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Static Structure Factors of Lamellar, Semicrystalline Polymer Chains. 1. Critical Test of an Analysis Technique

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ABSTRACT: Numerically exact transfer matrix formulas to compute static structure factors and gyration radii of individual polymer chains are derived. These formulas have been specifically derived to compute structure factors of model semicrystalline polymers but are also well suited to many other model polymers. They are applied here to test the validity of a technique due to Fischer et al.[1] that is intended to extract information on intramolecular clustering from neutron-scattering data. The Fischer technique, because of several incorrect assumptions, does not seem to work as intended.

1. Introduction

Neutron scattering by isotropic mixtures of semicrystalline polymers has been applied by a number of workers to probe single chains in the semicrystalline environment.[2] Fischer and co-workers[1] have published a technique for the analysis of neutron-scattering data from semicrystalline polymers that, if correct, would provide information on some aspects of the internal structure, such as the number and size of intramolecular clusters, tie chains, etc. This technique assumes the existence of intramolecular clustering within the crystalline domains and then seeks to extract information on cluster number and size from intermediate-angle neutron-scattering data. In this paper we present numerically exact calculations of the static structure factor of a model polymer chain to examine the validity of the Fischer technique. We construct a model with well-defined clusters of known size, and whose structure factor can be calculated rigorously, and then determine whether or not the Fischer technique can successfully determine the number and size of clusters. The technique fails to measure those quantities for the model considered and, therefore, cannot be applied meaningfully to semicrystalline polymer systems.

Scattering experiments carry structural information in the structure factor

$$S(\mathbf{q}) = (N+1)^{-2} \sum_{j=0}^{N} \sum_{k=0}^{N} \langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk}) \rangle \tag{1}$$

where $N + 1$ is the number of scattering centers in the chain (labeled from 0 to N), with each sum ranging over all the scattering centers present. The vector $\mathbf{r}_{jk}$ is the displacement between the jth and the kth center. Historically, model structure factors of individual chains have proven difficult to calculate; the number of model polymer chains with exactly calculated structure factors is very small. Most theoretical progress either has been by Monte Carlo simulation[3] or has required simplifying assumptions such as a lack of correlation at certain $\mathbf{q}$ values between different chain segments.[1] We point out in this paper the existence of a class of single-chain models with exactly soluble structure factors. The technique is practically identical with the transfer matrix approach applied so successfully to polymer properties beginning in the 1960s and summarized under the name rotational isomeric states model in Flory's book.[4]

The approach considered here was first applied by Thorpe and Schroll[5] and then by Schroll, Walker, and Thorpe[5] to calculate characteristic functions of chains on the diamond lattice. We extend it in this and a later paper[6] to semicrystalline polymers.

We derive the general formalism for calculating structure factors in sections 2–5. In section 6, we review the derivation of the Fischer analysis, with special attention to the various assumptions employed and to the range of wavenumbers for which the analysis might possibly be expected to be valid. In section 7, we introduce the model employed to test the Fischer analysis and present matrices needed to compute the structure factor and the radius of gyration according to the formalism presented in sections 2–5. In section 8, we present the results of a number of calculations, and in section 9 we draw a number of conclusions.

2. Structure Factors: Preliminary Matrix Expressions

Equation 1 may be written

$$S(\mathbf{q}) = (N+1)^{-1} + 2(N+1)^{-2}\mathcal{R} \sum_{0\le j<k\le N} \langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk}) \rangle \tag{2}$$

since it will always be true that

$$\mathcal{R}\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk}) \rangle = \mathcal{R}\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{kj}) \rangle$$

Here $\mathcal{R}$ indicates that you should take the real part of what follows. The first term in eq 2 represents the single particle terms ($j = k$) in eq 1; the second term includes contributions from all unique pairs of scattering centers. We consider only single-chain scattering, for which we may write

$$\mathbf{r}_{jk} = \sum_{l=j+1}^{k} \mathbf{r}_l \tag{3}$$

The vector $\mathbf{r}_l$ represents the displacement between neighboring scattering centers along the chain contour. We refer to each vector $\mathbf{r}_l$ as a bond, while recognizing that,

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for many models, the vector $\mathbf{r}_l$ may span chain segments comprising a number of covalent bonds with many internal degrees of freedom. Furthermore, we assume that the average appearing in eq 2 can be performed in two separate steps:

$$\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle = \langle\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle_{\mathrm{i}}\rangle_{\mathrm{e}} \tag{4}$$

The average $\langle ...\rangle_{\mathrm{i}}$ extends over all degrees of freedom internal to the bond. We furthermore assume that the internal state of one bond does not influence the internal state of any other bonds, permitting us to write

$$\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle_{\mathrm{i}} = \langle \prod_{l=j+1}^{k} \exp(i\mathbf{q}\cdot\mathbf{r}_l)\rangle_{\mathrm{i}} = \prod_{l=j+1}^{k} \langle \exp(i\mathbf{q}\cdot\mathbf{r}_l)\rangle_{\mathrm{i}} \tag{5}$$

Our next assumption is that each bond, once we have averaged over its internal degrees of freedom, will be found in a particular element of a discrete set of states. That is to say that $\langle \exp(i\mathbf{q}\cdot\mathbf{r}_l)\rangle_{\mathrm{i}}$ can take on only one of a discrete set of values. Any one of these values represents the Fourier transform of the probability distribution function of the vector $\mathbf{r}_l$ when $\mathbf{r}_l$ is confined to one of these states. The model calculations given below clarify what is meant by "internal" and "external" degrees of freedom.

We now introduce the following shorthand notation:

$$\langle \exp(i\mathbf{q}\cdot\mathbf{r}_l)\rangle_{\mathrm{i}} \equiv B(\sigma_l) \tag{6}$$

Note that $B(\sigma_l)$ is an implicit function of $\mathbf{q}$. The symbol σ_l represents the state in which the vector $\mathbf{r}_l$ is found. For example, if each $\mathbf{r}_l$ can take on at most n states, then we can take σ_l to be an integer between 1 and n.

We may also write

$$\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle_{\mathrm{i}} = \prod_{l=j+1}^{k} B(\sigma_l) \tag{7}$$

It is now necessary to apply the average $\langle ...\rangle_{\mathrm{e}}$ to the quantity in eq 7. This average is performed over all discrete states accessible to each vector $\mathbf{r}_l$. We limit ourselves to models in which the state of one bond can at most influence the state of only its two neighbors. Specifically, we let $A(\sigma_l,\sigma_{l+1})$ represent the probability that bond $l + 1$ assumes the state σ_{l+1} given that bond l is found in state σ_l. We also let $J(\sigma_1)$ be the probability that the first bond is found in the state σ_1. The probability, therefore, that the entire chain of N bonds assumes a particular sequence of states $(\sigma_1, \sigma_2, \sigma_3, ..., \sigma_N)$ is just

$$J(\sigma_1)\, A(\sigma_1,\sigma_2)\, A(\sigma_2,\sigma_3)...A(\sigma_{N-1},\sigma_N) \tag{8}$$

Now, to generate $\langle\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle_{\mathrm{i}}\rangle_{\mathrm{e}}$, we have only to multiply the probability of a particular sequence, eq 8, by the value of $\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle_{\mathrm{i}}$ in that sequence, eq 7, and then sum over all possible sequences, or over all possible states of each vector.

$$\begin{aligned}\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle = {} & \textstyle\sum_{\sigma_1}\sum_{\sigma_2}...\sum_{\sigma_N}\sum_{\sigma_{N+1}} J(\sigma_1)\, A(\sigma_1,\sigma_2)\, A(\sigma_2,\sigma_3)... \\ & A(\sigma_j,\sigma_{j+1})[B(\sigma_{j+1})A(\sigma_{j+1},\sigma_{j+2})][B(\sigma_{j+2})A(\sigma_{j+2},\sigma_{j+3})]... \\ & [B(\sigma_k)\, A(\sigma_k,\sigma_{k+1})]A(\sigma_{k+1},\sigma_{k+2})\, A(\sigma_{k+2},\sigma_{k+3})... \\ & A(\sigma_{N-1},\sigma_N)\, A(\sigma_N,\sigma_{N+1})\, F(\sigma_{N+1})\end{aligned} \tag{9}$$

At this point, the summation over the as yet undefined state σ_{N+1} and the two quantities $A(\sigma_N,\sigma_{N+1})$ and $F(\sigma_{N+1})$ should appear superfluous. If we were to simply erase those three symbols, we would obtain a completely valid expression in terms of only previously defined quantities. This means that whatever definition is given to the state σ_{N+1} and to the quantities $A(\sigma_N,\sigma_{N+1})$ and $F(\sigma_{N+1})$, it must be such that this simple erasure is a valid algebraic manipulation. This occurs if we define $F(\sigma)$ to be unity for all values of σ and if we define $A(\sigma_N,\sigma_{N+1})$ to be the unit tensor. Our reason for inclusion of these additional terms becomes obvious if we consider the case $k = N$. In eq 9, each B term is paired with an A term. Without the appearance of $A(\sigma_N,\sigma_{N+1})$, we would be unable to pair $B(\sigma_N)$ with an A term. Also note that we can define $A(\sigma_N,\sigma_{N+1})$ as any tensor having $F(\sigma_{N+1})$ as an eigenvector with unit eigenvalue.

We now define a more succinct matrix notation. Let $\mathbf{A}_l$ represent the matrix of elements $A(\sigma_l,\sigma_{l+1})$, and let $\mathbf{J}$ and $\mathbf{F}$ represent the row and column vectors containing $J(\sigma_1)$ and $F(\sigma_{N+1})$, respectively. Also assume that $B(\sigma_l)$ $A(\sigma_l,\sigma_{l+1}) \equiv C(\sigma_l,\sigma_{l+1})$ is an element of a matrix $\mathbf{C}_l$. In this notation, we have

$$\langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle = \mathbf{J}\mathbf{A}_1{}^{(j)}\mathbf{C}_{j+1}{}^{(k-j)}\mathbf{A}_{k+1}{}^{(N-k)}\mathbf{F} \tag{10}$$

where we have employed Flory's[4] serial matrix product notation

$$\mathbf{A}_m{}^{(n)} = \mathbf{A}_m\mathbf{A}_{m+1}...\mathbf{A}_{m+n-1}\ (n \text{ factors}) \tag{11}$$

$\mathbf{F}$ is an eigenvector of each $\mathbf{A}_l$ having eigenvalue 1. For example

$$\textstyle\sum_{\sigma_N} A(\sigma_{N-1},\sigma_N)\, F(\sigma_N) = F(\sigma_{N-1}) \tag{12}$$

since the state σ_{N-1} has a unit probability of being followed by some state. Therefore, we may write the following for the structure factor:

$$S(\mathbf{q}) = (N+1)^{-1} + 2(N+1)^{-2}\mathcal{R}\sum_{0\le j<k\le N} \mathbf{J}\mathbf{A}_1{}^{(j)}\mathbf{C}_{j+1}{}^{(k-j)}\mathbf{F} \tag{13}$$

Equation 12 also means that $\mathbf{A}_N$ can be set equal either to the unit matrix or to any other $\mathbf{A}_l$, whichever is more convenient.

In those cases for which $\mathbf{A}_1 = \mathbf{A}_2 = \mathbf{A}_3 = ...\mathbf{A}_N$ and $\mathbf{C}_1 = \mathbf{C}_2 = \mathbf{C}_3 = ...\mathbf{C}_N$, we have

$$S(\mathbf{q}) = (N+1)^{-1} + 2(N+1)^{-2}\mathcal{R}\sum_{0\le j<k\le N} \mathbf{J}\mathbf{A}^j\mathbf{C}^{k-j}\mathbf{F} \tag{14}$$

3. Structure Factors: Eigenvector Expansions

When $S(\mathbf{q})$ is given by eq 14, important expressions can be obtained by expanding $\mathbf{J}$ and $\mathbf{F}$ in terms of the eigenvectors of $\mathbf{A}$ and $\mathbf{C}$, respectively. Let $\mathbf{x}_\mu$ represent one of the contravariant eigenvectors of $\mathbf{A}$ having eigenvalue α_μ:

$$\mathbf{x}_\mu\cdot\mathbf{A} = \alpha_\mu\mathbf{x}_\mu \tag{15}$$

As shown above, one of the α_μ values will always equal 1. Also let $\mathbf{y}_\nu$ represent one of the covariant eigenvectors of $\mathbf{C}$ having eigenvalue γ_ν:

$$\mathbf{C}\cdot\mathbf{y}_\nu = \gamma_\nu\mathbf{y}_\nu \tag{16}$$

Let p_μ and r_ν be chosen to satisfy

$$\mathbf{J} = \textstyle\sum_\mu p_\mu\mathbf{x}_\mu \tag{17}$$

$$\mathbf{F} = \textstyle\sum_\nu r_\nu\mathbf{y}_\nu \tag{18}$$

Furthermore, define

$$g_{\mu\nu} = p_\mu r_\nu \mathbf{x}_\mu\cdot\mathbf{y}_\nu \tag{19}$$

Then we may write

$$S(\mathbf{q}) = (N+1)^{-1} + 2(N+1)^{-2}\mathcal{R}\textstyle\sum_{\mu\nu} g_{\mu\nu}T_{\mu\nu} \tag{20}$$

where

$$T_{\mu\nu} = \sum_{k=1}^{N}\sum_{j=0}^{k-1}\alpha_\mu^{\ j}\gamma_\nu^{\ k-j} \tag{21}$$

Equation 21 yields the following:

$$T_{\mu\nu} = N(N+1)/2 \quad \text{if } \alpha_\mu = \gamma_\nu = 1 \tag{22}$$

$$T_{\mu\nu} = \gamma_\nu(\gamma_\nu - 1)^{-2}[N - N\gamma_\nu - \gamma_\nu + \gamma_\nu^{\ N+1}] \quad \text{if } \alpha_\mu = 1 \text{ and } \gamma_\nu \neq 1 \tag{23}$$

$$T_{\mu\nu} = (1 - \alpha_\mu)^{-2}[N - N\alpha_\mu - \alpha_\mu + \alpha_\mu^{\ N+1}] \quad \text{if } \alpha_\mu \neq 1 \text{ and } \gamma_\nu = 1 \tag{24}$$

$$T_{\mu\nu} = \alpha(1 - \alpha_\mu)^{-2}[1 - \alpha_\mu^{\ N} - N\alpha_\mu^{\ N} + N\alpha_\mu^{\ N+1}] \quad \text{if } \alpha_\mu = \gamma_\nu \neq 1 \tag{25}$$

and

$$T_{\mu\nu} = \frac{\gamma_\nu}{\gamma_\nu - \alpha_\mu}\left[\frac{\gamma_\nu - \gamma_\nu^{\ N+1}}{1 - \gamma_\nu} - \frac{\alpha_\mu - \alpha_\mu^{\ N+1}}{1 - \alpha_\mu}\right] \quad \text{if } \alpha_\mu \neq \gamma_\nu \text{ and neither equals 1} \tag{26}$$

4. Structure Factors: Supermatrix Expressions

Flory shows how a series of the form of eq 13 can be placed in a "supermatrix" form.[7] The result is

$$S(\mathbf{q}) = (N+1)^{-1} + 2(N+1)^{-2}\mathcal{R}\mathbf{J}\mathbf{T}_1\mathbf{U}_1^{(N)}\mathbf{T}_2\mathbf{F} \tag{27}$$

where $\mathbf{U}_j$ is the "supermatrix"

$$\mathbf{U}_j = \begin{bmatrix} \mathbf{A}_j & \mathbf{C}_j & \mathbf{C}_j \\ \mathbf{0} & \mathbf{C}_j & \mathbf{C}_j \\ \mathbf{0} & \mathbf{0} & \mathbf{E} \end{bmatrix} \tag{28}$$

and where $\mathbf{E}$ is the identity matrix of the same order as $\mathbf{A}_j$ or $\mathbf{C}_j$, $\mathbf{0}$ is the matrix of the same order having all zero elements, and

$$\mathbf{T}_1 = (\mathbf{E}\ \ \mathbf{0}\ \ \mathbf{0}); \quad \mathbf{T}_2 = \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \\ \mathbf{E} \end{bmatrix} \tag{29}$$

5. Gyration Radii

Calculation of gyration radii by these techniques is a well-established procedure.[3] Nevertheless, previously published techniques are not immediately applicable to the models we consider, so it has been necessary to derive a set of radius of gyration formulas that accompany the matrix equations already given in this paper. However, the derivation is rather lengthy and is therefore given in the supplementary material accompanying this paper.

6. Derivation of Fischer's Analysis

As discussed above, we intend to apply the formalism developed in the last few sections to test the Fischer technique.[1] In order to focus upon the assumptions implicit in that technique, we give here a rederivation. We have altered somewhat the original notation but have remained faithful to the derivation found in their paper.

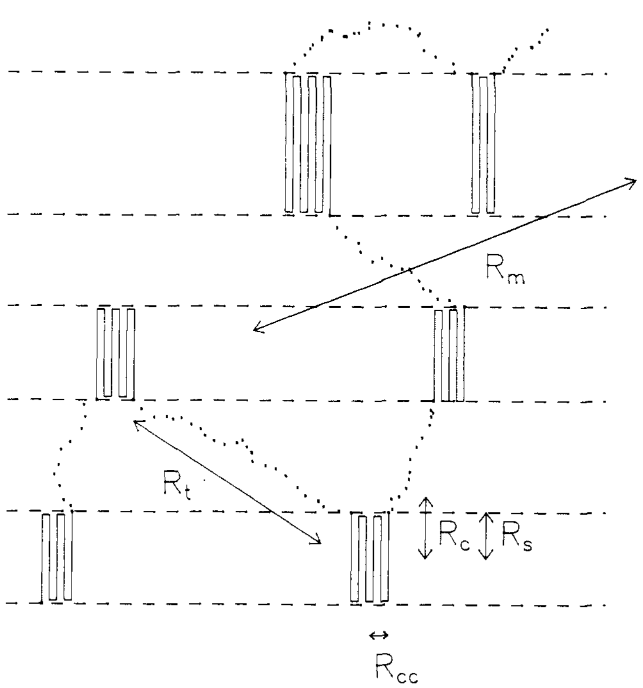

Figure 1. Schematic diagram of a chain in a semicrystalline system showing the definition of several different length scales.

Figure 1 displays the conception of a polymer molecule in a semicrystalline environment assumed by the Fischer analysis. Three assumptions underpin the analysis. It may be argued that the original publication did not actually state these assumptions explicitly. It is our contention, however, that they are implicit in the mathematical derivation and cannot be ignored. For example, eq 35 cannot be written without them. The first two assumptions are as follows:

A1. Polymer molecules in the semicrystalline state separate into well-defined clusters. A single cluster contains all those sequential crystalline stems that are joined by adjacent, or nearly adjacent, folds. Each cluster is connected to the succeeding cluster by a longer, amorphous fold or by a tie. We assume that each molecule contains ν clusters. Although the folds within each cluster appear in Figure 1 as strictly adjacent folds, we can, if preferred, assume that individual clusters also contain non-adjacent, yet short, folds.

A2. The scattering due to the amorphous spacers (amorphous folds or ties) can be neglected. This assumption is emphasized in Figure 1 by drawing such portions of the molecule as dotted curves.

It must be noted that these two assumptions are potentially contradictory. A2 can be satisfied by going to high crystallinities, i.e., by shortening the spacers between clusters. However, then the clustering becomes less well-defined.

To avoid immiscibility problems, neutron-scattering studies are typically performed on rapidly quenched samples, which consistently have relatively low crystallinities. Crystallinities around 50% are common. For such samples, A2 asks us to neglect half the molecule.

We define the static structure factor of any collection of N scattering centers to be

$$S(q) = N^{-2}\sum_{j=1}^{N}\sum_{m=1}^{N}\langle\exp(i\mathbf{q}\cdot\mathbf{r}_{jm})\rangle \tag{30}$$

$\mathbf{r}_{jm}$ is the separation between the jth and mth scattering centers. The sum runs over all pairs of scattering centers. The structure factor is normalized by the N^{-2} factor so that $S(0) = 1$. The wavevector $\mathbf{q}$ represents the momentum transfer between incident and scattered neutrons. The brackets $\langle\ldots\rangle$ denote an ensemble average over all possible structures of the object. In experiments, the neutron beam always illuminates a polycrystalline sample, which means that the average ⟨...⟩ includes all possible orientations of an individual chain. Therefore, the structure factor is written as function of the magnitude of **q** only. To second order, we have

$$S(\mathbf{q}) = 1 - q^2 R_g^{\,2}/3 \tag{31}$$

for R_g the radius of gyration of the object.

We now introduce the following length scales (see Figure 1):

R_m	radius of gyration of the entire molecule
R_t	mean separation of clusters
R_c	radius of gyration of one cluster
R_s	radius of gyration of one crystalline stem
R_{cc}	radius of gyration of the stem centers within one cluster

(The radius R_{cc} is defined as the set of points lying at the intersection of the stems with a plane normal to the stems.) We expect the following inequalities to hold:

$$R_m > R_t > R_c > R_s > R_{cc} \tag{32}$$

At high enough molecular weights, thef irst equality reads $R_m \gg R_t$, but the distinction appears not to be important. Assumption A1, stated mathematically, becomes

$$\text{A1. } R_t \gg R_c \tag{33}$$

We also note that

$$R_c^{\,2} = R_s^{\,2} + R_{cc}^{\,2} \tag{34}$$

rigorously, since cross terms vanish.

If the molecule is well clustered, ($R_t \gg R_c$) and if scattering from the amorphous domains is negligible, then at large enough q ($q \gg R_t^{-1}$), interference between scattering centers on different clusters is negligible, so that we may write

$$\nu S_m(q) = S_c(q) \tag{35}$$

where $S_m(q)$ is the structure factor of the entire molecule, and $S_c(q)$ is the structure factor of a single cluster.

The third assumption is that the structure factor $S_c(q)$ is factorizable:

$$\text{A3. } S_c(q) = S_s(q)\, S_{cc}(q) \tag{36}$$

Here, $S_s(q)$ is the structure factor of a single stem, and $S_{cc}(q)$ is the structure factor of all the stem centers within a single cluster. This factorization would be rigorously valid for all vectors **q** if the ensemble average did not include orientational averaging, since cross-terms cancel by orthogonality. However, as stated above, semicrystalline polymer scattering includes the orientational average, so the above factorization, it turns out, is only valid to second order in q. We find from numerical calculations that the factorizability of eq 36 is valid only in the range $q < R_c^{-1}$. Combining eqs 35 and 36 implies

$$\frac{S_s(q)}{S_m(q)} = \frac{\nu}{S_{cc}(q)} \tag{37}$$

Equation 37 is expected to be valid in the range $R_t^{-1} \ll q < R_c^{-1}$ only. The lower bound is imposed since eq 35 is invalid at low q, and the upper bound is imposed because eq 36 is invalid at high q.

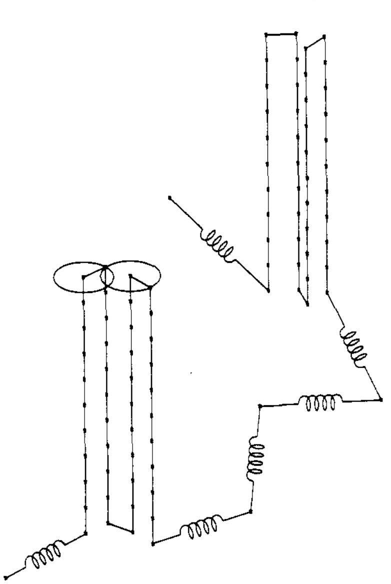

Figure 2. Schematic diagram of the model chain for which the structure factor has been calculated.

In the range $q < R_{cc}^{-1}$, we may write

$$S_{cc}(q) = 1 - q^2 R_{cc}^{\,2}/3 \tag{38}$$

implying, finally, that

$$\frac{S_s(q)}{S_m(q)} = \nu[1 + q^2 R_{cc}^{\,2}/3] \tag{39}$$

in the range $R_t^{-1} \ll q < R_c^{-1}$. Fischer et al., apparently because they accepted eq 36 to be valid at all q, argued that eq 39 should hold over the wider range $R_t^{-1} \ll q < R_{cc}^{-1}$.

Therefore, if the two assumptions, A1 and A2, are valid, then plots of $S_s(q)/S_m(q)$ vs q^2 should be linear in the range $R_t^{-1} \ll q < R_c^{-1}$ and permit measurement of R_{cc} and ν. Since $S_s(q)$ can be inferred from independent measurements, this procedure seems to provide the possibility of measuring the number and size of clusters within a molecule.

7. The Model

We consider a model, shown schematically in Figure 2, in order to test the applicability of the Fischer analysis. The model consists of a set of clustered stems: Each stem consists of M bonds each of unit length organized into a rigid rod. Q such stems are laid together in a mutually parallel fashion. The first stem in each cluster is arbitrarily designated to point up, the second down, etc. Each of these Q stems within a cluster are separated by one lateral step, of length d, which represents a tight fold. Each lateral step points in an arbitrary direction normal to the stems. Then separating each cluster are P Gaussian steps, each of rms length a. These model, of course, the amorphous runs between clusters. We let this basic structure repeat itself ν times, to generate a molecule of ν clusters. We let N represent the total number of steps in the chain.

This model may not apply too well to semicrystalline polymers, since no effort has been made to force different clusters to lie in lamellar arrays. However, it should provide an excellent test of the Fischer analysis. For example, we can begin with a structure satisfying both assumptions A1 and A2 by setting $P = 1$ and letting a be much larger than the size of a cluster. Then we can examine the effect of assumption A2 by gradually "turning on" the scattering from the amorphous parts of the chain, which we do by increasing P and decreasing a in such a way that $Pa^2 = R_t^{\,2}$ is constant. Alternatively, we can

Table I
Summary of the Different Structures for Which $S(k)$ Has Been Calculated

	M	Q	P	ν	n	d	a^2	$R_t^2 = Pa^2$
A	25	4	1	10	1040	1	10000	10 000
B	25	4	20	10	1230	1	500	10 000
C	25	4	50	10	1530	1	200	10 000
D	25	4	90	10	1930	1	111.11	10 000
E	25	4	1	10	1040	1	100	100
F	25	4	20	10	1230	1	5	100
G	25	4	50	10	1530	1	2	100
H	25	4	90	10	1930	1	1.1111	100

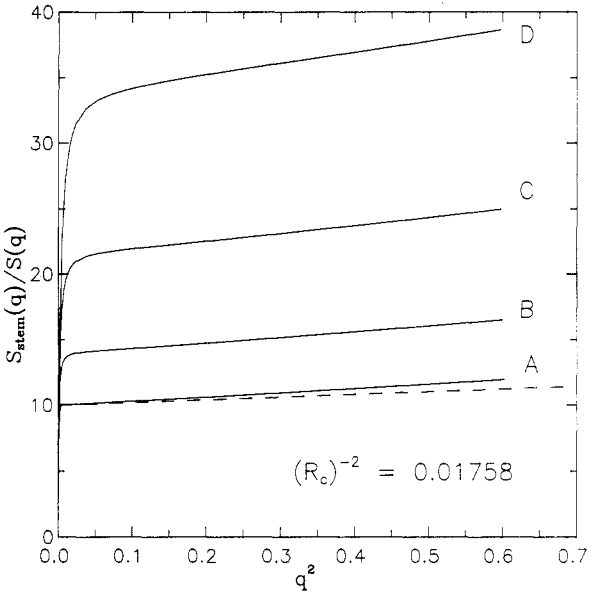

Figure 3. Plots of $S_s(q)/S_m(q)$ as a function of q^2 for model calculations A-D.

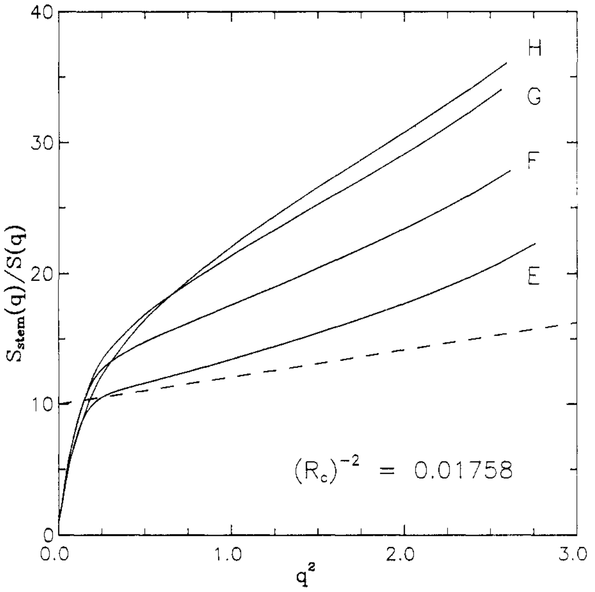

Figure 4. Plots of $S_s(q)/S_m(q)$ as a function of q^2 for model calculations E-H.

examine the effect of assumption A1 by using smaller values of Pa^2.

The structure factor of this model can be calculated rigorously by the techniques given in sections 2-5. We begin by defining a square matrix **A**. Each row of **A** corresponds to one of the steps in a single repeat unit of the chain. For example, the first M rows of **A** correspond to the M up steps of the first stem. The next row corresponds to the lateral step between the first and second stems. Then the next M rows correspond to the M down steps of the second stem. We continue in such a way until all steps in one repeat unit are accounted for. For example, the last P rows correspond to the P Gaussian steps in the amorphous spacer. In each repeat unit there are $MQ/2$ up steps, $MQ/2$ down steps (to avoid proliferation of special cases we only consider even Q), $Q - 1$ lateral steps, and P Gaussian steps. Therefore, the order of **A** is $(M + 1)Q + P - 1 \equiv n$. The entry $A_{\mu\sigma}$ of **A** is the probability that step σ follows step μ, so we make the following assignments:

$$A_{\mu,\mu+1} = 1 \quad \text{for } \mu = 1, 2, 3, ..., n - 1 \tag{40a}$$

$$A_{n1} = 1 \tag{40b}$$

$$\text{all other } A_{\mu\sigma} = 0 \tag{40c}$$

The **C** matrix is obtained by multiplying each row of **A** by one of the following four Fourier transforms, depending on the step to which each row corresponds.

$$\text{up steps: } \phi(\mathbf{q}) = \exp(iq_3) \tag{41}$$

$$\text{down steps: } \phi(\mathbf{q}) = \exp(-iq_3) \tag{42}$$

$$\text{lateral steps: } \phi(\mathbf{q}) = J_0(d\kappa);\ \kappa^2 = q_1^{\ 2} + q_2^{\ 2} \tag{43}$$

$$\text{Gaussian steps: } \phi(\mathbf{q}) = \exp(-a^2q^2/6) \tag{44}$$

Here $\mathbf{q} = (q_1,q_2,q_3)$ is the wavevector, and q_3 is its component in the "up" direction. The row matrix **J** is defined with its first element as 1, and all other elements as 0. This is equivalent to assuming that all chains in the ensemble start at the first up step of the first stem. All elements of the column matrix **F** are set to unity.

We set n equal to the number of steps in one repeat unit and ν equal to the number of repeat units. Therefore

$$N = n\nu \tag{45}$$

is the total number of steps in the chain.

With **A**, **C**, **J**, and **F** defined as above, the structure factor of this chain is given by eqs 27-29.

Note from eqs 41-44 that $S(\mathbf{q})$ is a function of only q_3 and κ, not q_1 and q_2 independently. (This simplification is obtained by permitting the lateral steps to point arbitrarily in the plane.) It follows that the orientational average is an integration over a single variable

$$S_m(q) = \frac{1}{2}\int_0^{\pi} \sin\theta \, d\theta \, S(\kappa,q_3) \tag{46}$$

where $q_3 = q\cos\theta$ and $\kappa = q\sin\theta$. In our calculations, this integral was performed numerically.

We can apply the analysis of sections 2-5 to obtain the following results:

$$S_s(q) = (M+1)^{-2}\left[(M+1) + 2\sum_{j=1}^{M}(M+1-j)\frac{\sin(jq)}{jq}\right] \quad (47)$$

$$R_s^2 = M(M+2)/12 \quad (48)$$

$$R_{cc}^2 = \frac{d^2(Q-1)(Q+1)}{Q} \quad (49)$$

In section 3 we give alternative expressions for $S(\mathbf{q})$ in terms of the eigenvectors and eigenvalues of **A** and **C**. This approach is in principle faster than the matrix multiplication approach, especially in cases where the diagonalization is simple. However, for large values of N, we found the eigenvalue algorithm to be subject to numerical instabilities, and so all the computations reported here were performed with the matrix multiplication version, eq 27. (We did perform a number of preliminary calculations, at small N, independently by both approaches, to verify our computer code.) It may be possible, with machines of higher precision, to avoid these instabilities. Therefore, we report in passing that matrices of the general form of **A** or **C** in eqs 40–44 can be easily diagonalized. $\mathbf{A}^n$ or $\mathbf{C}^n$ simply multiply any vector by a constant, from which it follows that both **A** and **C** have characteristic equations of the form

$$\lambda^n = \text{constant} \quad (50)$$

8. Results

We calculated $S_m(q)$ according to eqs 27–29 and $S_s(q)$ according to eq 47 for eight different structures summarized in Table I. The results of these calculations for the ratio $S_s(q)/S_m(q)$ are shown in Figures 3 and 4. Also shown in Figures 3 and 4 is the Fischer analysis prediction: $\nu(1 + q^2R_{cc}^2/3)$. For all eight structures, eqs 34, 48, and 49 imply $R_s^2 = 56.25$, $R_{cc}^2 = 0.625$, $R_c^2 = 56.875$, $R_c^{-2} = 1.76 \times 10^{-2}$. The first structure in Table I, labeled A, satisfies both the crucial assumptions: It is well clustered ($R_t^2 = Pa^2 = 10^4$), and scattering from the Gaussian spacers is absent ($P = 1$). It is not surprising, therefore, that the curve for $S_s(q)/S_m(q)$ for this particular structure agrees well with the dashed curve, especially in the region $R_t^{-2} \ll q^2 < R_c^{-2}$.

The three structures, B–D, still satisfy the clustering assumption, since the Gaussian spacer in all three cases has the same size as that of structure A ($R_t^2 = 10^4$). However, it is obvious from Figure 3 that the scattering from the Gaussian spacer is important and cannot be neglected. Structure B has a rather diffuse concentration of scatters in the Gaussian spacers (only about one scattering center in six is in a spacer) but still does not agree with the prediction of eq 39. Structures D and H have practically equal numbers of scattering centers in the stems and in the Gaussian spacers, so, in that sense, they correspond to semicrystalline polymers of about 50% crystallinity.

None of the four structures E–H agree well with eq 39 anywhere in the interval $q^2 < R_c^{-2}$. These are not nearly so well clustered, since we do not have $R_t \gg R_c$. The curve for structure E appears to extrapolate nicely to eq 9 at low q, but it is not clear what significance, if any, this has, since these structures are not too well clustered, and since there is still no agreement in the crucial region $R_t^{-2} \ll q^2 < R_c^{-2}$. In any case, the curves for structures F–H clearly indicate that once scattering from the amorphous spacers is "turned on", any hope for agreement is lost.

9. Discussion

This paper reports calculations of the structure factor of a model polymer. These calculations examine the validity of a technique due to Fischer and co-workers[1] for analyzing neutron-scattering data by semicrystalline polymers. These calculations indicate that the Fischer technique is invalid. There can be no doubt that plots of $S_s(q)/S_m(q)$ are linear in q^2 in a certain q region, at least for the samples analyzed by Fischer et al.[1] However, it is not clear what, if anything, these linear regions indicate.

We have also presented a general matrix formalism that permits computation of certain single-chain structure factors. It is hoped that this formalism will be useful in other applications. We have also applied it to calculate the structure factors of model semicrystalline chains obeying gambler's ruin statistics on the simple cubic lattice. That report will appear shortly.[6]

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Supplementary Material Available: Derivation of equations for computing radii of gyration (13 pages). Ordering information is given on any current masthead page.

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