Single-Chain Structure in Model Polyethylene Melts

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ABSTRACT: The rotational isomeric state (RIS) model is usually considered to be an excellent description of the single-chain structure of polymer chains both in the melt and in Θ solvents. The manifestation of this single-chain structure (commonly measured by scattering experiments) is the correlation function $\omega(r)$, which is the probability that two sites on the same chain are separated by a distance r. The evaluation of $\omega(r)$ from the RIS model requires laborious statistical averages, and, as a consequence, various approximations of $\omega(r)$ are of importance. Previous approximation schemes have focused on the long-wavelength regime. However, many physical phenomena and properties are very sensitive to local correlations and understanding such behavior requires an approximate $\omega(r)$ which is accurate on all length scales. We present such an approximation here and compare it to both computer simulation and previous, more coarse-grained approaches.

I. Introduction

We have recently engaged in detailed theoretical investigations of the intermolecular site–site probability distribution functions in dense polymer melts.[1-4] These distribution functions play a central role in the understanding of phenomena such as the equation of state, phase behavior, and interfacial properties.[5,6] In addition, they can be directly probed by X-ray and neutron diffraction methods.[1,7,8] In this paper we consider the intramolecular correlations of a single chain in the melt. Here, as in ref 1, our focus is simple hydrocarbons where the elementary chemical unit, or "site", is taken to be an effectively spherical CH_2 group.

Several different types of pair distribution functions arise in the study of polymer statistics. The total site–site correlation function $S(r)$ is the ensemble-averaged probability density that sites will be found in volume elements separated by r (less the mean-field ρ^2 contribution where ρ is the site density). Its Fourier transform divided by the density is the static (total) structure factor $\hat{S}(k)$, which may be measured by, for instance, X-ray scattering. The intrachain correlation function $\omega(r)$ is the probability density of finding two sites *on the same chain* separated by a distance r. It is also useful to define the probability density between two specific sites on the same chain $\omega_{ij}(r)$ which when summed over j and averaged over i is $\omega(r)$. The Fourier transform of $\omega(r)$, $\hat{\omega}(k)$, may be measured by isotopically labeling a small fraction of chains in a melt and using neutron-scattering methods.[8-10] Finally, the interchain correlation function, $g(r)$, is defined such that $\rho g(r)$ is the chain-averaged probability density of finding two sites *on different chains* separated by a distance r. It may be deduced from the experimental $S(r)$ and $\omega(r)$ through the relation $S(r) = \rho\omega(r) + \rho^2 h(r)$, where $h(r) \equiv g(r) - 1$.

The RISM ("Reference Interaction Site Model") integral equation approach of Chandler and Andersen,[11] as extended to polymers ("polymer-RISM" or "PRISM") by Curro and Schweizer,[2] can be used to calculate $\hat{S}(k)$ and $g(r)$ if $\omega(r)$ is known. While the calculation of the structure factor of polyethylene was our primary goal in ref 1, we also found it necessary to develop an accurate approximation for $\omega(r)$ (or equivalently, $\hat{\omega}(k)$) which reflected the detailed chemical structure of the chains. This new approximation scheme is the subject of the present paper. Indeed, the quantitative agreement for polyethylene between the structure factor predicted by PRISM and that measured by X-ray diffraction experiments[1] is a direct result of our accurate description of $\omega(r)$.

Rather than presenting our approximation as an isolated case, we also discuss in section II a number of computationally-convenient methods for determining $\omega(r)$ with the intent of highlighting the improved accuracy of our approach. The exact evaluation of $\hat{\omega}(k)$ for moderately sized chains through Monte Carlo simulation is discussed in section III. Section IV compares the various approximations to the simulation results and comments on the influence of their differences on the structure factor, $\hat{S}(k)$, of the melt. A concluding discussion is contained in section V.

II. Approximation of $\omega(r)$

The structure of a chain in the melt is very different than that of a single, isolated chain or of a chain in a good solvent. The excluded-volume interactions between sites which swell the isolated chain are effectively screened out in the melt.[12] That is, the melt acts as a Θ solvent for itself. Flory took advantage of the screening of long-range excluded volume by describing the single-chain melt structure with a model (the rotational isomeric state (RIS) model)[13] which has only *local* interactions. In particular, polyethylene can be described using a gauche–trans energy of 500 cal/mol (with an additional 2000 cal/mol for two adjacent gauche bonds of opposite sign), a carbon–carbon bond length L of 1.54 Å, a bond angle of 112°, and gauche conformations located at ±120° relative to the trans. We have focused our attention here on behavior at 413 K, which is close to the experimental melting point of the linear homopolymer at atmospheric pressure.

While it does seem that the RIS model provides an excellent description of the single-chain structure,[13] it is

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difficult to evaluate $\omega(r)$ for the model. The structural properties conveniently calculated by the transfer matrix methods[13] of the RIS model are the moments $\langle r_n^2\rangle$, $\langle r_n^4\rangle$, etc., and not the underlying distribution function $\omega(r)$. Here r_n is the distance between two sites separated by n consecutive bonds along the chain, and $\langle\ \rangle$ indicates an ensemble average. The most common solution to this problem is to make use of simple model chains (Gaussian, freely jointed, etc.) with analytically computable $\hat{\omega}(k)$ and to adjust the parameters of the model polymers so that their first few moments duplicate those of the RIS chains. Such an approach is useful and correct for describing the relatively long-wavelength behavior of polymers which is insensitive to chemical length-scale information. However, for the physical problems mentioned in the Introduction, one requires a representation accurate on *all length scales*. In addition to describing the methodology we have developed, we briefly review several previous approximation schemes for comparative purposes. The various approximations considered are as follows.

(1) Gaussian Approximation.[14] This is the simplest, most coarse-grained model of a polymer chain. Each site is bonded to its neighbors by Hookean springs of entropic origin, and all nonbonded interactions are absent. The corresponding $\hat{\omega}(k)$ of the Gaussian model is given exactly[3,14] by

$$\hat{\omega}(k) = \frac{1 - e^{-2x/N} - \frac{2}{N}e^{-x/N}(1 - e^{-x})}{(1 - e^{-x/N})^2} \tag{1}$$

where $x = k^2R_g^2$, R_g is the radius of gyration of the Gaussian chain, and N is the number of sites in the chain. In applying eq 1 to real polymers, the usual procedure[14] is to replace R_g with the radius of gyration of the actual polymer of interest.

(2) Debye Approximation.[14,15] This is a widely used approximation to the Gaussian distribution valid for $x \ll N$ (i.e., $k \ll 1/L$). Physically, this simplification arises from the neglect of the discrete nature of the Gaussian chain on segmental length scales and is given by

$$\hat{\omega}(k) = \frac{2N}{x^2}(e^{-x} - 1 + x) \tag{2}$$

Since in the absence of long-range, excluded-volume interactions all sufficiently-long chains are Gaussian on long wavelengths, $k \ll 1/L$ (and real polymer chains in a melt fall into this category[12]), both the Gaussian and Debye representations describe this region well.

(3) Yoon–Flory Moment Expansion.[16] The above two approximations utilize only a single characteristic of the real chain (namely, R_g) and, thus, cannot be expected to reflect structural variations over a spectrum of intramolecular length scales or to capture departures from ideal Gaussian statistics. However, it is possible to expand $\hat{\omega}(k)$ in the moments $\langle r_n^2\rangle$, $\langle r_n^4\rangle$, etc. The higher moments are cumbersome to evaluate in practice, and the state of the art in the calculation of $\omega(r)$ for polyethylene from a knowledge of the moments is a tour de force by Yoon and Flory,[16] utilizing moments through $\langle r_n^8\rangle$.

Yoon and Flory expanded $\hat{\omega}(k)$ as

$$\hat{\omega}(k) = 1 + \frac{2}{N}\sum_{n=1}^{N-1}(N-n)e^{-k^2\langle r_n^2\rangle/6}\left[1 + \sum_{i=2}\left(\frac{k^2\langle r_n^2\rangle}{3}\right)^i g_{2i;n}\right] \tag{3a}$$

where

$$g_{4;n} = -\frac{1}{2^3}\left[1 - \frac{3\langle r_n^4\rangle}{5\langle r_n^2\rangle^2}\right]$$

$$g_{6;n} = -\frac{1}{2^4}\left[1 - \frac{3\langle r_n^4\rangle}{5\langle r_n^2\rangle^2} - \frac{1}{3}\left(\frac{1 - 9\langle r_n^6\rangle}{35\langle r_n^2\rangle^3}\right)\right] \tag{3b}$$

and

$$g_{8;n} = -\frac{1}{2^6}\left[1 - \frac{3\langle r_n^4\rangle}{5\langle r_n^2\rangle^2} - \frac{2}{3}\left(\frac{1 - 9\langle r_n^6\rangle}{35\langle r_n^2\rangle^3}\right) + \frac{1}{6}\left(\frac{1 - 3\langle r_n^8\rangle}{35\langle r_n^2\rangle^4}\right)\right]$$

For polyethylene, through the $\langle r_n^8\rangle$ moment level, this expansion is still poorly converged,[16] even in the reasonably long (or "intermediate") wavelength region where this sort of expansion is expected to work well.

In our work, we are interested in the behavior of $\hat{\omega}(k)$ not only at small k but also at short wavelengths where the delta function nature of $\omega(r)$ makes a description by moments impractical. We have addressed this problem by treating the short-range local structure explicitly and then describing the long-range structure by RIS moments. We decompose $\omega(r)$ as

$$\omega(r) \equiv \frac{1}{N}\sum_{\alpha,\beta}\omega_{\alpha\beta}(r) = \frac{1}{N}\sum_{\alpha}\left\{\sum_{|\alpha-\beta|\le 5}\omega_{\alpha\beta}(r) + \sum_{|\alpha-\beta|>5}\omega_{\alpha\beta}(r)\right\} \tag{4}$$

where $\omega_{\alpha\beta}(r)$ is the distribution function for sites "α" and "β", and explicit end effects are retained. The $\omega_{\alpha\beta}(r)$'s in the $|\alpha - \beta| = n \le 5$ summation result from an explicit enumeration of all Boltzmann weighted rotational isomeric states, while the contributions in the $|\alpha - \beta| > 5$ summation are calculated for a "simpler" (more coarse-grained) model chain whose parameters are selected so that its first several moments agree with those of the RIS model.[17] We have found that explicit enumeration through 5 bonds represents a good compromise between accurately representing the short-range structure (one bond beyond the "pentane" effect[13]) while retaining computational convenience.

The accuracy of this "splice" between short- and long-range correlations depends upon the model used to describe the large n contributions. If we adopt a specific model "Y", the $\hat{\omega}(k)$ calculated through eq 4 is referred to as the result of the "Y-patch" approximation. We now consider a number of approximation schemes of this type.

(4) Gaussian-Patch I Approximation. The sites separated by more than 5 sites are viewed as being members of a Gaussian chain, described by eq 1. We are assured that both long- and short-wavelength behavior is correctly described by this approximation. Indeed, this can be said for all our "patched" approximations. Thus, it is the intermediate wavelength regime which is of importance in assessing the accuracy of an approximation based on eq 4.

(5) Gaussian-Patch II Approximation. In the above approximation, the model chain parameters are based solely upon the global chain behavior (i.e., R_g). Here the nonenumerated sites are again bonded by Gaussian springs

$$\hat{\omega}_{\alpha\beta}(k) = e^{-\langle r_n^2\rangle k^2/6} \tag{5}$$

where $|\alpha - \beta| > 5$ but now the Gaussian parameters are selected *for each* n so that the $\langle r_n^2\rangle$'s of the Gaussian chain are exactly those of the RIS model.

Table I
Second and Fourth Moments of Polyethylene for 293 K < T < 500 K[a]

$n < 10$	$n > 10$
$\frac{1}{C_n} = A + B\frac{1}{n}$	$\frac{1}{C_n} = A + B\frac{1}{n} + C\frac{1}{n^2}$
$\frac{1}{D_n} = D + E\frac{1}{n} + F\frac{1}{n^2}$	$\frac{1}{D_n} = D + E\frac{1}{n} + F\frac{1}{n^2}$
$A = 0.062542 + 0.00016311T$	$A = 0.075943 + 0.00016686T$
$B = 1.3606 - 0.00021396T$	$B = 0.7793 - 0.00004175T$
$D = -0.0052554 + 0.00002344T$	$C = 5.365 - 0.0035796T$
$E = 0.27998 + 0.0004127T$	$D = \frac{3}{5}A^2$
$F = 1.4692 - 0.00065476T$	$E = 0.13243 + 0.00028452T$
$C_n = \langle r_n^2\rangle/nl^2$; $D_n = \langle r_n^4\rangle/n^2l^4$	$F = 2.2857 + 0.000065533T$

[a] n is the number of bonds; l is the bond length.

(6) Koyama-Patch Approximation. In order to force equality of the RIS chain and the model chain through both the second and fourth moments $\langle r_n^2\rangle$ and $\langle r_n^4\rangle$ for *all* n, a non-Gaussian model must be used. One such model may be motivated by realizing that a chain segment of length n is more flexible than a rod and stiffer than a Gaussian bond. A simple interpolation between these two extremes is the convolution of the distribution function for a rod and a Gaussian bond which (in Fourier space) is

$$\hat{\omega}_n(k) = \frac{\sin(B_nk)}{B_nk}e^{-A_n^2k^2} \tag{6}$$

where A_n and B_n are selected to correctly give $\langle r_n^2\rangle$ and $\langle r_n^4\rangle$. This is the Koyama distribution.[18,19] The Koyama distribution was originally developed to describe continuous wormlike chains and more recently has been modified to describe the discrete pearl-necklace model.[4] The relevant formulas are given in ref 4 and will not be repeated here. Either wormlike or pearl-necklace Koyama distributions will capture the long-wavelength behavior of RIS chains; however, our Koyama-patch[1] is able to capture the more-detailed short-wavelength nature of these chains as well.

The most difficult aspect of these approximation schemes is the calculation of the RIS moments required to fix A_n and B_n in eq 6. We numerically calculate $\langle r_n^2\rangle$ out to $n = 99$ and $\langle r_n^4\rangle$ out to $n = 29$ using standard Flory transfer matrix methods.[13] Moments for higher n's are evaluated by a parabolic fit to the calculated moments where we have carefully extrapolated the $\langle r_n^2\rangle$ to get the correct infinite-chain limit and have also constrained the infinite-chain limit of $\langle r_n^4\rangle$ to obey the exact relationship $\langle r_\infty^4\rangle = (5/3)\langle r_\infty^2\rangle^2$. Because polyethylene is such a ubiquitous material, we report in Table I interpolations of moments calculated for 293 K ≤ T ≤ 500 K. We believe these interpolations to be accurate to within 2%. At 413 K, the values of the characteristic ratio $C_\infty = 6.9$ and its derivative $d\ln C_\infty/dT = -0.00115$ (1/K) are well within the ranges suggested by Flory[13] (6.7 ± 0.3 and −0.0011 ± 0.0001 (1/K), respectively). It is common for C_∞ to be estimated at various temperatures through the first-order Taylor series for $\ln C_\infty$ (e.g., $\ln(C_\infty(T)) = \ln(C_\infty(413)) + (d\ln C_\infty/dT)(T-413)$). However, we have evaluated C_∞ directly over a wide range of temperatures and found that the accuracy of the Taylor series approximation becomes unacceptable for temperatures differing from 413 K by more than a few tens of degrees. In particular, for $T = 293$ K, the Taylor series leads to a value of $C_\infty = 7.88$, while our explicit, long-chain extrapolation gives $C_\infty = 8.03$ and the interpolated expression in Table I gives $C_\infty = 8.01$.

III. Simulation

Within the RIS approximation, "exact" $\hat{\omega}(k)$ functions were computed by means of Monte Carlo generation of chain conformations.[16,20] Conformations of chains containing from 100 to 1000 bonds (101 to 1001 sites) were generated in Markov fashion using a priori and conditional bond conformation probabilities[13] calculated from the standard polyethylene statistical weights.

For the purpose of calculating the intramolecular structure factor, each backbone (i.e., carbon) atom in the chain was treated as a scattering center, and $\hat{\omega}(k)$ was computed using the expression

$$\hat{\omega}(k) = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\sin(kr_{ij})}{kr_{ij}}\right\rangle \tag{7}$$

where N is the number of sites in the chain, r_{ij} is the distance between sites i and j in a given conformation, and the angle brackets denote an average over all conformations. Typically, from 200 to 3000 conformations were generated for each chain length to achieve $\hat{\omega}(k)$ values with a sufficiently small statistical uncertainty. (Such a small number of conformations is sufficient in part because, in the Markov scheme, each chain conformation is uncorrelated with subsequent ones.)

These calculations differ from those of Yoon and Flory[16] in the following respect. Yoon and Flory used Monte Carlo generation of chain conformations in conjunction with eq 7 only for sequences up to 100 bonds ($|i-j| < 100$). For $|i-j| \geq 100$, they used a moment expansion and standard RIS matrix techniques to estimate the contribution of these longer sequences to $\hat{\omega}(k)$. By contrast, in the current study, entire chain conformations were explicitly generated for all chain lengths. Even so, the Kratky function, $k^2L^2\hat{\omega}(k)$, obtained by this method differs by at most 7% from that in ref 16 (for $N = 1001$).

IV. Comparison of Theory to Simulation

We have simulated chains varying in length from 101 to 1001 sites, and we concentrate on the two extremes here. Figure 1 shows a comparison of $\hat{\omega}(k)$ of a 101-site chain found by simulation to that found by the Koyama-patch methodology where (as discussed in section II) the local correlations have been explicitly enumerated through 5 bonds using the RIS model and the longer range correlations approximated by eq 6. Results are plotted in standard Kratky[21] form ($k^2L^2\hat{\omega}(k)$ vs kL). The agreement between simulation and theory for $kL > 1$ is nearly perfect (we have compared out to $kL = 23$), and this level of agreement for $kL > 1$ holds for *all* the chains for which we simulated this high-k region ($N = 101$–801). The insert magnifies the "intermediate scaling" region over which there is greatest disagreement. The Koyama-patch approximation slightly underestimates $\hat{\omega}(k)$ in this region corresponding to a slightly too stiff chain.

For the 1001-site chains, we have concentrated our simulation efforts on the $kL < 1$ region and taken the Koyama-patch $\hat{\omega}(k)$ for k outside the simulated region to be quantitatively accurate (as was explicitly demonstrated for $N \leq 801$). Accordingly, we refer to the simulation at small k plus the Koyama-patch at high k as the "true" or "exact" $\hat{\omega}(k)$.

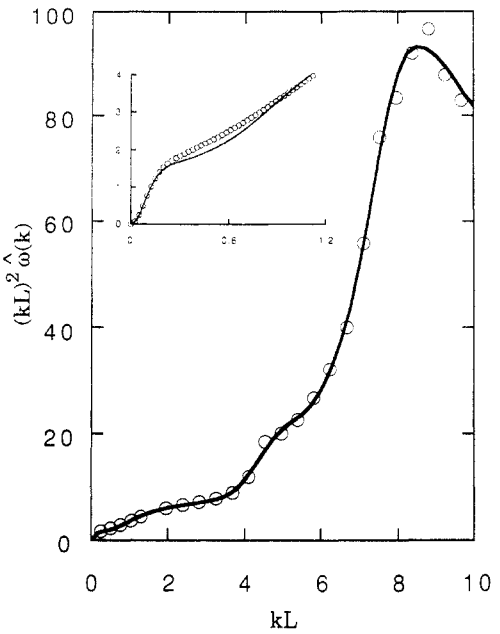

Figure 1. Kratky plot for a 101-site RIS chain. The solid line is the Koyama-patch approximation, and the circles are simulation results. For the region $kL < 1.2$, the error in the simulation is less than the diameter of the circles in the inset. For the region $kL > 1.2$, the error is within a few diameters of the circles in the main figure.

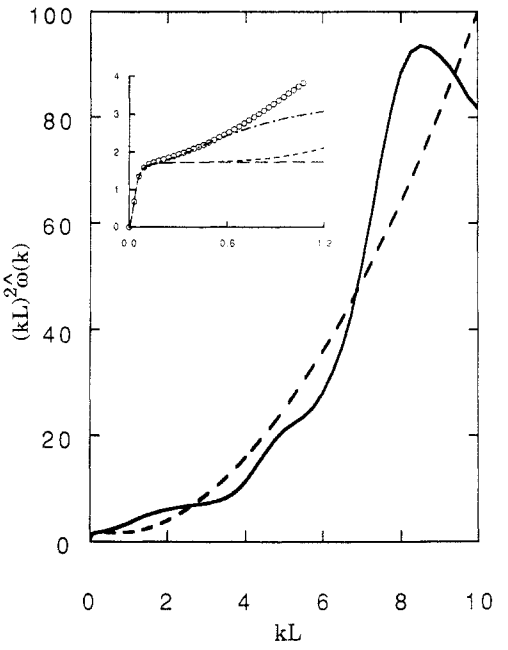

Figure 2. Kratky plot for a 1001-site RIS chain. In the main figure the dashed line is for the equivalent Gaussian chain, and the solid line is the "exact" RIS curve (that is, simulation results at small k and the Koyama-patch at higher k). In the inset the short dashed line is for the equivalent Gaussian chain, the long dashed line is the Debye approximation for the equivalent Gaussian chain, the dot-dashed line is the moment expansion of Yoon and Flory[16] through $\langle r_n^4 \rangle$, and the circles are simulation results. The exact RIS curve will oscillate about the Gaussian curve for all k values larger than shown. The Debye approximation will remain a constant for all k values larger than shown. The Yoon–Flory approximation through $\langle r_n^4 \rangle$ becomes identical with the Gaussian approximation for $kL > 4$.

Figure 2 compares this exact single-chain structure factor to the $\hat{\omega}(k)$ of both the equivalent Gaussian chain and the Debye approximation for $N = 1001$. As expected, they are in good agreement (by construction) with simulation in the long-wavelength (small-wavevector) regime; however, both are in poor agreement in the short- and, as

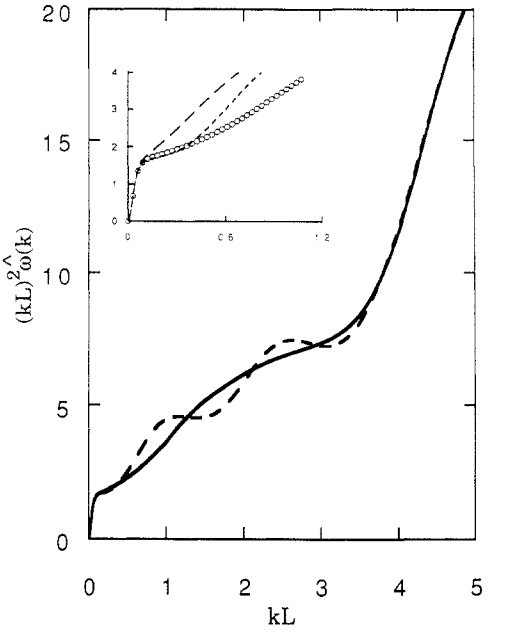

Figure 3. Kratky plot for a 1001-site RIS chain. In the main figure the dashed line is the Gaussian-patch using only $\langle r_\infty^2 \rangle$, and the solid line is the exact RIS curve. In the inset the short dashed line is the Gaussian-patch using only $\langle r_\infty^2 \rangle$, the long dashed line is the Gaussian-patch using the full $\langle r_n^2 \rangle$, and the circles are simulation results. Both Gaussian-patches become identical for $kL > 1.2$.

shown in the inset, in the intermediate-wavelength region. Notice, however, that the Gaussian function captures the general shape of the curve, while the Debye approximation is flat for $kL > 1$—a consequence of the approximations made in going from eq 1 to eq 2.

The Yoon–Flory moment expression through $\langle r_n^4 \rangle$ is also compared to the true $\hat{\omega}(k)$ in Figure 2 for a 1001-carbon chain. The moment expansion becomes very much like the Gaussian approximation at short wavelengths. The expansion would need to be taken to very high moments to capture the delta function nature of this region. Indeed, the expansion through $\langle r_n^8 \rangle$[16] only serves to worsen the agreement with simulation.

The Gaussian-patch I approximation is compared to the true $\hat{\omega}(k)$ in Figure 3. For $kL > 4$, the agreement is quantitative. It is the $0.1 < kL < 4$ "intermediate-wavelength regime" which is difficult to describe, because this region is dominated neither by very short nor by very long wavelength behavior. The Gaussian-patch II approximation is also presented in the inset of Figure 3. Clearly, there is still difficulty in the $0.1 < kL < 4$ region.

Finally, in Figure 4 the full Koyama-patch is shown for 1001-site chains. The region of disagreement between simulation and theory is reduced to $0.1 < kL < 0.8$, implying that including the information contained in the fourth RIS moment via the Koyama distribution results in an accurate description of the single-chain structure. However, as was true for the $N = 101$ chain, the Koyama-patch tends to underestimate $\hat{\omega}(k)$ slightly and, hence, to overestimate the "plateaulike behavior".

Figure 5 displays the structure factors predicted by PRISM integral-equation theory[1] using the exact and the Koyama-patch $\omega(r)$'s for 801-site chains at a density of 0.7796 g/cm^3. Here CH_2 groups have been represented by hard-spherical sites of diameter 3.9 Å. Judging by the agreement in both the $\hat{\omega}(k)$'s and the $\hat{S}(k)$'s, the Koyama-patch approximation is quite accurate.

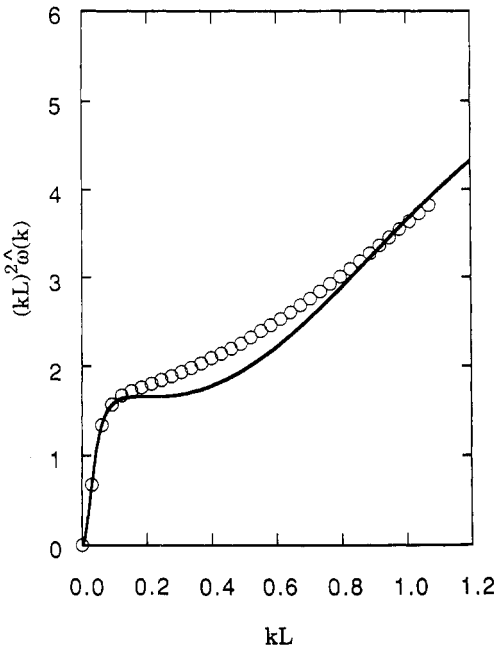

Figure 4. Kratky plot for a 1001-site RIS chain. The solid line is the Koyama-patch, and the circles are simulation results.

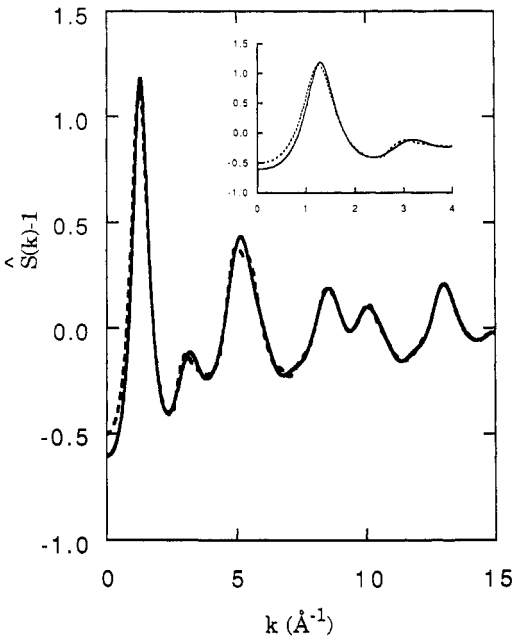

Figure 5. Total structure factors for 801-site chains calculated using PRISM theory. The solid line is computed using the Koyama-patch $\hat{\omega}(k)$, and the dashed line is calculated from the true $\hat{\omega}(k)$. The inset contains an expansion of the amorphous halo region.

V. Discussion

A Kratky[21] plot is intended to bring out the universal "plateau" region (where $\hat{\omega}(k) \sim 1/k^2$), and this feature is clearly seen in the Gaussian $\hat{\omega}(k)$ (Figure 2). The existence of the plateau region is considered to be a hallmark of polymeric correlations. It indicates that the chains are long enough to display self-similar, ideal random-walk statistics. However, to the best of our knowledge, there are no published simulation studies which show a plateau for the RIS model of polyethylene. Yoon and Flory[16] clearly state that the correct (i.e., simulated) behavior of the RIS chains they consider does not show a plateau. It is only their approximate $\hat{\omega}(k)$'s which plateau. Just as in the Yoon–Flory work, the plateau in our Koyama-patch approximation should be attributed to inaccuracies in the approximation scheme.

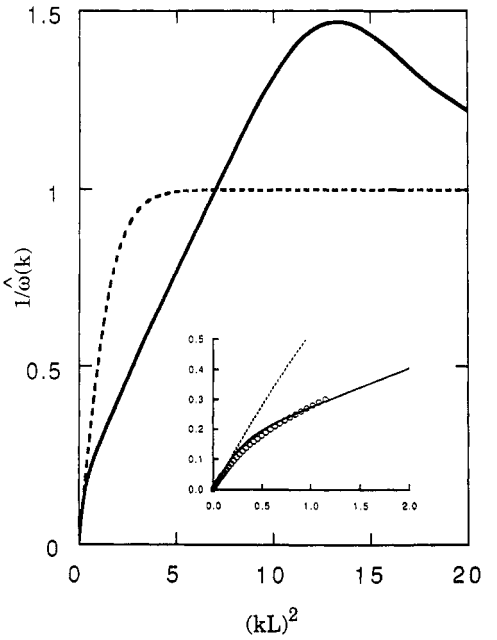

Figure 6. Ornstein–Zernike plot for a 1001-site chain. The solid line is the Koyama-patch approximation, the dashed line is the Gaussian chain, and the circles are simulation results. The region usually accessible to experiment is $(kL)^2 \lesssim 0.15$ where all the curves look Gaussian. Notice the well-defined intermediate wavelength regime for $(kL)^2 = 1$–10.

In and of itself, the lack of a plateau in a simulation of an RIS chain is not surprising. It simply indicates that the chain simulated was too short to show true "high" polymeric behavior. On the other hand, scattering experiments on polyethylene chains 5–10 times the length of the longest chains we have simulated do show a well-defined plateau.[9,10] These are difficult experiments and have only been performed for relatively small k. For chains of effectively 5786 sites, Fischer et al.[9] find a plateau through $kL = 0.38$, while, for chains of effectively 8143 sites, Schelten et al.[10] find a plateau only through $kL = 0.15$ (at which point the errors in the measurement become large).

Experimental difficulties aside, it does appear that polyethylene chains of 5000–10 000 CH_2 units exhibit plateau behavior. RIS chains of this length are too long for us to comfortably simulate. However, we have performed *preliminary* simulations at $N = 4001$ and see no evidence of the development of a plateau. Careful simulations on polyethylene chains on the order of 10^4–10^5 carbons are required to definitively settle the question of the quantitative adequacy of the RIS model in the intermediate scaling regime. Moreover, careful experiments in the degree of polymerization range of 1000–10 000 would be valuable to establish how long a polymer is required in order for the self-similar scaling regime to emerge.

Often, experimental data are presented in "Ornstein–Zernike" or "Zimm" form (i.e., $1/\hat{\omega}(k)$ versus k^2) which transforms the plateau region into a linear curve and permits easy evaluation of the radius of gyration (see eq 2). This is made clear by Figure 6 where the Gaussian $\hat{\omega}(k)$ of Figure 2 is plotted along with the results of simulation and the Koyama-patch approximation. Plotted in this manner, the Koyama-patch and simulation are all but indistinguishable. As seen in the inset, for both simulation and theory, the commonly probed experimental region ($(kL)^2 < 0.15$) appears completely Gaussian (i.e., linear). The most interesting aspect of this plot, however, is the markedly non-Gaussian behavior of RIS chains

(evaluated with the Koyama-patch) in the higher wavevector part of the intermediate regime, a regime which, unfortunately, is not as well experimentally documented. Here the function develops a secondary linear behavior (*with a different slope from the smaller k region*).

Regardless of the resolution of the small disagreement between simulation, experiment, and our Koyama-patch approximation, the intra and intermolecular structures predicted through the different paths are very similar, and the Koyama-patch is the first approximation which predicts accurate single-chain structures with relative computational ease.

Generalization to more chemically complex polymers is feasible. By combining the Koyama-patch approximation for the single-chain structure with the polymer RISM and density functional[6] formalisms, one now has the ability to rapidly and accurately calculate the intermolecular packing, bulk properties, and crystallization of chemically realistic models of dense polymer fluids. The Koyama-patch scheme may prove to be especially valuable in the context of the recently-developed "self-consistent" polymer RISM theory[22] where single-chain conformation and interchain packing are determined in a coupled, *iterative* manner, thereby allowing an ab initio determination of "nonideality" effects in polymer liquids and alloys.

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References and Notes

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