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Monte Carlo Prediction of the Structure Factor of Polyethylene in Good and Θ-Solvents

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ABSTRACT: Using Monte Carlo techniques on a united atom model of polyethylene, we predict the structure factor of a single polymer chain $g(q)$ at all length scales for Θ and good solvent conditions. The solvent quality is included in the nonlocal monomer−monomer potential of mean force through an ad hoc parameter controlling the balance between repulsive and attractive contributions. Chains up to 4096 C−C bonds have been treated to get, in the "intermediate" regime of q, the well-established scaling law $g(q) = Aq^{-1/\nu}$ where ν is the Flory exponent depending upon the quality of the solvent. For the q range above the scaling regime, the flexible rod model of Porod−Kratky is found to apply satisfactorily.

I. Introduction

The prediction of polymer structural properties in terms of an "atomic" model has received considerable attention in the sixties under the impetus of Flory and his collaborators, a work gathered in the classical book *Statistical Mechanics of Chain Molecules*.[1] At a time when the study of condensed phase systems at the molecular level was limited by computer power to simple fluids modeled by Lennard-Jones or hard sphere systems, Flory and collaborators were studying polymer melts on the basis of a detailed and specific "chemical" model. For a wide variety of polymer species such as vinyl chains or even polypeptides, single chain structural properties like the mean square end-to-end distance were predicted for realistic polymer molecular masses. The chain structure factor was predicted a few years later by a Monte Carlo scheme for chains up to 1000 C−C bonds.[2]

The key point behind such an incredible "tour de force" was the drastic mathematical simplification which consists of disregarding the monomer−monomer nonlocal interactions (sometimes called inappropriately "long-range" interactions) in the chain free energy. Such an elimination of solvent-mediated excluded volume forces is indeed (partially) justified for chains in a Θ-solvent, i.e. at a thermodynamic point where repulsive and attractive contributions to the two-body interactions accidentally cancel each other.[3] What makes this model even more important and useful is that it is relevant in the study of individual chains in polymer melts (at any temperature) on the basis of the well-accepted Flory conjecture that such chains are close to a Θ-point environment. This assumption, tested experimentally since then by neutron scattering, is still a matter of debate, however: see ref 4 for a recent discussion on this important topic and ref 5 for an example of a massive simulation test of this hypothesis on medium size chains (up to 100 methylene units).

"Chemical" models typically treat polymer conformations in terms of a set of N dihedral angles $\{\gamma_i\}_{i=1,N}$ controlling the internal rotation of one part of the molecule in respect to the other around the ith individual bond of the chain skeleton of N bonds. In Flory modelization, bending angles and covalent bonds are treated as fixed geometrical parameters. In the absence of nonspherical side groups, the interaction model of a linear polymer is written as a sum of two types of contributions: (i) single specific rotational angle contributions $U(\gamma_i)$ deal with effective "1−4" interactions, namely between atoms separated by three covalent bonds; (ii) "two-body" interaction terms $U(\gamma_i,\gamma_{i+1})$ introduce neighbor correlations resulting from 1−5 interactions between atoms separated by four covalent bonds such as the well-known pentane effect in polyethylene. This "local" or "short-range" interaction scheme yields what Flory called the "unperturbed" dimensions of the chain as the environment, i.e. the rest of the chain and the surrounding chains, has a neutral role on the average. In order to further simplify the statistical problem, the number of conformations was drastically reduced by allowing each dihedral angle variable to adopt a limited number of values corresponding to local minima of the torsion (free) energy: this is the basis of the so-called rotational isomeric state (RIS) approximation.

The above mathematical simplifications opened the path to both analytical and numerical developments in various aspects of single polymer statistical problems with the possibility to treat a broad class of polymer species. Let us mention analytical treatments exploiting the expression of the polymer partition function (end-to-end distance, total dipole, ...)[1] or the Monte Carlo estimation of the single chain structure factor for rather long polymers requiring modest computational efforts given that the number of conformations is limited and that the chain internal energy grows linearly with the number of bonds.[2]

The traditional RIS model is still commonly used today; however, doubts about the quantitative predictability of models restricted to local interactions are growing. An example is provided by the intermodel contradictions for the mean dimensions of a vinyl polymer like polypropylene at the Θ-point.[6] A different but related problem is the apparent sensitivity of the polymer size to the specific division between local and nonlocal interactions, namely the cutoff distance adopted along the polymer contour for monomer−monomer interactions.[7] The first observation shows that, within the framework of a Θ-point chain model (neglecting nonlocal forces), the choice of parameters describing both the rotational energy and the coupling between

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adjacent dihedral angles is largely ad hoc, especially in the presence of side groups. For the RIS model to be quantitatively realistic, the local interaction scheme must incorporate the average effect of correlations with more distant parts of the chain: this free energy character of the local interactions shows that fixing the model parameters requires more than a good ab initio potential calculation. More fundamentally, the second point illustrates that the distinction between "local" and "nonlocal" interactions has no strong basis; i.e. it is not based on a length or an energy scale separation for example.

The Flory approach to polymer statistics has received renewed interest recently from several groups exploiting new ideas requiring present time computer power. Vacatello and collaborators[8,9] have proposed a quasi continuous dihedral angle version of the RIS model. The elements of a 72 × 72 matrix describing a discretized conjoint distribution of consecutive dihedral angles within a polymer at the Θ-point is estimated from a preliminary Monte Carlo simulation of a corresponding oligomer in vacuum. On the basis of a very detailed atomistic potential avoiding any interaction cutoff, the conformations of consecutive dihedral angles in the central part of the oligomer are statistically analyzed in order to produce a probability distribution supposed to be transferable to the corresponding polymer at the Θ-point. This methodology was applied to polyisobutene (PIB) and to polyethylene (PE): in each case, the experimental chain structure factor of relatively low molecular weight polymers was satisfactorily reproduced.

Rigby and Stepto[10] have also used Monte Carlo techniques to study the expansivity of polymers when excluded volume effects are added to the RIS model. These excluded volume forces act between monomers which are close in space although distant from each other along the polymer contour. These forces combine a short-range repulsive part (hard sphere excluded volume) and an attractive part at medium range in space, the latter part (chosen proportionnal to r^{-6}) being weighed by an adjustable parameter. In this approach, Θ-point conditions are fixed at a preset absolute temperature defined relative to the energy scale introduced by the "realistic" local potential model (i.e., the gauche–trans energy difference in saturated hydrocarbons). According to earlier studies of off-lattice polymer coarse-grained models,[11-13] Θ-point conditions are found by adjusting the available parameter in the attractive part of the nonlocal forces until the average size of the polymer grows as $N^{0.5}$ in the long chain size limit.

Achieving Θ-point conditions through an exact compensation between repulsive and attractive contributions of binary nonlocal forces has been further exploited by Sariban et al. These authors consider a realistic chemical model of PE expressed in terms of continuous dihedral angles[14,15] and incorporate the solvent effect in the nonlocal forces between methylene groups through a Lennard-Jones potential with an ad hoc parameter modulating the attractive part. Such an approach is presented as a step forward in the prediction of chain properties on the basis of a specific atomistic model. The authors indeed envisage that such a technique will open new perspectives for the computer-aided molecular modeling of macromolecular systems,[15] but this remains to be checked on various polymer species outside the simple PE case.

Before closing this long introduction about Flory's approach and recent developments on the prediction of polymer structure on the basis of chemical models, let us stress the importance of the polymer single chain structure factor in the present context. Experimentally accessible by various scattering methods, it is a central quantity which probes polymer structure at all length scales,[16] as beautifully illustrated by the atactic polystyrene neutron scattering study of Rawiso, Dupplessix, and Picot.[17] As mentioned earlier, the first RIS model prediction of a structure factor was published on PE[2] and since then this quantity is used for testing the potential model prediction against experiments.[8,9,18]

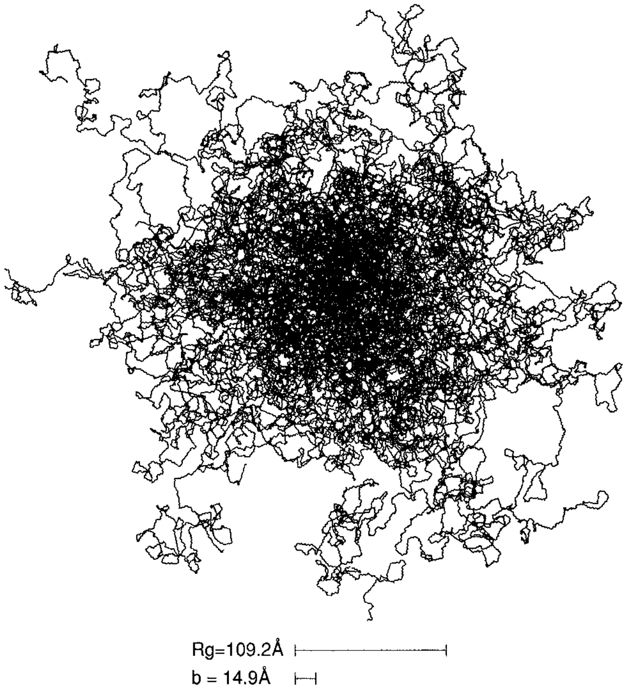

Figure 1. Superposition of the projections onto the *xy* plane of 20 independent conformations of the 4096 C–C bond PE chain at 400 K close to the Θ-point (the center of mass of all conformations is superposed at the center of the figure). The radius of gyration R_g and the Kuhn segment length *b* (twice the persistence length) indicate the two relevant length scales.

In the present work, we predict the structure factor of a long PE polymer at 400 K for various solvent qualities on the basis of a realistic atomistic potential of the polymer. Figure 1 gives an idea of the larger polymer size used in the present work, namely for a chain of 4096 C–C bonds close to the Θ-point. We adopt the potential model proposed by Sariban et al.[14,15] which requires a Monte Carlo sampling limited to the polymer degrees of freedom. The original aspect of our work lies in the ability to follow the structure factor $g(q)$ over the whole scattering vector q range pertinent to (long) polymers. Starting from the Guinier regime probing the global size of the polymer, we go down in space scale through the scaling regime typical of flexible polymers in solvent up to the local scale at 1 $Å^{-1}$ probing distances between bonded atoms! A crucial point to note is that we are dealing with much longer chains than in earlier studies, in fact with real polymer sizes, as proven by the observation of the asymptotic scaling regime expected for long linear polymers. The range of q over which this scaling behavior is detected is discussed in detail for different solvent qualities.

An important point in this work being the study of solvent quality influence on $g(q)$, we encountered the "practical" difficulty to assess the Θ-solvent state for very long chains on the basis of a model including explicit nonlocal interactions. We apply a method close to the one proposed some time ago by Binder and coworkers to determine the Θ-point temperature for chains on a diamond lattice[19] and more recently for coarse-grained chain models in continuous space.[13,20] This method rests on the expected universal behavior linking polymer size and departure from the Θ-point transition point resulting from the tricritical nature of the phase transition between a swollen and a collapsed chain state. See refs 21 and 22 for a recent discussion on this subject. We conduct a set of runs at a preset temperature of 400 K by probing the Θ-point region for different chain lengths, meaning here that the ad hoc parameter in the nonlocal forces was given a set of values in the neighborhood of the Θ-point value estimated by Sariban et al. on the basis of a shorter chain analysis.[14] Our final estimate of the Θ-point value of the parameter is found by optimizing a universal plot gathering all data relative to long chains.

The paper is organized as follows: In the next section, we establish the model and the two Monte Carlo techniques used to sample single chain conformations, namely the CBMC (configurational biased Monte Carlo) method and a modification of the pivot algorithm. The achievement of Θ-point conditions is specifically treated in section III. This section closes with an estimate of the persistence length (equivalently the Kuhn segment length) of PE at 400 K. Section IV describes the structure factor for Θ and good solvent conditions and its comparison with appropriate theoretical predictions such as Gaussian chain and flexible rod models. Section V deals with a closer analysis of the scaling regime. A general discussion and some conclusions are gathered in the last section.

II. Chain Model and Monte Carlo Techniques

We adopt a PE chain model very close to the one used by Sariban et al.[14] The $N + 1$ united atoms modeling methylene groups which are located at carbon positions $\{\boldsymbol{R}_i\}_{i=0,N}$, are connected by rigid bonds of length $l_{CC} = 1.54$ Å and rigid bending angles $\gamma = 109.7°$. A butane-like torsion potential with three preferred conformations (one trans and two gauche) deals with so-called "1−4" interactions: we adopted the "CHARMM" butane potential model[23] as this empirical function apparently reproduces ab initio predictions the most closely.[24] Interactions between methylene units separated by four C−C bonds are modeled according to the standard Lennard-Jones potential with values $\epsilon/k_B = 51.8$ K and $\sigma = 3.74$ Å: this completes the "local potential" model. For nonlocal interactions between methylene units separated by more than four C−C bonds, we adopt the modified Lennard-Jones interaction,

$$u(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \beta\left(\frac{\sigma}{r}\right)^{6}\right) \qquad (1)$$

with a β value adjusted according to solvent quality, the other parameters being taken identical to those chosen for the 1−5 interactions. To speed up calculations, interactions are neglected beyond a cutoff distance of 10 Å (6 Å when only repulsive interactions are considered, i.e. when $\beta = 0$). At ordinary melt or solution temperatures, β can be given values ranging from $\beta = 0$ when good solvent conditions prevail to $\beta = 1$, which corresponds to the collapsed chain case. Θ-solvent conditions at temperature T are fixed by a value $0 < \beta_\Theta(T) < 1$ defined as the value for which the polymer size increases as the square root of the molecular mass in the large polymer size limit. Let us note that Sariban et al. determined a value $\beta_\Theta = 0.53 \pm 0.03$ at 400 K.[15] On the basis of our analysis on much longer chains detailed in the next section, we find $\beta_\Theta = 0.505 \pm 0.005$ for an almost identical model.

Two Monte Carlo techniques have been exploited. The first is based on the configurational biased Monte Carlo (CBMC) method[25] in terms of "reptation" moves of the chain with a move "amplitude" corresponding to a segment of l monomers (typically, for PE, $l = 32$). At one end of the chain (each end being chosen with equal probability), the segment consisting in the last l monomers is eliminated while, at the other end of the chain, a new segment of l monomers is grown sequentially via a biased procedure which, among various dihedral angles attempts, favors low-energy elementary contributions. An attempted move is accepted on the basis of the ratio of the so-called Rosenbluth weights of the constructed and the deleted segments in such a way that the bias is corrected for. The second method uses the pivot algorithm wherein one bond of the chain is selected at random and the corresponding dihedral angle modified to a new value leading to the global rotation of one part of the chain with respect to the other.[5,26] Note that to enhance the acceptance rate in both MC methods, any dihedral angle is selected between 0 and 2π in a distribution proportional to $\exp(-V^T/k_BT)$ where V^T is the "butane" torsional potential and k_B is the Boltzmann constant. Without entering into further computational details, let us just mention that the CPU time required to generate on a CRAY YMP a new (independent) conformation at the Θ-point by CBMC is ≈20 s and ≈190 s for 1024 and 4096 bond chains, respectively. Most of the runs on PE were performed by the CBMC method, as this method is slightly more efficient. More details about these techniques will be published elsewhere.[27] A minimum of details are mentioned here as the chain lengths considered are quite unusual. This also allows us to indicate that the present results have been crosschecked by using two largely independent Monte Carlo techniques. Each production run is typically based on 1000 independent configurations, and error bars on averages represent a single standard deviation.

III. Adjustment of Θ-Point and Good Solvent Conditions

As mentionned in the Introduction, simulating polymers with nonlocal interactions at Θ-point conditions is not a trivial matter. For our specific polymer model, we need to fix the ad hoc parameter β to a value as close as possible to β_Θ (see eq 1) which is defined as the value leading to a perfect compensation between attractive and repulsive nonlocal interactions at 400 K. As the specific criteria to achieve this compensation is related to the long chain asymptotic behavior of the end-to-end distance, the Θ-point localization is necessarily approximate.[13]

The value β_Θ was selected on the basis of an analysis of the square end-to-end distance average $R_N{}^2$ for different chain lengths N and different β values close to the expected Θ-point value.

In Figure 2, we gather all results of the ratio $C_{N,N} \equiv R_N{}^2/Nl_{CC}{}^2 \equiv \langle(\mathbf{R}_N - \mathbf{R}_0)^2\rangle/Nl_{CC}{}^2$ for polymers consisting of N C−C bonds. We also report $C_{n,N}$ defined by the following intrachain mean square distances

$$C_{n,N} = \frac{1}{N - n + 1}\sum_{i=0}^{N-n}\frac{\langle(\mathbf{R}_{i+n} - \mathbf{R}_i)^2\rangle}{n{l_{CC}}^2} \qquad (2)$$

Given our purpose and the size of chains considered, we assume that $C_{n,N} \approx C_{n,n}$; namely, we expect the

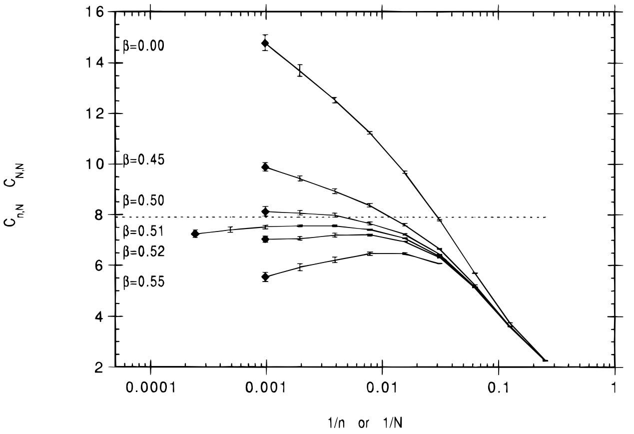

Figure 2. Global plot of Monte Carlo results at 400 K for different chain lengths and different values of the ad hoc parameter β regulating the solvent quality. The ratio $\langle R^2\rangle/Nl_{CC}^2$ is represented as $C_{N,N}$ (lozenges) for chains of size N and by ordinary points for $C_{n,N}$, namely subparts of size n in chains of size N. The estimated Θ-point value for C_∞ is shown by the broken line.

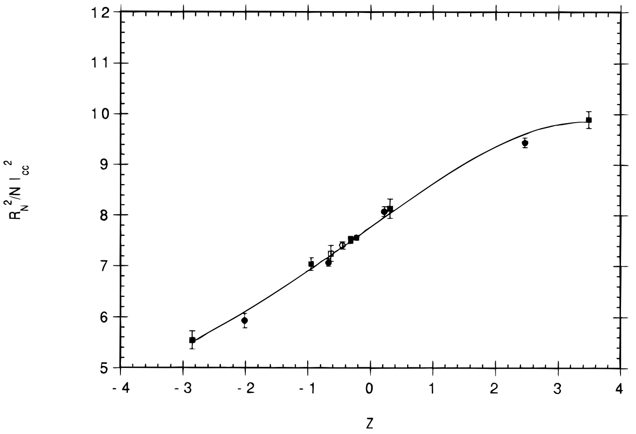

Figure 3. Universal behavior $\langle R_N{}^2\rangle/Nl_{CC}{}^2$ versus $Z = tN^{1/2}$ for chains with $N = 512$ (filled circles), $N = 1024$ (filled squares), $N = 2048$ (open circles), and $N = 4096$ (open squares) assuming $\beta_\Theta = 0.505$ in $t = (\beta_\Theta - \beta)/\beta_\Theta$. The continuous line is a polynomial fit to the data to help guide the eye.

average distance between monomers separated by n bonds within a longer chain to be representative of chains of length $N = n$. By plotting our results as a function of $1/N$ (or $1/n$), we look for the β value which leads to an asymptotically constant value of $C_{N,N}$ as $1/N$ tends to zero. From Figure 2, it appears that $\beta_\Theta(400) = 0.505 \pm 0.005$. This is confirmed by a plot of $C_{N,N}$ and $C_{n,N}$ versus β for each chain length[13] in which one looks for a fixed point through which should pass all curves relative to sufficiently long chains.

As pointed out recently,[13,20,21] the determination of Θ-point temperature in finite chain simulation studies can be made more systematic by exploiting phase transition scaling theory predictions. As solvent quality varies with temperature accross the Θ-point, theory predicts that $\mathrm{d}\ln(R_N)/\mathrm{d}T \propto N^{1/2}$ for sufficiently long chains. The transition can then be traced on finite chains through the universal behavior $R_N{}^2/Nl_{CC}{}^2 = f(tN^{1/2})$ where $f(Z)$ is a crossover scaling function where t is a measure of the relative departure from the Θ-point temperature. In the present context, it appears reasonable to measure the departure from Θ-point thermodynamic conditions through the quantity $t = (\beta_\Theta - \beta)/\beta_\Theta$. Figure 3 shows convincingly the existence of such universal behavior: all data $R_N{}^2/Nl_{CC}{}^2$ for chain sizes $N \geq 512$ (data already shown in Figure 2) are plotted against Z by assuming, as suggested by Figure 2 data, that $\beta_\Theta(400)=0.505$. The β_Θ value is thus again confirmed. In our experience with polyethylene and polypropylene,[27] such a plot is recommended as it is systematic to perform and allows an easier estimation of the precision on the results.

Direct inspection of Figure 2 then immediately confirms that the 4096 bond chain Monte Carlo calculation conducted with $\beta = 0.51$ corresponds to solvent conditions on the bad solvent side with a departure from the Θ-point characterized by $Z = tN^{1/2} \approx -0.5$. As Figure 3 indicates, this departure from the Θ-point is characterized by a ≈5% decrease of the dimension of the chain.

Figure 3 finally leads to the following estimate

$$C_\infty \equiv \lim_{N\to\infty} \frac{\langle(\mathbf{R}_N - \mathbf{R}_0)^2\rangle_0}{Nl_{CC}{}^2} = 7.9 \pm 0.2 \qquad (3)$$

where $\langle\ldots\rangle_0$ denotes a conformational average at the Θ-point.

This value is quite higher than the experimental range 6.8−7.1 for PE at 400 K[28] but is perfectly in agreement with results obtained earlier with the same model.[14,15] Refinement of potential is not our objective in this work. However, tracing the origin of the discrepancy between experimental and theoretical predictions is a subject of concern for the future in order to validate the present methodology and/or the model for absolute quantitative predictions of polymer size at the Θ-point.

In the following, the flexibility of the PE chain will be characterized by the Kuhn segment b defined by $b = \lim_{N\to\infty} \langle(\mathbf{R}_N - \mathbf{R}_0)^2\rangle_0/L$ where L is the polymer contour length.[1] We obtain $b = 14.9 \pm 0.4$ Å by assuming that $L = Nl_\infty \sin(\gamma/2)$.

Good solvent conditions were modeled by simply setting β to zero in the interaction law 1. Analysis of log−log plots of the average radius of gyration R_g versus N for $N = 128$, 256, 512, and 1024 gives the expected scaling laws, namely $R_g = (1.28 \pm 0.07)\,N^{(0.59\pm0.01)}$ and $R_N = (3.3 \pm 0.2)\,N^{(0.58\pm0.01)}$ if expressed in Å.

IV. The Chain Structure Factor

For a PE polymer with $N + 1$ diffraction centers located at carbon positions $\{\boldsymbol{R}_i\}_{i=0,N}$, the chain structure factor is given by

$$g(q) = \frac{1}{N+1}\sum_{i=0}^{N}\sum_{j=0}^{N}\langle\exp(-i\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j))\rangle \qquad (4)$$

In an isotropic medium, $g(q)$ is only a function of the modulus of $\mathbf{q}$.

The $g(q)$ functions for a PE chain in a good solvent (1024 C−C bonds) and in a Θ-solvent (4096 C−C bonds) are shown in Figures 4 and 5, respectively. The relevant q range is divided into three regions I−III corresponding to low, intermediate, and high q regimes. Quite arbitrarily, the limits we indicate in both figures are the boundaries of the q domain over which the curve displays a strict scaling behavior. The "straight line" portion in the log−log plots of $g(q)$ in region II indeed correspond to $g(q) = Aq^{-1/\nu}$ with $\nu = 0.5$ or $\nu = 0.59$ for Θ or good solvent conditions, respectively. This point will be analyzed in detail with the help of a Kratky plot in the next section. At present, we simply want to emphasize that the adopted polymer lengths in the simulations are large enough for $g(q)$ to display such a scaling regime: clearly the low and high q regimes are

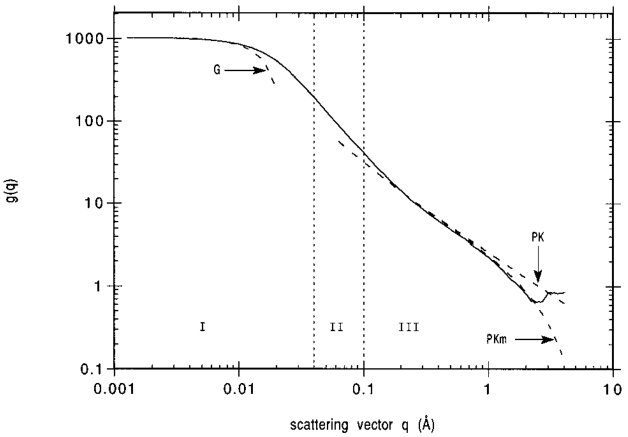

Figure 4. Structure factor of a 1024 bond PE chain in good solvent conditions at 400 K. The continuous line represents our Monte Carlo results. Broken lines represent theoretical predictions, namely the Guinier expansion at low q (noted G) and the Porod–Kratky model for flexible rods at high q using a Kuhn statistical segment of $b = 14.9$ Å, noted PK. The Porod–Kratky prediction modified to take the finite size of the rod into account is indicated by PKm.

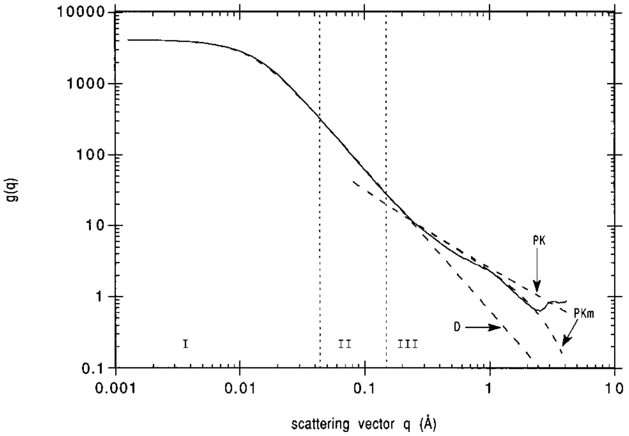

Figure 5. Structure factor of a 4096 bond PE chain close to the Θ-point at 400 K. The continuous line represents our Monte Carlo results. Broken lines represent theoretical predictions, namely the Debye prediction for ideal chains at low and intermediate q (denoted by D) and the Porod–Kratky model for flexible rods at high q denoted by PK. The Kuhn segment $b = 14.9$ Å is the only input parameter in both theories. The Porod–Kratky prediction modified to take the finite size of the rod into account is indicated by PKm.

therefore disconnected and can be analyzed separately. The Guinier regime $g(q) \approx (N + 1)(1 - ((qR_g)^2/3))$ valid at low q was computed on the basis of the average radius of gyration $R_g = 75.1$ Å for the good solvent case and $R_{g0} = 109.2$ Å for the 4 times larger chain close to the Θ-solvent. As Figure 4 shows, it applies as long as $qR_g \leq 0.7$. The ideal (Gaussian) chain model is known to be an excellent approximation of chains at the Θ-point or in melts for length scales larger than b. More explicitly, if we divide the whole chain into consecutive sets of n C–C bonds, the distribution of vectors joining methylene units separated by n C–C bonds, namely $\mathbf{r}_n = (\mathbf{R}_{i+n} - \mathbf{R}_i)$ should approach, as n increases, a product of three-dimensional Gaussian function

$$\psi(\mathbf{r}_n) = \left(\frac{3}{2\pi h_n^{\,2}}\right)^{3/2} \exp\left(-\frac{3\mathbf{r}_n^{\,2}}{2h_n^{\,2}}\right) \tag{5}$$

with

$$h_n^{\,2} = \langle \mathbf{r}_n^{\,2} \rangle = n l_{\mathrm{CC}}^{\,2} C_\infty \tag{6}$$

The chain form factor $P(q) = g(q)/g(0)$ for ideal chains (model describing a polymer structure as a sequence of independent Gaussian segments down to vanishing length scales) is given by the Debye function

$$P_{\mathrm{D}}(q) = \frac{2}{x^2}(x - 1 + \exp(-x)) \tag{7}$$

with

$$x = q^2 R_{g0}^{\;2} = q^2 \frac{bL}{6}$$

In Figure 5, we show the Debye prediction $g(q) = (N + 1)\,P_{\mathrm{D}}(q)$ based on eq 7 with x expressed in terms of the Kuhn segment value $b = 14.9$ Å. The agreement is excellent over regions I and II even if a small discrepancy can, however, be detected at low q, as the next section will show.

The local regime observed for any solvent quality above 0.2 Å^{-1} is usually described by the wormlike model of Porod and Kratky which in the regime $q > 1/b$ gives, for a chain contour length L, the asymptotic expression[29]

$$g_{\mathrm{PK}}(q) = \frac{N+1}{qL}\left(\pi + \frac{4}{3qb}\right) \tag{8}$$

This model can be modified to take into account the finite thickness of the coil, namely in multiplying $g_{\mathrm{PK}}(q)$ by a corrective factor $\phi(q) = \exp(-q^2 R_c^{\,2}/2)$ where R_c is an effective radius of diffraction centers in respect to a zero thickness thread model.[17] Results with and without the coil thickness correction are shown in Figures 4 and 5 for both the good solvent and Θ-solvent cases. The b parameter has been fixed to its known value and the radius of the coil has been taken as the distance between a single methylene unit center and a hypothetical thread crossing all C–C bonds in their midpoint, namely $R_c = {}^1/_2 l_{\mathrm{CC}} \cos(\gamma/2)$. For both solvent qualities, $g(q)$ rather abruptly quits the coil scaling behavior to approach rather closely, although imperfectly, the wormlike chain regime around the q value where scaling and PK theoretical curves intersect. This "length scale" transition is observed around $q \approx 0.2$ Å^{-1} which corresponds to a length scale of ≈30 Å. This value is quite reasonable as it is 2 times b! For q values above 1 Å^{-1}, the standard wormlike chain model is clearly no longer valid, as the zigzag structure of the C skeleton of the chain begins to appear: the modified theory, taking chain thickness into account, works extremely well as long as q remains below $2\pi/d$ where d corresponds to δ peaks in C–C distance distribution for first and second neighbor atoms. Note, finally, that $g(q)$ is not significantly sensitive to solvent quality in the high q range.

V. Refined Analysis of the Scaling Regime

In order to discuss more precisely the q range over which scaling is observed, we show in Figure 6 the (modified) Kratky plot of $g(q)q^{1/\nu}$ versus q for both solvent qualities using standard exponents $\nu = 0.5$ or $\nu = 0.59$ for Θ or good solvent conditions, respectively. Experimental observations[17] suggest that the scaling regime starts around $5/R_{g0}$ or $3/R_g$ for Θ or good solvent conditions, respectively, and ends up around a few times $1/b$. This fully agrees with the simulation results. Pragmatically, the good solvent scaling regime is easier to detect by simulation as it requires shorter chains to be observed. Chains of 1000 C–C bonds usually taken for $g(q)$ RIS estimations at the Θ-point[2,8,9] were thus a few times too short to display the scaling behavior.

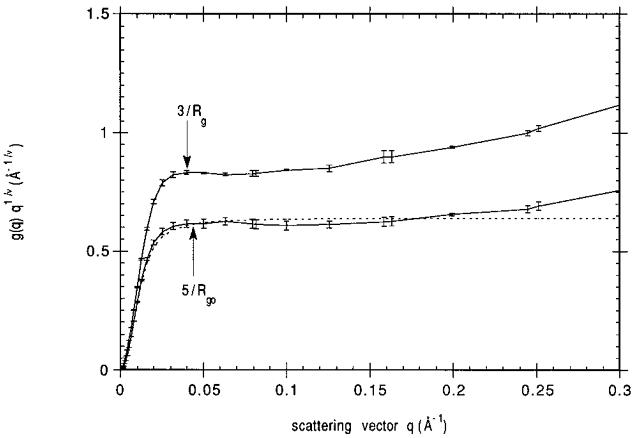

Figure 6. (Modified) Kratky plot, namely $g(q)q^{1/\nu}$ versus q for Θ-point $\nu = 0.5$ and good solvent case $\nu = 0.59$. Continuous lines represent good solvent (upper curve) and Θ-solvent (lower curve) conditions. The broken line represents the Debye theory prediction for an ideal chain. The expected lower limits of the plateaus characterizing scaling behavior are indicated by arrows. Error bars were estimated from the dispersion of curves obtained from three mutually orthogonal directions of **q**.

The height of the plateaus in the Kratky plots provides an estimate of the universal constants P_∞ defined by scaling behavior

$$\frac{g(q)}{N+1} = P_\infty (qR_g)^{-1/\nu} \qquad (9)$$

For good solvent conditions ($\beta = 0$, $N = 1024$), P_∞ is estimated from eq 9 using the plateau value $g(q)q^{1/\nu} = 0.82$ and the chain radius of gyration estimated from the Monte Carlo conformational average. One obtains the value $P_\infty = 1.21$, which agrees with experimental estimates.[17,30]

For the long chain case near the Θ-point ($\beta = 0.51$, $N = 4096$), the check of P_∞ requires some care as a result of the slight shift between thermodynamic conditions used in the simulations and the actual true Θ-point. We proceed by comparing the simulation curve for $g(q)$ with the Debye prediction (for which $P_\infty = 2$) based on the expected polymer size at the Θ-point, namely $R_{g0} = \sqrt{bL/6} = 113.2$ Å. Figure 6, which compares simulation results and the Debye function, shows plateau values of $g(q)q^{1/\nu}$ in mutual agreement.

Actually, a careful analysis of the behavior of the Monte Carlo curve $g(q)q^{1/\nu}$ for $q \leq 0.05$ Å^{-1} indicates that agreement with the Debye prediction is not fully satisfactory in this q range which probes the global dimension of the chain. The radius of gyration computed in the simulation, namely 109.2 Å, is indeed 4% smaller than the Θ-point radius of gyration assumed in the Debye function.

In the practice, the unavoidable shift in thermodynamic conditions the respect to the true Θ-point conditions alters the $g(q)$ in a nonuniform way over the q range and the low q regime appears to be more affected than the higher q part. This behavior is easy to interpret as a finite size scaling effect connected with the de Gennes' blob concept for a chain near the Θ-point.[16,21] The chain we consider is very long (4096 C−C bonds), and the blob size is lower than the chain length. Indeed, within statistical error, the structure of chain segments probed in the intermediate q range appears ideal (within the blob) while the slightly bad solvent conditions start showing up as larger and larger chain segments are considered, ending finally with a too short radius of gyration by 4% with respect to ideality. We can roughly (and rather subjectively) estimate the "blob" size of the PE chains considered in this experiment by observing that the structure factor deviates from the Θ-point Debye curve below $q = 0.05$ Å^{-1}, that is on a length scale of ≈125 Å. Using eq 3, one then gets a number of methylene units per blob of $N_{\mathrm{blob}} \approx 850$.

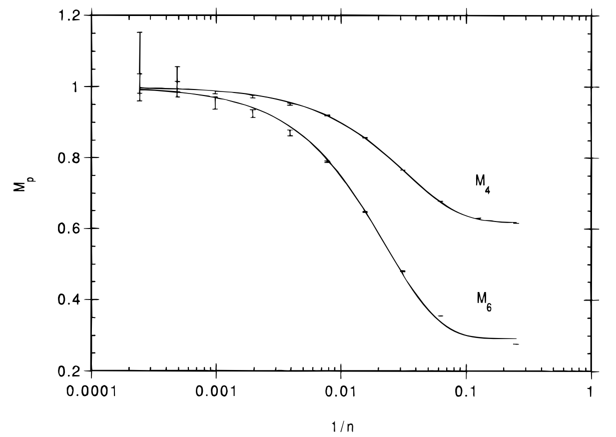

Figure 7. Moments $M_4 = 3\langle r_n^4\rangle/5\langle r_n^2\rangle^2$ and $M_6 = 9\langle r_n^6\rangle/35\langle r_n^2\rangle^3$ (defined to be equal to 1 for the Gaussian case) as a function of $1/n$ for the large chain size case ($N = 4096$) close to the Θ-point conditions. To guide the eye through the points, continuous lines represent polynomial fits forced to reach unity as $1/n$ tends to zero.

Our conclusion is thus that the Gaussian chain model should probably be, as expected, an extremely good approximation of the structure factor $g(q)$ for polymers at the Θ-point. What limits a quantitative check over a wide q range is the need of both long chains ($N \gg 1$) and a very small relative shift $t = (\beta_\Theta - \beta)/\beta_\Theta$ from the Θ-point conditions, subject to the condition that $tN^{1/2}$ must remain much smaller than 1.

As the present simulation work is concerned with polymers modeled at the chemical level in the presence of nonlocal forces, the observed q upper limit for the validity of the Gaussian chain model should be representative of the situation with real polymers. This suggests a direct analysis of the convergence of an atomic model of a polymer with "rigid" covalent bonds and angles toward a Gaussian chain behavior as n increases (as the length scale gets larger): this point is not trivial in the sense that the presence of nonlocal forces in our model prevents the use of a central limit theorem argument to explain Gaussian behavior at large length scales. Following standard practice,[1] we evaluate the second moment $\langle r_n^2\rangle$ discussed earlier and the moment ratios $M_4 = 3\langle r_n^4\rangle/5\langle r_n^2\rangle^2$ and $M_6 = 9\langle r_n^6\rangle/35\langle r_n^2\rangle^3$ defined to be unity for a Gaussian distribution given in eq 5. In Figure 2, it can be observed that $\langle r_n^2\rangle$ divided by nl_{CC}^2 approaches C_∞ up to a few percent as n reaches 100. As shown in Figure 7, M_4 and M_6 have already reached 0.96 and 0.89, respectively, for chains of 256 bonds. In agreement with the $g(q)$ behavior discussed earlier, these results again confirm the widely accepted view that real (finite) chains close to Θ-points are very close to ideal chains on length scales larger than a few times b.

VI. Discussion and Conclusions

While calculations of the structure factor of a single polymer chain for coarse-grained models have already a long history,[7,11,12] calculations of this central quantity on the basis of "atomic" or "chemical" models have always been performed with variants of the Flory RIS model. In such a model, the nonlocal (excluded volume) interactions are fully neglected and the results are therefore representative of Θ-point chains. For lack of computer power, the chains considered were systematically too short to display the whole set of length scale regimes, missing in particular the power law scaling behavior for the intermediate q regime.[2,9] This implies that the "local" and the "global" chain regimes were not properly disentangled.

We have reported in this paper Monte Carlo calculations of the single chain structure factor $g(q)$ of a polyethylene (PE) polymer in a noncrystalline phase on the basis of a specific "chemical" model including both realistic local interactions (e.g. torsions) and nonlocal effective (solvent mediated) interactions between all methylene pairs. Both Θ-point and good solvent conditions were considered. On the basis of sufficiently long chains, the expected static polymer scaling laws characterizing random or self-avoiding walks, respectively, have been carefully investigated. For chains close to the Θ-point, the Debye function for Gaussian (ideal) chains[16] and the des Cloizeaux asymptotic expression for the Porod−Kratky wormlike chain model[29] are found to reproduce very closely the chain structure factor in the lower and in the higher part of the q range, respectively. No parameter adjustment is involved in these theoretical predictions. Indeed, in addition to the polymerization degree N and related polymer contour length L, the single input parameter in both theories is the Kuhn statistical segment b.

Let us stress again that Monte Carlo simulations of a chain in a solvent with nonlocal interactions cannot be performed exactly at the Θ-point because such a thermodynamic point is defined by asymptotic properties of polymers as $N \rightarrow \infty$. The problem at first sight looks even more acute for long polymers as the transition between the swollen coil state and the collapsed chain becomes sharper as N increases. However, as phase transition scaling theory predicts size effects accross the transition point, namely $\mathrm{d}\ln(R_N)/\mathrm{d}T \propto N^{1/2}$, the Θ-point can in principle be determined from finite chain behavior. In the present context, we exploit a direct analogy between temperature and the β ad hoc parameter (weighing the attractive part of the nonlocal forces). Our data collected at 400 K for different chain lengths and for different β values were found to follow a universal behavior $R_N^2/N_{\mathrm{CC}}^2 = f(tN^{1/2})$ where t is a measure of the relative departure from the Θ-point thermodynamic state through the quantity $t = (\beta_\Theta - \beta)/\beta_\Theta$. In this way, we have a practical recipe to estimate C_∞ and β_Θ in a systematic way which exploits the whole set of runs. Such a method has been found to work not only for PE (see Figure 2) but also for polypropylene.[27]

In the Introduction, we indicated deficiencies of the RIS approach which, to a large extent, are linked to the arbitrariness in any clear-cut division between local and nonlocal with the explicit intention of neglecting the second ones when modeling Θ-point chains. The resulting "cutoff" problem in defining the local interaction character is a byproduct of the particular modelization: local interactions are described at the atomic length scale while, in the RIS approach, nonlocal interactions have a coarse-grain nature as the repulsive and attractive parts of nonlocal interactions cancel at all length scales. With the type of model we follow in the present work[10,14,15] the exact compensation between repulsive and attractive nonlocal interactions is obtained thanks to a control parameter in the nonlocal (but short range in space) interaction. In the future, we hope to participate in the efforts covering a large variety of polymers, to test whether the latter method effectively leads to more robust estimates of polymer average structures at the Θ-point: this conjecture is plausible as it is reminiscent of the widely accepted idea that so-called "specific solvent effects" have a minor effect on chain dimensions at the Θ-point. More specifically, we are presently investigating whether the methodology described in the present paper can clarify the link between polymer dimensions at the Θ-point and chain tacticity in the polypropylene case.[6,27]

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