional angles) decays exponentially along the chain backbone and thus has no influence on the long range conformation. However, recent theoretical [4, 5] and computational [5–9] results for models of long and flexible polymer chains indicate that there exist deviations from ideal behavior. These deviations stem from the incompressibility of the melt which leads to an incomplete screening of the excluded volume interactions by the surrounding chains. The non-ideality of the chains impacts the conformational properties of polymer melts on intermediate length scales. Static quantities such as the bond-bond orientational correlation function, the pair distribution function and its Fourier transform, the form factor, show deviations from the ideal chain hypothesis.

The non-ideality of polymer chains has been extensively studied by means of highly flexible coarse-grained models, such as the bond fluctuation model (BFM) and bead spring model (BS). The results from the coarse grained simulations concur with the analytically predicted deviations [5–9]. These models are so close to the idealized chain (highly flexible and the units (beads) are point-like), that deviations from ideality caused by residual excluded volume interaction are easily identified as such. Real polymers, on the other hand, have a non-negligible stiffness and monomer cross-section. These finite size effects skew the chain properties so that they can no longer be approximated by idealized chain models, which in turn makes it more delicate to differentiate the effects of the residual excluded volume.

To this date residual excluded volume effects have not been experimentally investigated. The work at hand attempts to bridge the gap between coarse-grained simulations and experimental data by implementing an atomistically realistic polymer model. To differentiate between effects caused by chain stiffness and monomer cross-section, and those caused by the incomplete excluded volume screening we additionally employ a chain model that neglects all excluded volume effects, namely the rotational isomeric state model [3]. The insight - gained from the simulations - on how the residual excluded volume affects the structure of real chains can then be directly applied to the analysis of experimental data.

We had to choose one exemplary polymer for this study and the





choice fell on Polyisobutylene (PIB) $\text{CH}_3\text{-[4C8H]}_N\text{-H}$ for a number of reasons. It is a polymer whose conformational and dynamic properties have been exhaustively studied both experimentally [10–33] and theoretically [28, 34–40]. For our purposes it is important that the polymer is flexible and has no electrostatic interactions as this would slow down the simulations considerably. We implemented a recently published united atom model of PIB by Tsolou et al. [40], which reproduces the static and dynamic quantities of PIB extremely well.

The presented work focuses on a specific polymer, however we feel that the potential is much broader. Revealing the corrections to chain ideality for PIB should lend confidence to the possibility to detect these universal corrections also in other polymers, thereby stimulating further research in this field, not only for homopolymers but also for polymer blends [41] or polymers in confined geometry (films [42, 43] or pores [44]) where the corrections are predicted to be much larger than in the three-dimensional bulk [4, 43].

The computational challenge of this work is to simulate very long PIB chains. This is necessary to distinguish the effects of chain stiffness and cross-section from the effects of non-ideality. We work with the united-atom (UA) model introduced by Tsolou et al. [40]. Explicit hydrogen atoms do not influence the chain structure and the eight additional particles per monomer would only slow down the simulation. In chapter 3 the UA model is thoroughly discussed and the chain and melt properties analyzed.

In chapter 4 we introduce the computational methods used to tackle the challenge of equilibrating systems consisting of chains of up to $N = 350$ monomers — over four times longer than what has been simulated up to this date. In the same chapter we discuss how we added the explicit hydrogen atoms to our UA model in an effort to correctly reproduce the structure factor as it is measured in small angle neutron scattering experiments (SANS). The final computational method we introduce is the Rotational Isomeric State Monte Carlo “RIS-MC” model. This model is true to chemical detail, but neglects excluded volume interactions, making it a valuable counterpart to the molecular dynamics simulations.

To set the simulations into experimental context, SANS measurements of PIB were performed by our collaborator, and analyzed in the scope of this thesis. Chapter 5 details the challenges of interpreting the SANS data and the comparison to the simulation.

The result of this work is discussed in chapter 6, where we analyze the simulation data in the light of non-ideality effects and attempt to do the same with the experimental data comparing both to theoretical predictions.

Flory’s ideality hypothesis is manifested in the 1983 publication by Hayashi et al. [17] which shows that the RIS predictions and the SANS data concur. By reproducing the RIS model according to Vacatello and Yoon [39] and evaluating the effect of polydispersity on the scattering picture we are able to shed a new light onto the past results.

An overview of the results of this thesis and an outlook onto future





projects is given in the final chapter 8.



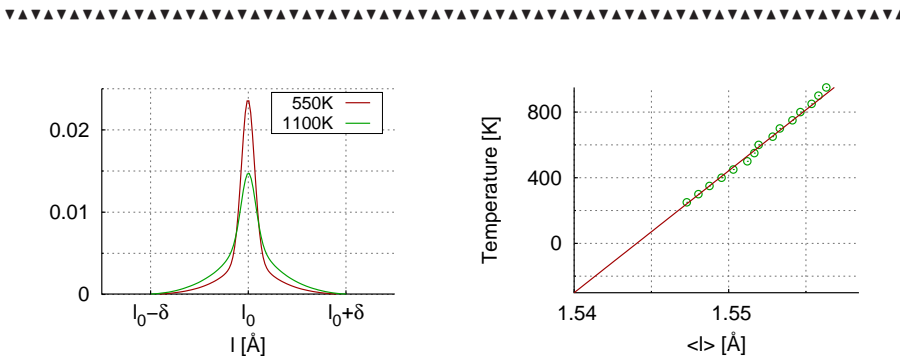


Figure 3.5: The images above show the temperature dependency of the bonds. The left-hand-side shows the bond-length distribution for the bonds regulated with the SHAKE algorithm. The equilibrium length l_0 is 1.54\AA and the tolerance $\delta = 0.001\text{\AA}$. With rising temperature the distribution becomes wider, but does not exceed the tolerance. Even for temperatures as high as 1100K the SHAKE algorithm is stable. The plot to the right shows the mean bond-length of the harmonic bond at varying temperature. The red line is a guide to the eye and shows that a bond-length of 1.54\AA would be reached at the fictitious temperature of -300K , if the dependence would continue to be linear at even lower temperatures.

fig. 3.5 compares the bond-length distribution at different temperatures. Though the distribution becomes wider with rising temperature, the mean bond-length does not drift and the distribution does not exceed $l_0 + \delta$. This proves that even at very high temperatures, here 1100K , the SHAKE algorithm is reliable. For the harmonic bond the equilibrium value of $l_0 = 1.50\text{\AA}$ is suggested. Tsolou et al. argue that due to the steric repulsion of the methyl groups the bond will stretch and its resulting mean value will be equal to that of the SHAKE bonds. Our analysis shows that the bond is stretched even further, exceeding 1.54\AA at all temperatures. On the right in fig. 3.5 the temperature dependence of the mean harmonic bond length is plotted. The extrapolation to low temperatures indicates that a bond length of 1.54\AA cannot be reached under normal circumstances. Most simulations were performed at 550K . At this temperature the harmonic bond has a mean length of 1.552\AA and is 0.012\AA longer than the SHAKE controlled bonds. The deviation is less than 1%, so we continued with the suggested parameters.

Angle potentials

The angles defining the architecture of the PIB monomer have been studied by x-ray scattering [50]. The results show that the angles inside the monomer are dihedral angles of 109.47° (angles a)-f) in fig. 3.6) and the interdial backbone angle (angle g) in fig. 3.6) has a mean value of 128° . To construct the monomer six angle potentials must be applied to each monomer and an additional angle potential regulates the backbone angle connecting two monomers. All seven angles, a) through g), are shown in fig. 3.6. They are regulated by a harmonic bending potential

$$U_{\text{angle}}(\theta) = K_\theta(\theta - \theta_0)^2 \quad (3.4)$$

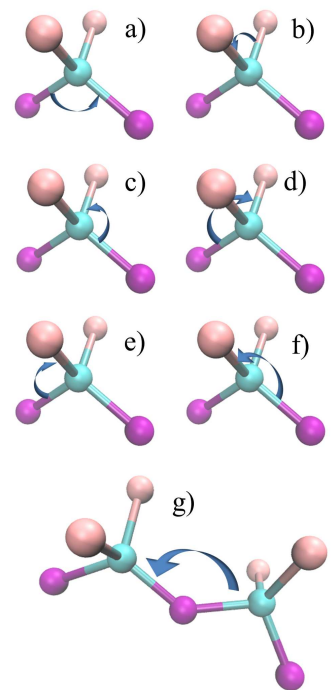


Figure 3.6: The panels above are to help visualise the seven applied angle potential. All angles a) through f) are set to the tetrahedral value, while the backbone angle g) is wider.

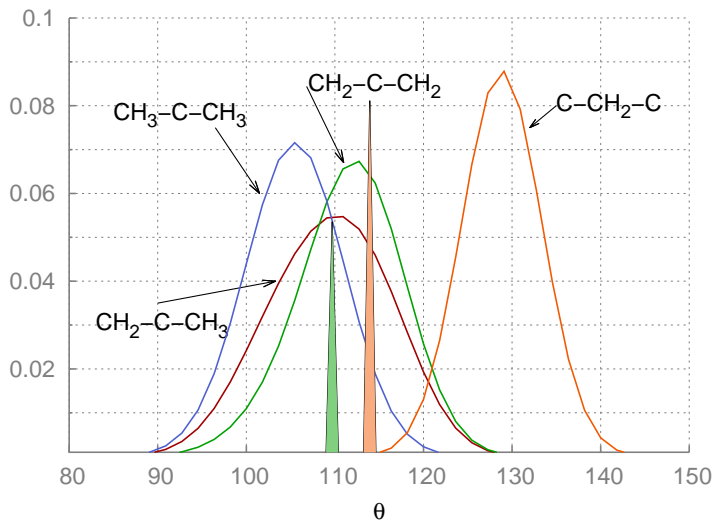


Figure 3.7: The angle distributions are distorted from their equilibrium values 109.5° and 114° due to the excluded volume interaction of the beads. The mean values of the backbone angles are $\theta^a = 112^\circ$ and $\theta^g = 129^\circ$ at 550K. The filled curves are the expected distributions for the tetrahedral angle (green) and the interdiad angle (orange). They are calculated with $\exp(-U_\theta/k_B T)$ and for reasons of legibility not drawn to scale.

where the bending constant K_θ is the same for each angle and can be found together with the equilibrium values θ_0 in table 3.1. As with the bonds the excluded volume interaction of the UA beads interferes with the applied potentials which leads to the mean angle widths being distorted from their chosen equilibrium values. All angles inside the monomer, connecting the methyl and methylene groups with the quaternary C atom, are set to the tetrahedral angle $\theta_0^{a-f} = 109.47^\circ$ while the bond angle between two monomers is set to the equilibrium value of $\theta_0^g = 114^\circ$. Methyl crowding stretches the backbone bond angles θ^a and θ^g further so that their mean values at 550K are 112° and 129° , respectively. Fig. 3.7 shows the distribution of all angles to visualise the distortion from the equilibrium values. Tsolou et al. published the value of $\theta^a = 110^\circ$ which contradicts our findings. For the average over all tetrahedral angles θ^{a-f} however we find 109° which leads to the assumption that Tsolou et al. calculated the mean over all six dihedral angles $\theta^{(a)-f}$ as opposed to only the intradiad back-bone angles θ^a . Though the mean angle widths slightly stray from the values found experimentally, it is not expected that this gravely influences the global chain structure.

Torsional potential

The probability distribution of the torsional backbone angles (ϕ) is of great importance to the structure and influences such key quantities as the chain stiffness. Section 4.3 discusses the torsional distribution in great detail. The backbone dihedral has two preferred states, the gauche



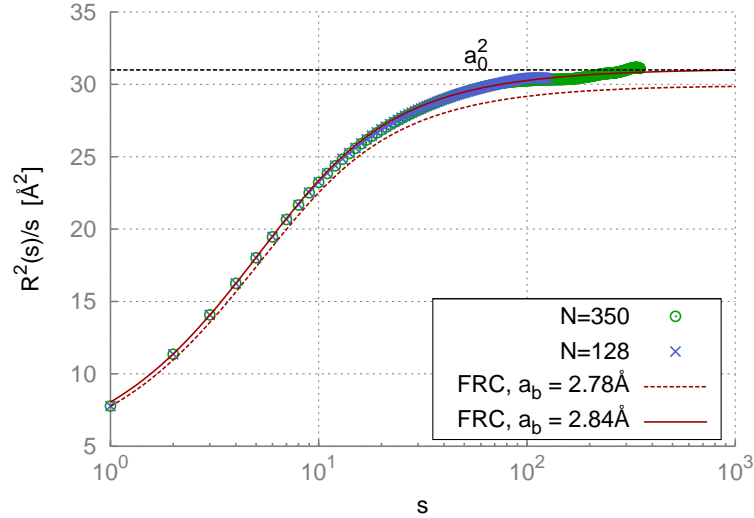


Figure 3.12: The intra chain distances with the fit of eq. (3.17) .

barostat. The equations of motion are those published by Shinoda [52] which are propagated by the time integration method introduced by Tuckerman [53] which is a slightly modified Verlet integrator. The integration step length is set to 2 fs if not indicated otherwise. LAMMPS calls for damping parameters of the temperature and pressure. These parameters are in time units and influence how strongly fluctuations from the goal values of temperature and pressure are damped. It is important to choose these parameters with care as to avoid oscillations in the system. The temperature damping constant is $t_{\text{damp}} = 300\text{fs}$ for all systems and temperatures. The pressure damping constant p_{damp} was chosen depending on the size and density of the system by

```
Lammps sample code:
fix all npt temp 550.0
550.0 300.0 iso 0.9869
0.9869 20000.0
```

$$p_{\text{damp}} = \frac{3}{2\pi} \frac{M^{5/6}}{\sqrt{k_B T}} (\nu n_{\text{atoms}})^{1/3} \quad (3.18)$$

where $M = 23.3 \times 10^{-27}\text{kg}$ is the average mass per UA bead, k_B is the Boltzmann constant, T is the temperature, n_{atoms} is the total number of UA beads in the System and ν is the specific volume of the system. In all performed simulations the pressure is set to 1 atm.

3.3.1 Static quantities

Given the nature of their research Tsolou et al. had to pay special attention that the density of the PIB melt is correctly reflected by the simulation. The density of polymer melts varies with chain length and temperature.

The end groups of polymer chains occupy a larger volume than intra-chain monomers that are flanked by neighbouring groups at each side. A melt that consist of short chains accommodates more chain-ends per unit volume then a melt of longer chains. Thus the volume is larger in the melt of short chains and the density is lower. The chain length



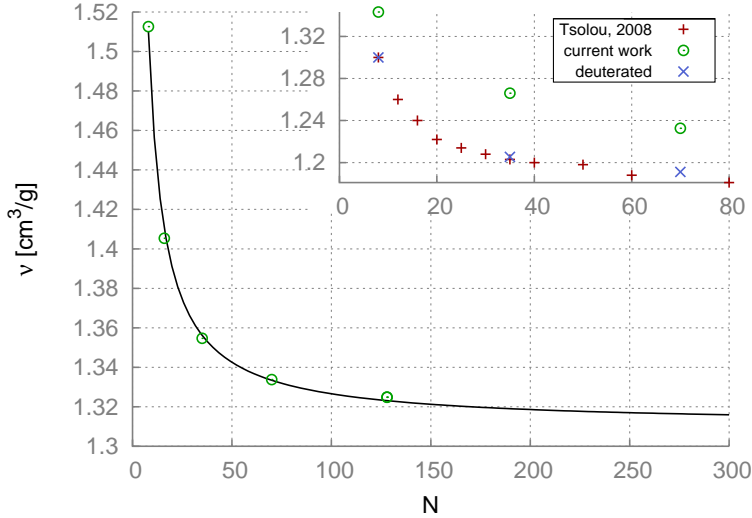


Figure 3.13: The specific volume ν is dependent on the chain length. The plot shows ν for different chain length at 550K. The line is the fit of eq. (3.19) to our data. Inset: To compare with Tsolou's data we evaluated the specific volume at 450K and notice that our data is off set to larger values compared to that presented by Tsolou. When the calculation is done for deuterated PIB our data coincides with that of Tsolou.

dependence of the specific volume ν is described by

$$\nu = \nu_{\infty} + \frac{\nu_0}{N} \quad (3.19)$$

with ν_{∞} being the limit for very large chains [31]. A fit of eq. (3.19) to our data produces $\nu_{\infty} = 1.31 \text{cm}^3/\text{g}$ and $\nu_0 = 1.60 \text{cm}^3/\text{g}$. Tsolou et al. conducted the bulk of their simulations at $T = 450\text{K}$, so to compare with their findings we also simulated three systems at 450K. Though the shape of the curve is the same as that published by Tsolou, our data is off set to a higher specific volume. Flabbergasted as to why this might be, we finally came to the conclusion that Tsolou et al. did their volume calculations for deuterated polymers ($\text{CD}_3\text{-[C}_4\text{D}_8\text{]}_N\text{-D}$), whereas we calculated the mass of the polymers with hydrogen ($\text{CH}_3\text{-[C}_4\text{H}_8\text{]}_N\text{-H}$). If we recalculate the specific volume replacing the mass of hydrogen with that of deuterium, our data coincides with that of Tsolou et al., see fig. 3.13. Polymer melts expand with rising temperature, so the specific volume is also temperature dependent. There are different empirical equations to describe the temperature dependence of ν . Eichinger and Flory [54] use the following equation to analyse their work

$$\nu_{\infty}^{\text{Flory}}(T) = (0.9297 - 5.123 \cdot 10^{-4}(T - 273) + 6.15 \cdot 10^{-8}(T - 273)^2)^{-1}. \quad (3.20)$$

Fetters et al. [31] proposed another empirical equation

$$\nu_{\infty}^{\text{Fetters}}(T) = 1.077 + 6.8 \cdot 10^{-4}(T - 273). \quad (3.21)$$

In fig. 3.14 both equations are compared to the data of a melt of chains with $N = 128$. At low temperatures, between 250K and 450K, the

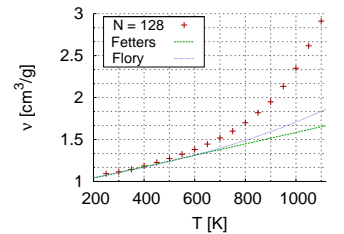


Figure 3.14: The specific volume of a polymer melt with $N = 128$ is studied at different temperatures and compared to predictions made by comparison to experimental data. At low temperatures the Fetters equation fits well, at higher temperatures the specific volume becomes very large.

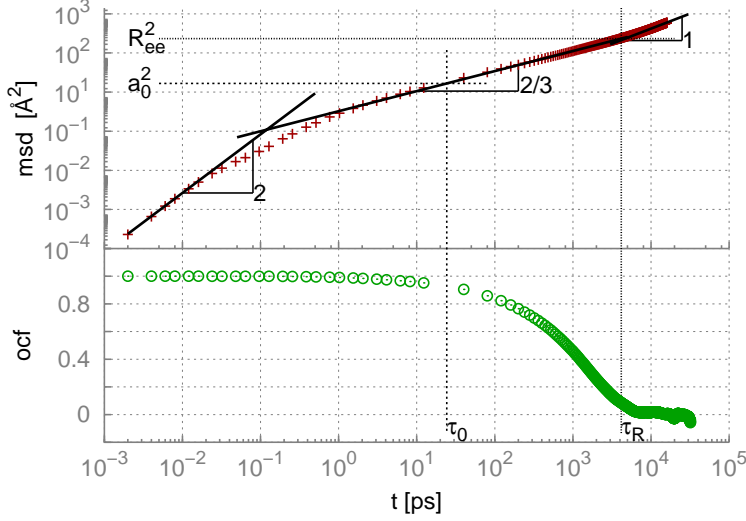


Figure 3.16: The plots above show the dynamics of a melt of 256 chains of length $N = 35$ at 550K. The upper panel shows the mean square displacement of all UA beads constructing the chain. The lower panel shows the orientational correlation function (ocf) of the end-to-end vector. The ocf is sufficiently decorrelated once the chain has diffused by R_{ee} . This time is called the Rouse time τ_R .

with ξ the friction coefficient, n the index number of monomers along the chain, and \vec{f}_n the random force of the Langevin equation. To solve eq. (3.24) we follow [1] and use the amplitudes of the vibrational modes, the Rouse modes, \vec{X}_p as generalised coordinates. Via time correlation it is possible to identify the relaxational times τ_p

$$\langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle \propto \exp -t/\tau_p, \quad t \gtrsim \tau_0 \quad (3.25)$$

with $\tau_N = \tau_0$ being the time it takes for a single monomer to relax and $\tau_1 = \tau_R$ is called the Rouse time and is the time it take for a chain to diffuse a distance of order R_{ee} . On time scales $\tau_0 \leq t \leq \tau_R$ the chains show viscoelastic properties and the mean square displacement is

$$\langle [\vec{R}(0) - \vec{R}(t)]^2 \rangle \propto t^{1/2}, \quad \tau_0 \ll t \ll \tau_R \quad (3.26)$$

On time scales larger than τ_R and distances greater than R_{ee} the motion of the coil is purely diffusive and can be described by Brownian motion.

$$\langle [\vec{R}(0) - \vec{R}(t)]^2 \rangle \propto t, \quad \tau_R \gg t. \quad (3.27)$$

Fig. 3.18 shows the different regimes of diffusive behaviours for a polymer melt and compares the mean square displacement (msd) with the orientational correlation function (ocf) of the end-to-end vector. The plot demonstrates that the chain configurations decorrelate for times $t \gg \tau_R$.

Fig. 3.17 compares the polymer motion in the viscoelastic regime for chains of different lengths. The shorter chains diffuse more quickly which is due to a number of reasons, the lower density and the higher

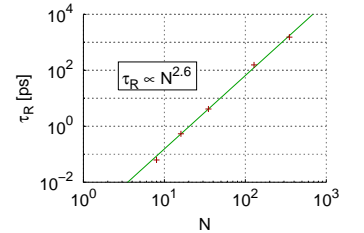


Figure 3.17: The Rouse time depends on the length of the chain, but in our simulation the dynamics is considerably slower then predicted ($\tau_R \propto N^2$ [2]).

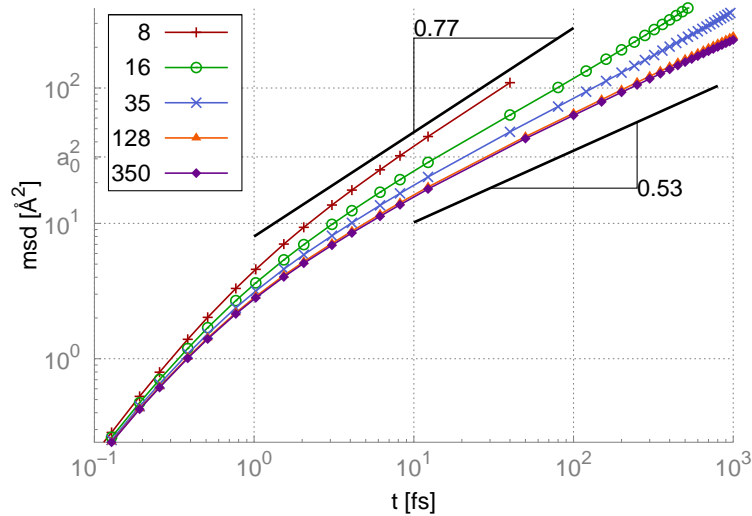


Figure 3.18: The plot compares the msd of all monomers on intermediate timescales for chains of different length at $T = 550$ K. While the earlytime regime is roughly independent of the chain length, the dynamics in the Rouse regime is much faster for shorter chains. For long chains the Rouse dynamics appears to converge towards $\text{msd} \propto t^{0.53}$.

mobility of the end groups to name two. For long chains the dynamics converges to $\text{msd} \propto t^{0.53}$ which is close to the Rouse model.

In our simulations we want to sample as many independent chain configurations as is feasible. To realize this it is important to estimate the Rouse times of the chains. The Rouse time is predicted to scale with the degree of polymerisation as $\tau_R \propto N^2$ for an unentangled chain. Fig. 3.17 in the margin shows the relaxation times at 550K for chains of different length. Our dynamics are considerably slower, with a $\tau_R \propto N^{2.6}$ behavior.



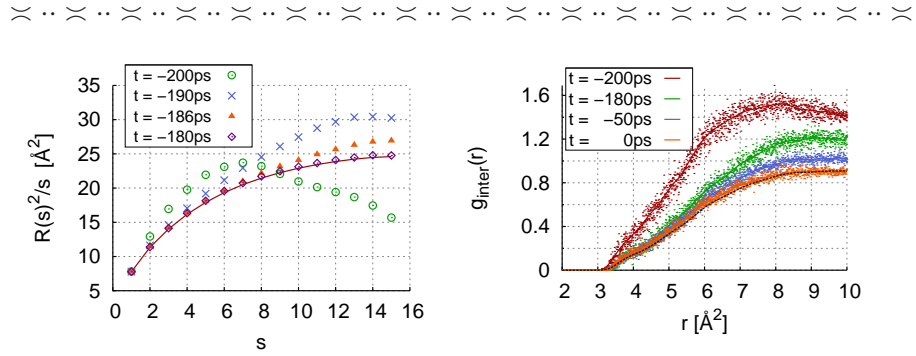


Figure 4.3: The panels above show the manner in which the chain structure develops during the deformation of the simulation box for a $N = 16$ system. The temperature is held at 550 K. Left: The internal distances equilibrate surprisingly fast. Just 20 ps after the setup the equilibrium value (solid red line) is reached. In all likelihood this is because the coil structure of the short chains in this example are predominated by the chain stiffness. Right: The inter-chain radial distribution approaches the mean value of an equilibrated melt (black dashed line) while the volume of the original all trans system is reduced.

renders PIB chains that resemble rods, see fig. 4.1. Other than the torsional angle all angles and bond lengths are set to their equilibrium values, θ_0 and l_0 , which, as discussed in section 3.1, are not equal to the mean values. Hence the monomer architecture is, albeit only weakly, distorted from its relaxed structure. The coordinates of one such chain are calculated and read into LAMMPS which then clones this chain with the command `replicate x y z`. In the following the all-trans method is demonstrated on a system with 256 chains of length $N = 16$. Fig. 4.1 shows this system after applying the command `replicate 4 8 8` to one single all-trans chain to generate 256 cloned chains. It is important to note that by setting up the system with a low density this method avoids any excluded volume overlap of either inter-chain or intra-chain nature.

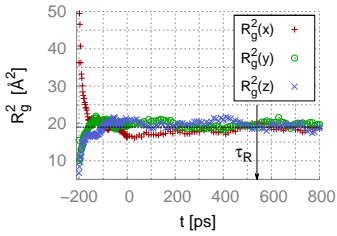


Figure 4.2: Above the time development of the radius of gyration x, y, z -components R_g^2 are shown for an all-trans setup of the $N = 16$ system. During the first 200 ps the system undergoes deformation. Starting from $t = 0$ the system equilibrates under standard conditions. The dashed line is the equilibrium value for $1/3 R_g^2$ and the arrow indicates the Rouse time of the system.

Warm-up, simulation box deformation and equilibration

Given that neither the local chain structure is overly distorted nor do the beads overlap, the warm-up procedure is straightforward. There is no need to cap or toggle the interaction potentials, merely the integration step length is reduced. The preliminary equilibration is done under `nvt` conditions with the Nosé-Hoover thermostat. Over the course of 3000 integration steps the integration step length is increased from 0.5 fs to 2 fs. This allows the local chain structure to relax while ensuring that no unproportionally large forces give rise to skewed monomer or chain topology. In return for avoiding bead overlap the starting volume of the simulation box is set to twice the normal size. Hence after the preliminary equilibration the volume must be reduced. Still working under `nvt` conditions, the simulation box is deformed to a cube with the `fix deform` command. The end volume of the box is calculated from the specific volume ν , which can be estimated from experimental

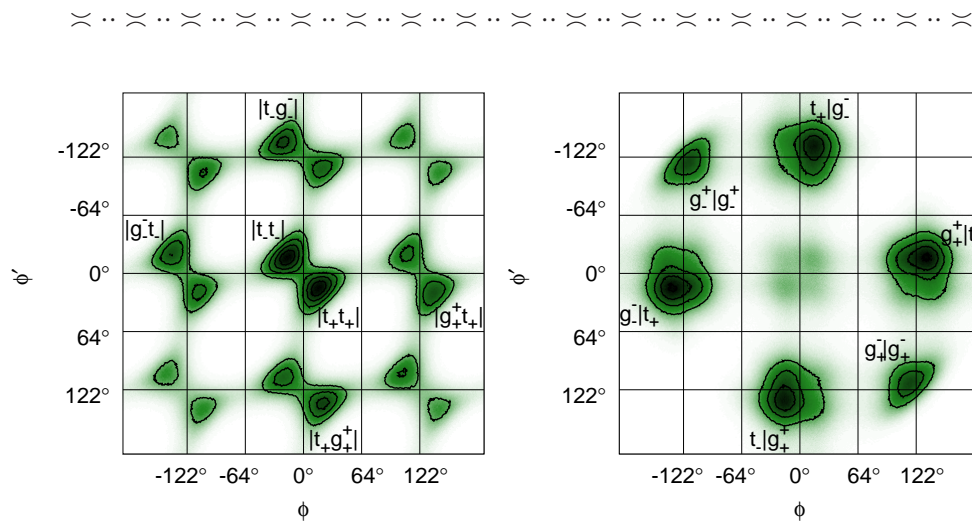


Figure 4.27: In the intradiad matrix to the left the splitting of the trans and gauche states is especially apparent. The interdiad matrix on the right provides us with essential information about the chain stiffness.

states: two trans states (t_- , t_+) and four gauche states (g_-^- , g_+^- , g_-^+ , g_+^+). In the trans state the bonds are arranged to be nearly planar, see fig. 4.25 while the bonds occupying one of the gauche states are strongly twisted, see fig. 4.26. The majority of the simulations performed in the scope of this work are run at 550K. At such high temperatures the splitting of the gauche states is hardly visible. Hence, fig. 4.23 shows the torsional distribution at 250 K as well as at 550 K. The distribution at 250 K is taken from a melt which is not fully equilibrated, since relaxation times at such low temperatures are very long. We can safely assume that the local configuration is adequately, but nevertheless the torsional distribution function is used for demonstrative purposes only.

For the homopolymer PIB there are two types of bond pairs: the pair centered at the methylene group, defining the intradiad matrix, and the pair flanking the quaternary C atom, which defines the interdiad matrix, see fig. 4.24. The bonds of each pair are correlated. Their joint probability distribution maps are shown in fig. 4.27. The chain ends influence the torsional distribution, so we dropped the contributions of six end monomers and calculated the probability maps from the remaining 232 bonds of a $N = 128$ system at 550 K. The intradiad probability distribution is qualitatively similar to that of previous RIS studies [37, 39]. The intradiad pairs prefer the $|tg|$ states which make up for 63.6% of the population followed by the $|tt|$ states which 19% of the pairs occupy. In general states with mixed classes, such as $|t_-g_+^-|$, are very unlikely. The interdiad map on the other hand is significantly different from the most recent RIS model of PIB presented by Vacatello et al. [39]. In our model it is more likely that the bonds of an interdiad pair occupy states of different classes. The Vacatello model on the other hand prefers interdiad pair that share a class. The pairs of $t_\alpha|g_\alpha$ constellation occupy 79% of the states in Vacatello's model as opposed to the 34.6% in our model. The most heavily populated states in our model are of the $t_\alpha|g^\beta$ type, accounting for 41% of the interdiad pairs.

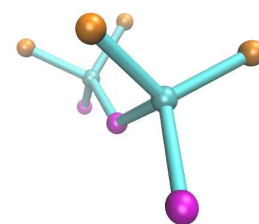


Figure 4.25: The pictured schematic PIB dimer is in trans conformation.

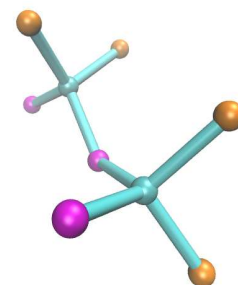


Figure 4.26: Here the dimer is in a gauche state.

5 | Neutron Scattering Methods

Over the last decades neutron scattering has contributed largely to our understanding of the structure and dynamics of soft matter systems. This is because thermal neutrons have a de Broglie wavelength that matches interatomic distances in ordered or disordered condensed matter structures. With small angle neutron scattering (SANS) the structure can be probed on a micrometer to nanometer length scale which matches well with typical size distributions in soft matter systems ranging from polymer aggregates, micelles, to nanopores. Furthermore, thermal neutrons have an energy which is on the same order of magnitude as quasiparticle excitations. With quasielastic neutron scattering (QENS) and neutron spin echo (NSE) techniques dynamical processes become accessible, such as local vibrations, librations, and diffusion that span time scales from pico- to milliseconds.

Scattering of thermal neutrons by matter is dominated by the interaction of neutrons with the nuclei of the matter. For each isotope the neutron-nuclei scattering potential is different. Hence the scattering amplitude or scattering length is specific to the isotope, not to the atomic number, as it is in x-ray scattering. Because the neutron is a spin 1/2 particle, the scattering can be coherent or incoherent. This is a unique property in neutron scattering. With the coherent cross section the pair correlation and structural information can be gained, whereas with the incoherent cross section the self-correlation is explored. For hydrogen and its isotope deuterium the distinction between coherent and incoherent scattering lengths and thus cross sections is of particular significance. The hydrogen nuclei has a spin 1/2, so the scattering is mostly incoherent. The deuterium nuclei has a total spin +1 and it scatters mostly coherently. The total nuclear spin for the carbon isotope ^{12}C is zero, so it scatters only coherently. Isotope labeling makes use of the large difference in the scattering lengths between hydrogen and deuterium. Most polymers and organic materials are composed of carbon and hydrogen. Selectively exchanging some hydrogen nuclei in the sample for deuterium offers the possibility of making structures visible that would otherwise be difficult to detect. The chemical properties, however, are almost unaffected by isotope labeling. Measuring the single chain conformation of polymers in bulk is an example of a quantity that can only be measured by neutron scattering. If the χ parameter, which measures the miscibility of hydrogen and deuterated polymer chains, is zero, they are fully mixed and entangled and probe the conformation in its unperturbed state[63, 64]. For the polymers studied in this thesis,

we assume the χ parameter to be close to zero.

This chapter gives a short introduction to scattering physics and explains the SANS experiment performed by our collaborators¹. The effects that chain length, stiffness and cross section have on the scattering picture are discussed on the example of chains generated with the rotational isomeric state (RIS) method. Taking these effects into account the form factor of the chains is extracted from the scattering intensity and the size of the chains is determined by comparing them to polyisobutylene (PIB) chains simulated with molecular dynamics (MD).

5.1 NEUTRON SCATTERING - THEORY

The key quantity in scattering experiments is the momentum transfer \vec{q} , that is the difference between the incident vector \vec{k}_i and the scattered wave vector \vec{k}_s

$$\vec{q} = \vec{k}_s - \vec{k}_i. \quad (5.1)$$

In the following only quasi elastic scattering experiments are discussed where there is no energy transfer between the neutron beam and the sample. Hence the wave length λ of the neutrons is unchanged by the scattering event and we can write

$$|\vec{k}_s| \approx |\vec{k}_i| = \frac{2\pi}{\lambda} \quad (5.2)$$

which leads to

$$|\vec{q}| = \frac{4\pi}{\lambda} \sin \vartheta \quad (5.3)$$

with 2ϑ the scattering angle. Because of this relationship \vec{q} is also referred to as the scattering vector.

The scattering amplitude $A(q)$ depends on the scattering length b_i of the particle located at \vec{r}_i

$$A(q) = \sum_{i=1}^{\mathcal{N}_m} b_i \exp[i\vec{q} \cdot \vec{r}_i] \quad (5.4)$$

where \mathcal{N}_m is the total number of particles that contribute to the scattering. Experimentally the amplitude is of course not accessible. Instead the Intensity $I(q) \propto |A(q)|^2$ is measured which implies that the phase is lost during the scattering event. Thus with scattering only pair correlations can be determined but not absolute positions of atoms or nuclei in space. The scattering intensity depends on the number of scatterers. To compare results from different samples the structure factor $F(q)$ is introduced with I_m the scattering intensity of a single scatterer

$$F(q) = \frac{I(q)}{I_m \mathcal{N}_m} = \frac{1}{\mathcal{N}_m} \sum_{i,j}^{\mathcal{N}_m} \exp[i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)]. \quad (5.5)$$

¹Prof. Mark Dadmun and Dr. Caleb Deyer, University of Tennessee, Knoxville

Since the scattering centers are small compared to the volume, we change to a continuum representation with $\sum_{i,j}^{\mathcal{N}_m} \rightarrow \int_V$ so that

$$F(q) = \frac{1}{\langle \rho \rangle} \int_V \exp[i\vec{q} \cdot \vec{r}] (\langle \rho(r)\rho(0) \rangle - \langle \rho \rangle^2) d^3\vec{r} \quad (5.6)$$

in which $\vec{r} = \vec{r}_i - \vec{r}_j$ and $\rho(r)$ is the local density of scatterers. From this equation it becomes apparent that scattering only takes place at density fluctuations.

To emphasize the relationship between the scattering picture and the structure of the sample eq. (5.6) can be written as

$$F(q) = \int_V \exp[i\vec{q} \cdot \vec{r}] (g(\vec{r}) - \langle \rho \rangle) d^3\vec{r}, \quad (5.7)$$

where $g(r)$ is the pair distribution function which is defined as [51, p. 391]

$$g(\vec{r}) = \frac{\langle \rho(\vec{r})\rho(0) \rangle}{\langle \rho \rangle}. \quad (5.8)$$

Eq. (5.7) shows the well known identity that the structure factor is the Fourier-transform of the pair distribution function.

In the following we describe a small angle scattering experiment on PIB chains. The samples investigated consist of a blend of deuterated and protonated PIB chains. As already mentioned, the scattering intensity is due to composition fluctuations. It is possible to directly probe the single chain scattering function, i.e. the form factor of a single chain by contrast variation of the blended PIB chains [64]. In the case of Gaussian chains the pair distribution function is

$$g(\vec{r}) = \left(\frac{3}{2\pi \langle \vec{r}^2 \rangle} \right)^{3/2} \exp \left(-\frac{3\vec{r}^2}{2\langle \vec{r}^2 \rangle} \right). \quad (5.9)$$

When plugging eq. (5.9) into eq. (5.7) the integral can be evaluated and the result is the Debye function $D(x)$ [51, p. 33]:

$$F(q) = \frac{2\mathcal{N}_m}{(qR_g)^4} \left[e^{-(qR_g)^2} - 1 + (qR_g)^2 \right] = \mathcal{N}_m D(Q = qR_g). \quad (5.10)$$

The Debye function can be approximated in the limits of very small and very large Q as

$$D(Q) = \begin{cases} 1 - Q^2/3 & \text{for } Q \ll 1 \\ 2/Q^2 & \text{for } Q \gg 1. \end{cases} \quad (5.11)$$

These approximations together with the Debye function are shown in fig. 5.1. The small Q range is also known as the Guinier regime. Scattering in the Guinier regime is often used to determine the radius of gyration and degree of polymerization of the chains. The larger Q -regime holds information about the internal coil structure. A $F(q) \propto 1/q^2$ behavior is expected for ideal chains, and hence scattering data of polymer systems is often shown in the Kratky representation, plotting $Q^2 F(q)$ vs. Q . The so-called Kratky plateau for $Q > 2\pi$ is often interpreted as proof of ideality in real chains. Though it has been noted, as is discussed in the following sections, that “[...] Kratky plots have to be interpreted with care” [63, p.252].

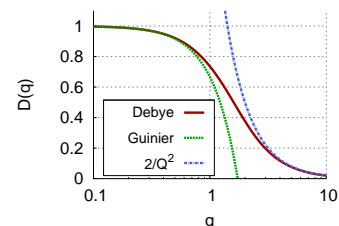


Figure 5.1: The Debye function (solid line) and its approximations, see eq. (5.11).

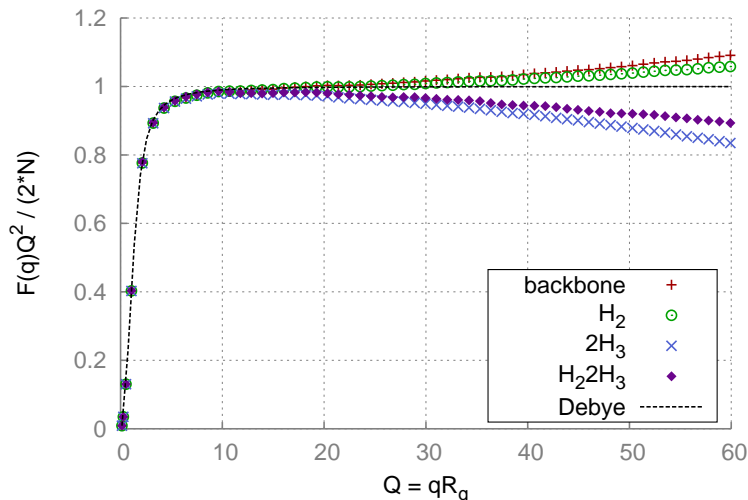


Figure 5.2: The figure above shows the influence of the chain cross-section on the structure factor. The structure factor has been calculated with respect to four different scattering centers. The data denoted as “backbone” is the structure factor solely regarding the carbon atoms along the backbone of the chain. With “H₂” we denote the structure factor gained by regarding only the hydrogen atoms belonging to the methylene group. The data denoted “2H₃” take only the hydrogen atoms belonging to the methyl groups into consideration, and the data denoted “H₂2H₃” take into account all hydrogen atoms of the chain. The solid line shows the Debye function eq. (5.10). All form factors are calculated from the rotational isomeric state (RIS) model with potentials derived from the molecular dynamics simulation of PIB at 550 K chains of length $N = 11200$.

5.1.1 The real chain

The section above discusses the structure factor of an ideal chain, neglecting effects of chain stiffness and cross-section that influence the scattering picture. In the following we quantitatively introduce properties of real chains that lead to deviations from the Debye curve. To distinguish between the different effects we resort to chains generated by the RIS-MC method detailed in section 4.3. These chains are unperturbed by excluded volume effects and are Gaussian for large N . Also the RIS-MC chains are generated much faster than the MD chains and hence it is possible to access an array of very long chain lengths.

The influence of labeling

Theoretical considerations of polymers often start from the idealization that polymers consist of point-like monomers that, strung together, form string-like coils. This is justified by assuming the cross-section, i.e. the girth, of the chain to be much smaller than the total chain length. Contrary to this belief, neutron scattering experiments on selectively labeled chains have shown that the cross-section strongly influences the form factor. That this effect is not limited to high q -values has been

demonstrated in the work of Rawiso et al. [65], who studied differently labeled polystyrene. They show that the form factor of backbone labeled polystyrene deviates from that with labeled phenyl rings for q -values as low as $q = 0.03\text{\AA}$. The influence of selective labeling on the form factor is also discussed in “Polymers and Neutron scattering” [63] in which the authors warn that the effects of chain stiffness and cross-section may superimpose, leading to a plateau in the Kratky regime that can be falsely interpreted as a sign of chain ideality. We study this effect by comparing the form factor of modeled PIB chains with different scattering centers, see fig. 5.2. For small Q -values the form factors for all four different types of labeling collapse onto the Debye curve, signifying ideal chain behavior. For larger Q -values the form factors deviate from the Kratky plateau. The backbone and methylene labeled chains show an upward deviation from the Kratky plateau, typical of a rod-like objects. The form factor of the methyl groups and the fully labeled chain (2H_3 and H_22H_3) show a downward deviation from the Kratky plateau. This type of labeling makes the cross-section of the chain visible. Scattering from the methyl groups is comparable to scattering from a tube-like object rather than from point-like monomers. The effect of the cross-section of the chain overpowers the stiffness effect.

Rawiso et al. introduced a method to derive the form factor of a point-like chain from the scattering signal of a chain with a notable girth using the following formula [65, eq.(37)]

$$F'(q) = F(q) \exp \left[-q^2 R_c^2 / 2 \right] \quad (5.12)$$

with $F(q)$ the original and $F'(q)$ the reduced form factor. The radius R_c is the radius of gyration of the chain with respect to the backbone axis. When considering the scattering signal of the hydrogen atoms of PIB, R_c can be approximated as a hollow cylinder with diameter equal to the distance between the methyl and methylene hydrogens. This estimation gives us the value of $R_c = 1.25\text{\AA}$. In fig. 5.3 this method is successfully applied to the RIS-MC chains to reduce the form factor of the fully labeled chain to that of the backbone labeled chain. This opens the possibility of treating chains as infinitely thin, even if their form factor was originally measured by labeling atoms that are located at a finite distance from the chains axis.

Finite length effects

The persistence length l_p of the RIS-MC chains of the current work (c.w.) is 4.13\AA , see chapter 7. It is expected that the chain stiffness affects the form factor on q -scales that probe distances comparable to l_p . Fig. 5.4 shows the form factor of RIS-MC generated chains ranging in lengths from $N = 350$ up to $N = 89600$. Only the backbone atoms are considered in this plot to avoid interfering effects caused by the chain cross-section. All chains, independent of their length, deviate from the Debye curve at approximately $q = 0.09\text{\AA}^{-1}$, which translates into a spacial distance of 70\AA . The radius of gyration of the two shorter chains shown in fig. 5.4 is smaller than 70\AA . The form factor of these chains

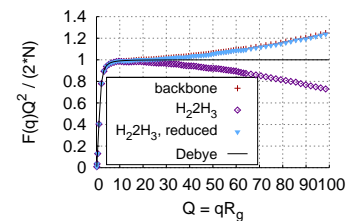


Figure 5.3: With the method explained in [65] the effect of the chain cross-section can be factored out.

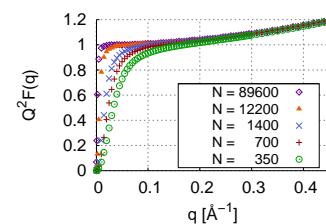


Figure 5.4: The form factor of the backbone deviates from the Kratky plateau of chains of varying length, demonstrating the influence of chain length on the form factor. The form factor is calculated from the backbone carbon atoms.

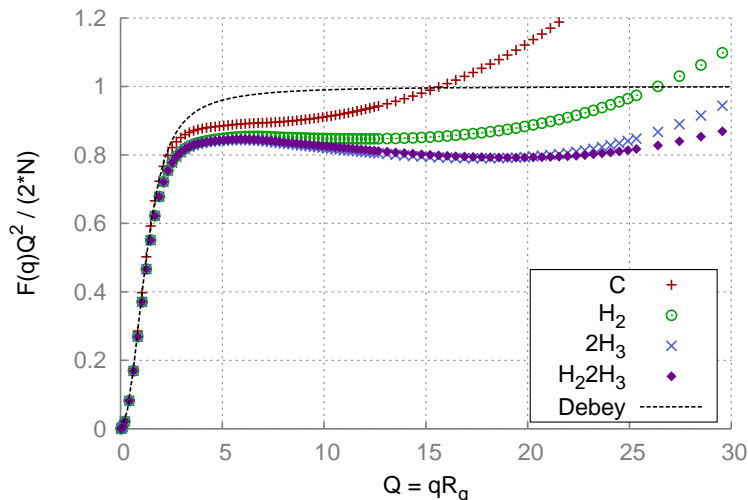


Figure 5.5: The plot shows the form factor of the $N = 350$ chains simulated with MD methods at 550 K. The notation of the different labeling is the same as in fig. 5.2.

shows no plateau in the Kratky regime. The Kratky plateau is only visible for much longer chains with $R_g > 70 \text{ \AA}$. The chain stiffness affects larger length scales than we assumed. The longest chains simulated by molecular dynamics are of length $N = 350$, hence the structure factor is strongly influenced by the chain stiffness. Additionally to the cross-section and the chain stiffness, the MD simulations of PIB also takes into account the excluded volume interaction. A quantity that is intrinsically neglected by the RIS-MC chains. In fig. 5.5 the form factor of the MD chains of length $N = 350$ is shown with different types of labeling. The excluded volume interaction leads to a depression in the Kratky region. All effects combined lead to an alleged Kratky plateau for the fully labeled chain, though this false plateau is at $Q^2 F(q) / (2N) \approx 0.8$ rather than 1. The absence of a real Kratky region for PIB chains of length $N = 350$ makes the analysis of the residual excluded volume effects more difficult.

5.2 NEUTRON SCATTERING - EXPERIMENT

5.2.1 The samples

The SANS measurements that are discussed in the following were performed by our collaborators, the group of Prof. Mark Dadmun from the University of Tennessee in Knoxville. Two different chain lengths were studied which will denote as “long” and “short” in the following. Protonated and deuterated polyisobutylene (h-PIB and d-PIB) samples were synthesized by Prof. Robson Storey (University of Southern Mississippi). The d-PIB samples are fully deuterated, meaning that all hydrogen atoms of the methyl and methylene groups are replaced by deuterium. The samples were dissolved in tetrahydrofuran (THF) and

	N_n	N_w	PDI
d-PIB, short	273	284	1.04
h-PIB, short	328	341	1.04
d-PIB, long	622	659	1.06
h-PIB, long	672	785	1.02

Table 5.1: The characteristics of the PIB samples measured by the MALL/SEC method directly after synthesis.

analyzed by multiangle laser light scattering (MALL) and size exclusion chromatography (SEC). The results for the number-average degree of polymerization N_n , the weight average N_w and the polydispersity index $PDI = N_w/N_n$ are listed in table 5.1.

Supposedly an error occurred during the analysis of the deuterated chains so that over half a year after the first analysis the samples were reevaluated using the 100% mass recovery method and the results presented in table 5.2 were obtained. As to this date confusion around the

	N_n	N_w	PDI
d-PIB, short	349	363	1.04
d-PIB, long	822	838	1.02

Table 5.2: Reevaluation of the deuterated chain leads to a higher degree of polymerization.

two different sets of data is not resolved and since the samples have been destroyed, performing a third analysis is impossible.

From the four chain types, a total of six samples were prepared. Four samples contain the purely protonated and deuterated samples while the remaining two contain a blend of the hydrogenated and deuterated PIB of one length. The structural information is gained from the blended sample since the protonated sample only scatters incoherently, while the deuterated sample scatters mainly coherently. The measurements of the pure samples are needed to subtract the incoherent scattering from the blended sample. The volume fraction ϕ of d-PIB in the blended samples was determined by the transmission intensity and is

$$\phi(\text{d-PIB,S}) = .503 \quad \phi(\text{d-PIB,L}) = .510. \quad (5.13)$$

The mixing properties of two polymers can be quantified by the Flory-Huggins parameter χ . A positive χ value leads to immiscibility, which can happen between deuterated and protonated polymer chains. F. Bates et al. [66] discuss the phenomena of demixing in deuterated and protonated polymers by the example of polybutadiene. In previous scattering experiments on d-PIB and h-PIB [17] the χ parameter was found to be zero, allowing for the chains to mix. For the samples at hand the density was measured and the relationship $\rho_D = 1.1\rho_H$ verified. This implies that the density of the deuterated monomers is only increased by the additional neutrons, but the monomer volume stays unchanged. Since immiscibility is often due to different monomer volumes, this anal-

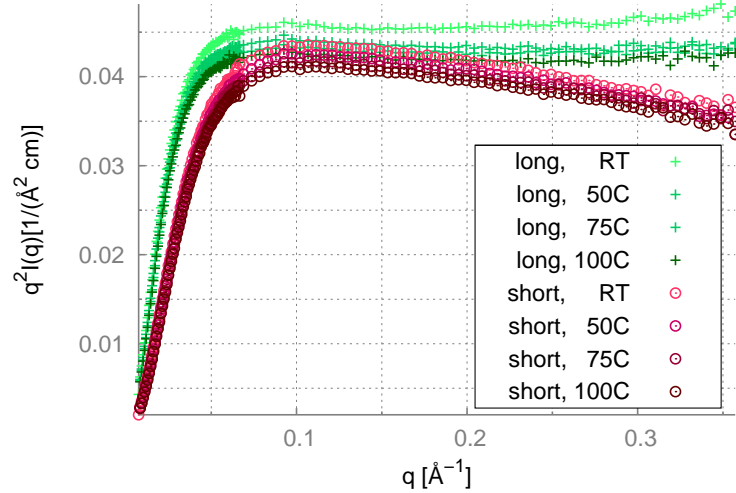


Figure 5.6: Intensity versus q after data reduction. The temperature dependence stems from the density variance.

ysis gives further weight to the assumption that $\chi = 0$ for d-PIB and h-PIB.

5.2.2 Neutron Scattering and Data Reduction

The scattering experiment took place at the 30m SANS machine **NG-7** at the National Institute of Standards and Technology (NIST) facility in Gaithersburg, Maryland. The scattering intensity was measured by a position sensitive helium detector. By varying the sample-to-detector distance it was possible to sample a q -range of 0.00829 \AA^{-1} to 0.3572 \AA^{-1} . The samples were placed in a heatable sample holder. The PIB samples themselves were contained in 1 mm thick cells. Both sets of samples were measured at four different temperatures: at room temperature ($\approx 25^\circ\text{C}$), 50°C , 75°C , and 100°C . The purpose of heating the sample was that the chain stiffness as quantified by C_∞ decreases with increasing temperature, rendering a more flexible polymer at higher temperatures. However, the effect is very weak and the difference of C_∞ at 100°C and 25°C is less than 1% according to Fetters et al. [31].

The scattering from the samples containing pure d-PIB and pure h-PIB as well as the blended samples were measured at each temperature. The scattering from the empty cell was also measured. Additionally the background events were measured by blocking the beam. The results from these measurements are then used to extract the coherent scattering of the blend by applying the following method of data reduction

$$I(q) = (I_{\text{blend}} - I_{\text{cell}}) - \phi(I_{\text{d}} - I_{\text{cell}}) - (1 - \phi)(I_{\text{h}} - I_{\text{cell}}) - I_{\text{background}}. \quad (5.14)$$

$I(q)$ is the intensity of the coherent scattering of the blended sample. The raw data after reduction is shown in fig. 5.6. The temperature dependency is clearly visible.

5.2.3 Data Analysis

After performing the data reduction described above the SANS measurements provide the coherent scattering intensity $I(q)$ of the blended sample. To extract the form factor from the scattering intensity we apply the random phase approximation (RPA) described in [63, p. 404].

$$I(q) = k_n \left[\frac{1}{v_H \phi_H F_H(q)} + \frac{1}{v_D \phi_D F_D(q)} - 2\chi/v_0 \right]^{-1}. \quad (5.15)$$

The factor $k_n = N_a (a_H/v_H - a_D/v_D)^2$ results from the incompressibility constraint of the melt. This is well justified because the composition fluctuations of the hydrogen and deuterium species are much larger than the density fluctuations of the melt. The parameters and functions appearing in eq. (5.15) have the following significance:

- N_a is the Avogadro Number: $N_a = 6.0221415 \cdot 10^{23} \text{ mol}^{-1}$.
- a_H and a_D are the coherent scattering lengths of the protonated and deuterated monomers. Their values are $a_H = -3.3408 \text{ fm}$ and $a_D = 79.952 \text{ fm}$.
- v_H and v_D are the volumes of the protonated and deuterated monomers. We take them as

$$v_H = \frac{m_H}{\rho_H} \quad \text{and} \quad v_D = \frac{m_D}{\rho_D}, \quad (5.16)$$

where $\rho_H = 0.928505 \text{ g/cm}^3$ and $\rho_D = 1.021355 \text{ g/cm}^3$ are the monomer densities of h-PIB and d-PIB. For ρ_H we use a parametrization of eq. (3.21) and applied the empiric relationship of $\rho_D = 1.1\rho_H$ which was verified for the samples at hand.

- The volume v_0 is an arbitrary reference volume. Following Beaucage et al. [67] we take $v_0 = \sqrt{v_H v_D} = 61.62845 \text{ cm}^3/\text{mol}$.
- χ is the Flory-Huggins (segment-segment) interaction parameter, as discussed above. Though it is known that for isotopic mixtures in general, we may not assume χ to vanish [66], [63, p. 137], density analysis of the samples at hand suggest χ to be zero in the case of d-PIB and h-PIB.

For the following analysis we rewrite eq. (5.15) as

$$I(q) = K(T) \left[\frac{\phi_D}{v_H/v_0} \frac{1}{F_H(q)} + \frac{\phi_H}{v_D/v_0} \frac{1}{F_D(q)} \right]^{-1}. \quad (5.17)$$

with the temperature dependent factor $K(T)$:

$$K(T) = \left[\frac{a_H}{v_H/v_0} - \frac{a_D}{v_D/v_0} \right]^2 \frac{\phi_H \phi_D}{v_0} = 0.176134 \rho_H(T). \quad (5.18)$$

The density is temperature dependent as is shown in eq. (3.21). We assume that the h-PIB and d-PIB chains of one sample have the approximate same chain length and polydispersity, which is justified when

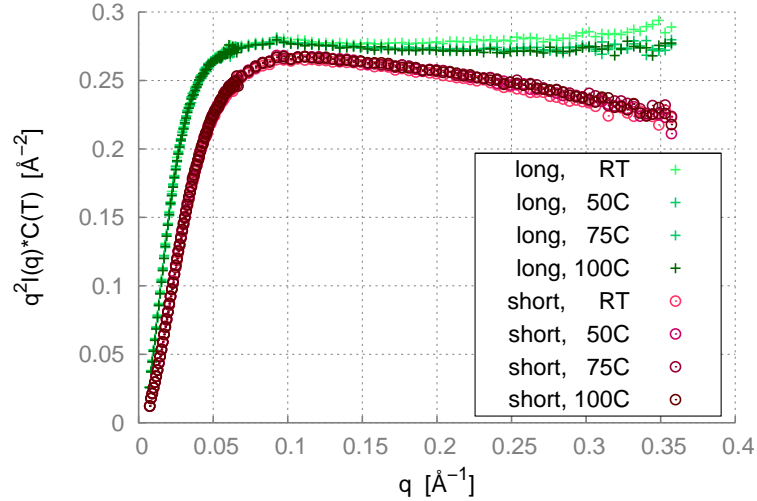


Figure 5.7: The Kratky plot for the structure factor of the chains at different temperatures collapse onto one master curve. This shows that only the density, but not the coil structure is influenced by the temperature in the studied regime.

assuming the first sample analysis to be true. Further we assume the form factors of h-PIB and d-PIB to be the same

$$F_H(q) = F_D(q) = F(q). \quad (5.19)$$

For eq. (5.17) this implies

$$\frac{1}{K(T)} I(q) = C(T) I(q) = F(q) \quad (5.20)$$

because

$$\frac{\phi_D}{v_H/v_0} + \frac{\phi_H}{v_D/v_0} = 1.00058. \quad (5.21)$$

When converting the intensity to the form factor with the temperature dependent proportionality factor $C(T)$ the curves for the different temperatures collapse with exception of the sample measured at room temperature, see fig. 5.7. The exact temperature the sample had during this measurement is not known. We approximated it to be 25°C, but since it is not coherent with the other data, this particular set of data will be dropped from further analysis.

Determining the coil size by a Guinier fit

Traditionally the chain size is extrapolated by fitting the Guinier approximation to the very small q values. This analysis method is applied to the data from every temperature separately. The chosen fit range is between $q^2 = 8 \cdot 10^{-5} \text{Å}^2$ and $q^2 = 15 \cdot 10^{-5} \text{Å}^2$. The mean values for the degree of polymerization and the coil size are summarized in the table of fig. 5.8 together with the fit itself. $R_{g,z}$ is the z-average radius of gyration. Surprisingly the degree of polymerization that is assigned to

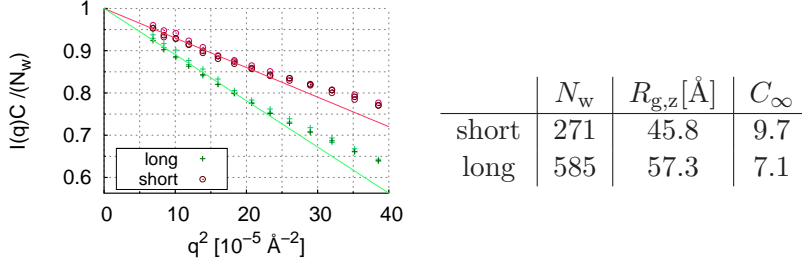


Figure 5.8: The values of chain length and radius of gyration gained from fitting the Guinier approximation at small q are listed in the table. The actual fit is shown in the plot on the left, where the data of all temperatures collapse onto one curve.

the chains from this fit is lower than what is expected from the previous analysis (cf. tables 5.1 and 5.2). The chain stiffness can be extracted from the fitted values by applying

$$C_\infty = 6R_g^2 \frac{1}{b_0^2 2N} \quad (5.22)$$

were $b_0 = 1.53 \text{ Å}$ is the bond length [2]. The values of the C_∞ are listed in the table of fig. 5.8. These values indicate that the PIB chains are stiffer than what is suggested in the literature [31], where $C_\infty \approx 6.5$.

To test the viability of the values extracted from the Guinier fit, we display them in a normalized Kratky plot together with the MD simulation data. The data is expected to collapse onto a master curve, but as can be seen in fig. 5.9 this is not the case. Though the longer chain coincide quite well with the simulation data, the form factor of the shorter chains lies above the Debye curve. This leads us to believe that in the q -region in which the Guinier fit is performed the real chain effect (cross-section, finite length, excluded volume) cause a deviation from the Debye curve.

Determining the coil size by comparison to the simulation data

Since the SANS measurements performed do not span lower scattering angles we resort to manually fitting the SANS data to the MD data of the longest simulated chains, that is $N = 350$. We do this by choosing the radius of gyration and the degree of polymerization so that the form factor of the SANS data and that of the MD data coincide. Fig. 5.10 shows the fitted SANS data together with the MD data. The results of the fit are summarized in the table of fig. 5.11.

The values returned by this method are in good agreement with the chain characterization done by SEC/MALLS (cf. table 5.1). In the normalized Kratky plot the data of the two real PIB samples and the simulated chains collapse onto one curve for small q -values, see fig. 5.11. Only by means of the united atom (UA) simulations of PIB and the consequential adding of the hydrogens could the SANS data be successfully interpreted. The traditional fit of the Guinier approximation at

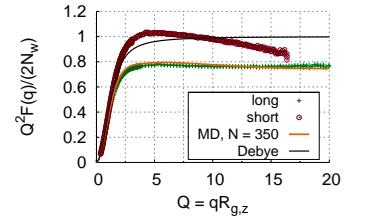


Figure 5.9: The Kratky plots are normalized with the values of the Guinier fit in fig. 5.8 and compared to the chains simulated with molecular dynamics.

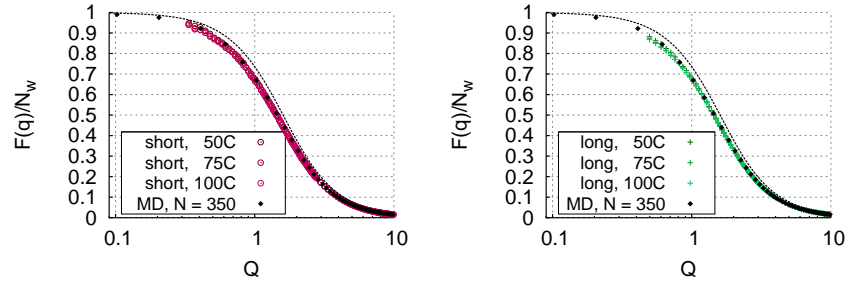


Figure 5.10: Manually fitting the SANS data to the $N = 350$ MD simulated chains in the low q -regime. The results are summarized in table 5.11

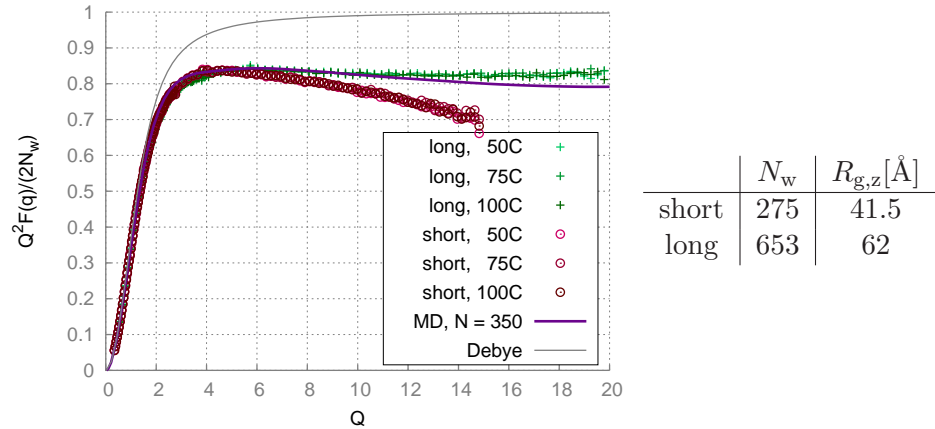


Figure 5.11: Comparison of the NS and MD data in Kratky representation. The values above are taken from the manual fit of the SANS data to the structure factor of the simulated chains at 550 K.

low q -values failed, because the cross-section of the chain influences the form factor even in the smallest q regime that was measured. In the following discussion the values of table fig. 5.11 will be used.



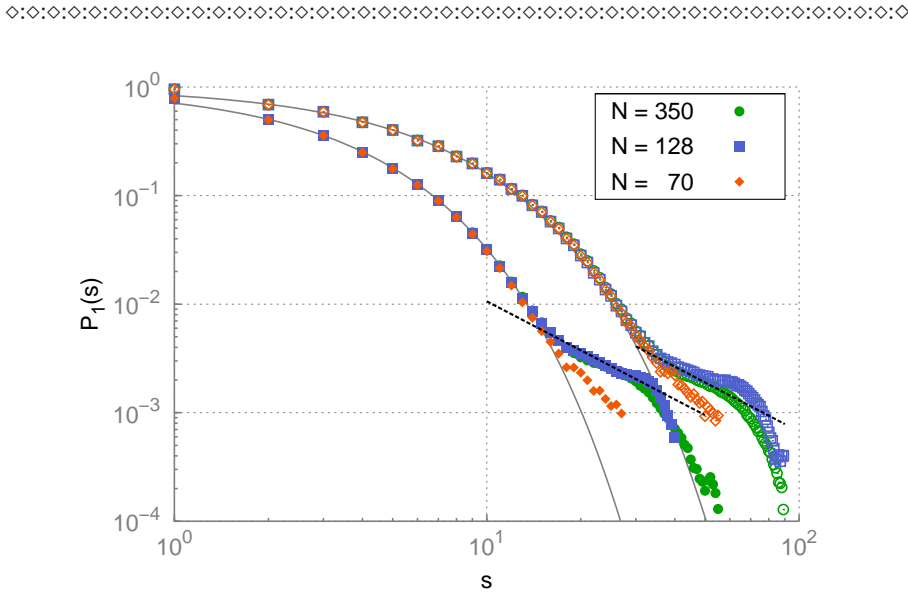


Figure 6.4: The figure shows the bond-bond correlation function for different chain lengths of PIB. The solid symbols represent the correlation between the monomers and the empty symbols represent the correlation between the backbone bonds. The dashed black lines indicate the $s^{-3/2}$ behavior expected for non-ideal chains. For chains of length $N = 70$ the influence of the residual excluded volume is almost lost in noise while it is clearly visible for longer chains with $N = 128$ and $N = 350$.

show the influence of the residual excluded volume effects on the chain structure in this manner. In lieu thereof we focus on the bond-bond correlation $P_1(s)$, see eq. (6.3), which is the second derivative of the intrachain distance function.

Perturbation calculation

As stated above the residual excluded volume interaction is very weak and can therefore be treated as a perturbation to the ideal chain. As detailed in [5, 6, 8, 73, 74] in first order perturbation any quantity \mathcal{A} that is under the influence of a small perturbation \mathcal{U} can be written as

$$\langle \mathcal{A} \rangle \simeq \langle \mathcal{A} \rangle_0 + \langle \mathcal{U} \rangle_0 \langle \mathcal{A} \rangle_0 - \langle \mathcal{U} \mathcal{A} \rangle_0 \quad (6.13)$$

where the averages denoted by $\langle \dots \rangle_0$ are performed over the unperturbed system. In our case we would like to study the bond-bond correlation function so $\mathcal{A} = P(s)$ and under the assumption that the information decays exponentially we write

$$\langle \mathcal{A} \rangle_0 \propto \exp(-s/s_p) \quad (6.14)$$

with s_p the number of segments per persistence length. As discussed in [8] the perturbation caused by the correlation hole effect leads to a power law dependency with

$$\langle \mathcal{U} \mathcal{A} \rangle_0 \propto - \left(\frac{s_p}{s} \right)^{3/2}. \quad (6.15)$$

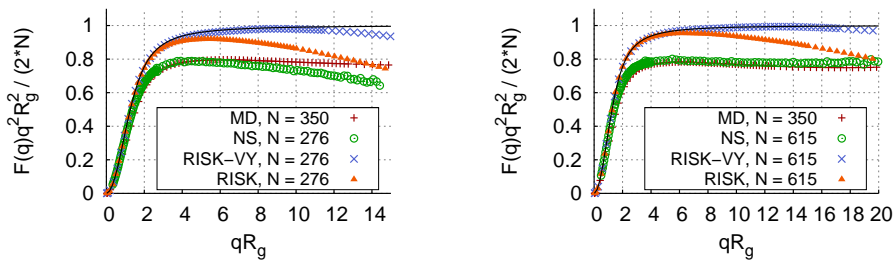
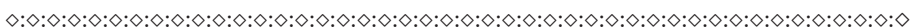


Figure 6.9: The plots show that the RIS-MC model does not correctly reflect the chain structure of PIB in the melt. The form factor of the MD-simulated PIB fits better.



7 | Retrospective

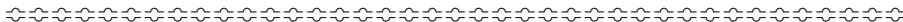
Neutron and x-ray scattering data of polymer coils in the melt or theta solution are commonly compared to the form factor of chains generated by the rotational isomeric state model (RIS). The RIS method which is discussed in 4.3 generates chains, which neglect excluded volume effects but are true to chemical detail. The foundation of the RIS theory lies within Flory’s’ ideality hypothesis which states that all excluded volume interaction is screened by the melt. In 1983 Hayashi et al. published a comparison between neutron scattering data and RIS theory for the form factor of polyisobutylene (PIB) [17]. The good agreement of RIS chains with the experimental data reinforced Flory’s ideality hypothesis. However, the RIS analysis in [17] is not as convincing as it might seem. As pointed out by DeBolt and Suter, it employed a wrong assignment of the backbone angles. In their Erratum [38], they propose a revised model, but just state that the new version gives indistinguishable results from the wrong one. However, no plot is given to support this point. Later, Vacatello and Yoon criticize [39] the refinement made by DeBolt and Suter. They argue that the DeBolt-Suter model is not really acceptable because it requires reallocated torsional states quite far from those of the energy minima originally deduced in Ref. [37]. Instead of the 4-state RIS model used in Refs. [17, 37, 38], Vacatello and Yoon (VY) suggest a 6-state RIS model (which is more consistent with our PIB model; see fig. 4.23) and show that this model also yields good agreement with experiment [39].

On the one hand, we have the good agreement between the Vacatello-Yoon RIS model and the Hayashi SANS (small angle neutron scattering) data reinforcing the ideality hypothesis. On the other hand, the current SANS data coincides with molecular dynamics (MD) simulations, strongly suggesting that residual excluded volume effects influence the coil structure. This calls for a reexamination of the Vacatello-Yoon model and the Hayashi SANS data.

In this chapter we discuss the most recent RIS model for PIB published by Vacatello and Yoon [39], and why it describes the scattering data of PIB so well. We also generate RIS chains with the torsional map gained from the MD simulations.

The RIS model by Vacatello and Yoon

In the following we compare the Vacatello-Yoon model with the RIS model which utilizes the probability distributions directly derived from

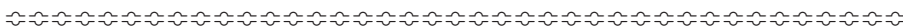


8 | Conclusion

In this thesis the effects of residual excluded volume interactions among real polymers in a dense melt were studied and successfully shown in atomistically realistic simulations and small angle neutron scattering (SANS) experiments. We successfully employed fine graining to reach equilibrium in very long chains. Computationally the greatest challenge was to generate fully equilibrated systems of atomistically realistic polymers. We tested a number of different methods of which fine graining proved to be the most effective. By developing a coarse-grained system with similar characteristics to PIB we utilized fine-grained to map the chemical detail onto the coarse-grained beads. With this method it was possible to simulate chains of length $N = 350$ — over four times longer than PIB chains that have been simulated to this date. From these simulations we were able to show the non-ideality effects that manifest themselves in the bond-bond orientation correlation function. It is the first time these deviations from ideality have been shown for a realistic polymer model and compared with real polymers.

With the help of the molecular dynamics simulations we could successfully analyze the SANS data collected by our collaborators, M. Dadmun et al. From the SANS data we could also derive the corrections to ideality, albeit only quantitatively, since the existing theory only takes string-like chains into account. These findings give confidence to the residual excluded volume theory. The SANS experiments from 1983 that once gave weight to Flory's ideality hypothesis were revisited and the rotational isomeric state simulations that accompanied them reproduced. By estimating the influence of polydispersity on the scattering picture it is possible to show that the 1983 data is in fact closer to the prognosticated non-ideal chains than it is to the ideal chains.

This thesis was successful in bridging the gap between theory and experiment, but there remains work to be done. Firstly the theory of residual excluded volume effects should be widened to include chains with finite monomer cross-section. Experimentally it is possible to synthesize longer chains than what was studied in this thesis. The longer the chains are, the easier it is to distinguish the effect of non-ideality, so more SANS measurements with longer chains should be performed. Powerful SANS machines are now available at several large scale neutron facilities and even more are anticipated to be installed at the European Spallation Source, such that comparison between theory and experiment is expected to make good progress in the near future.





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