Transfer Matrix Techniques for Computation of Single-Chain Structure Factors

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1. Introduction

Most polymer scientists are familiar with the transfer matrix techniques for computing statistical mechanical averages over ensembles of polymer chains, as discussed, for example, in Flory's book.[1] Apparently, many polymer scientists are unaware that these same techniques can be applied to compute characteristic functions and single-chain structure factors.[2−7] Structure factors are important both in the interpretation of light and neutron scattering experiments and for input into integral equation computations of polymer melt structure and thermodynamics.[7,8] The purpose of this Note is to demonstrate the feasibility of such computations by presenting a relatively simple computation for polyethylene.

The transfer matrix formalism permits us to sum over the properties of objects that we represent as sequences of states. The only conceptual adjustment required to adapt the formalism to structure factors is that we must consider sequences of directions in space, rather than sequences of rotational states. This means that the simplest applications of the technique require lattice embedding, which in turn implies that we can only easily treat the case for which bond angles are 109.5°, rather than the more realistic *ca.* 112°.

2. Walks on the Diamond Lattice

The following eight vectors include all possible steps on the diamond lattice: $\mathbf{a} = 3^{-1/2}(+1, +1, +1)$, $\mathbf{b} = 3^{-1/2}(-1, -1, +1)$, $\mathbf{c} = 3^{-1/2}(-1, +1, -1)$, $\mathbf{d} = 3^{-1/2}(+1, -1, -1)$, $\mathbf{a}' = -\mathbf{a}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = -\mathbf{c}$, and $\mathbf{d}' = -\mathbf{d}$. A particular polymer configuration is specified by listing a sequence of these vectors, i.e., α_1, α_2, ..., α_N, where each α_j is one of the eight vectors listed above. However, many sequences are not allowed, and the allowed sequences have different energies depending on the sequence of *trans* and *gauche* bonds found therein. All the following rules apply:

1. Only one of the four vectors **a**, **b**, **c**, or **d** is allowed in the first step of the walk.
2. Primed and unprimed vectors must alternate along the chain.
3. No vector may be followed by its own negative. (**a**′ may not follow **a**, etc.) Rules 2 and 3 imply that walks are three-choice, as required.
4. Whenever $\alpha_j = \alpha_{j-2}$, a *trans* interaction occurs, and we must add an amount E_t to the total energy.
5. Whenever $\alpha_j \neq \alpha_{j-2}$, a *gauche* interaction occurs, and we must add an amount E_σ to the total energy.
6. Whenever $\alpha_j = -\alpha_{j-3}$, a pentane interaction occurs, and we must add an amount E_ω to the total energy.

The total energy of a given sequence may be written

$$H = U_1(\tau_1) + U_2(\tau_1,\tau_2) + U_3(\tau_2,\tau_3) + U_4(\tau_3,\tau_4) + ... + U_N(\tau_{N-1},\tau_N) \quad (1)$$

The τ_1, τ_2, ..., τ_j, ... symbols represent the following discrete variables:

$$\tau_1 \in \{\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{d}\} \text{ (4 elements)}$$

$$\tau_2 \in \{(\mathbf{ab}')(\mathbf{ac}')(\mathbf{ad}')(\mathbf{ba}')(\mathbf{bc}')...\} \text{ (12 elements)}$$

$$\tau_3 \in \{(\mathbf{ab}'\mathbf{a})(\mathbf{ab}'\mathbf{c})(\mathbf{ab}'\mathbf{d})(\mathbf{ac}'\mathbf{a})...\} \text{ (36 elements)}$$

$$\tau_4 \in \{(\mathbf{a}'\mathbf{ba}')(\mathbf{a}'\mathbf{bc}')(\mathbf{a}'\mathbf{bd}')(\mathbf{a}'\mathbf{ca}')...\} \text{ (36 elements)}$$

$$\tau_5 \in \{(\mathbf{ab}'\mathbf{a})(\mathbf{ab}'\mathbf{c})(\mathbf{ab}'\mathbf{d})(\mathbf{ac}'\mathbf{a})...\} \text{ (36 elements)}$$

and so forth. τ_1 represents the possible states of α_1; τ_2 those of the possible states of α_1 and α_2; τ_3 those of α_1, α_2, and α_3; and each succeeding τ_j those of α_{j-2}, α_{j-1}, and α_j. Each energy term $U_j(\tau_{j-1},\tau_j)$ is defined to be $+\infty$ if τ_{j-1} and τ_j are incompatible; since τ_{j-1} and τ_j represent $(\alpha_{j-3}, \alpha_{j-2}, \alpha_{j-1})$ and $(\alpha_{j-2}, \alpha_{j-1}, \alpha_j)$, respectively, then τ_{j-1} and τ_j are incompatible if the last two entries of the first do not match the first two entries of the second. If its two τ arguments are compatible, then each U_j term is defined as follows: $U_1(\tau_1) = 0$. $U_2(\tau_1,\tau_2) = 0$. $U_3(\tau_2,\tau_3) = U_3(\alpha_1,\alpha_2,\alpha_3) = E_t$ or E_σ, depending on whether $\alpha_1 = \alpha_3$ or not. $U_j(\tau_{j-1},\tau_j) = U_j(\alpha_{j-3},\alpha_{j-2},\alpha_{j-1},\alpha_j)$, for $j \geq 4$, is set equal to E_t if $\alpha_{j-2} = \alpha_j$; to $E_\sigma + E_\omega$ if $\alpha_{j-2} \neq \alpha_j$ and $\alpha_{j-3} = -\alpha_j$; and to E_σ if $\alpha_{j-2} \neq \alpha_j$ and $\alpha_{j-3} \neq -\alpha_j$.

3. Partition Function

Define a set of matrices W_j such that $W_j(\tau_{j-1},\tau_j) = \exp[-\beta U_j(\tau_{j-1},\tau_j)]$ and $\beta = 1/k_BT$. Then the partition function may be written

$$Q = W_1 \cdot W_2 \cdot W_3 \; ... \; W_N \cdot J \quad (2)$$

where · represents the matrix product. This may also be written

$$Q = W_1^{(N)} \cdot J \quad (3)$$

if we employ Flory's[1] serial matrix product notation. Here W_1 is 1 × 4, W_2 is 4 × 12, W_3 is 12 × 36, each succeeding W_j is 36 × 36, and J is a column of 36 ones. Note that each W_j beyond W_4 is identical to W_4.

4. Structure Factor

Define a set of matrices as follows:

$$M_1(\tau_1) = W_1(\tau_1) \exp[i\mathbf{q} \cdot \alpha_1] \quad (4)$$

$$M_j(\tau_{j-1},\tau_j) = W_j(\tau_{j-1},\tau_j) \exp[i\mathbf{q} \cdot \alpha_j] \quad (5)$$

Here **q** is the wavevector. Each M_j is the same order as the corresponding W_j, although complex. Since primed and unprimed vectors alternate along the chain, M_{j+1} is the complex conjugate of M_j for any $j \geq 4$. Then

$$\langle \exp[i\mathbf{q} \cdot \mathbf{r}_{jk}] \rangle = Q^{-1} W_1^{(j)} \cdot M_{j+1}^{(k-j)} \cdot \mathbf{W}_{k-j+1}^{(N-k)} \cdot J \quad (6)$$

where we have again followed Flory's serial matrix product notation and where $\mathbf{r}_{jk}$ is the separation vector between nodes j and k of the walk.

We define the structure factor as

$$S(\mathbf{q}) = (N+1)^{-2} \sum_j \sum_k \langle \exp[i\mathbf{q} \cdot \mathbf{r}_{jk}] \rangle \quad (7)$$

where j and k each range over the integers 0, 1, 2, ..., N. Or we may write

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$$S(\mathbf{q}) = (N+1)^{-1} + 2(N+1)^{-2}\,\mathscr{R} \sum_{0\le j<k\le N} \langle \exp[i\mathbf{q}\cdot\mathbf{r}_{jk}]\rangle \quad (8)$$

The first term in eq 8 results from the $j = k$ terms. (It is appropriate to carry the $j = k$ terms when computing structure factors for radiation scattering, but inappropriate for structure factors appearing in integral equation theory. Obviously, the differences are slight for large N and only involve a constant term and a normalization.) The symbol $\mathscr{R}$ indicates that we take the real part of what follows.

The sum in eq 8 is performed with the supermatrix scheme presented by Flory:[1]

$$S(\mathbf{q}) = (N+1)^{-1} + 2(N+1)^{-2}Q^{-1}\,\mathscr{R}\, T_{\mathrm{L}}\cdot S_1{}^{(N)}\cdot T_{\mathrm{R}}\cdot J \quad (9)$$

where

$$T_{\mathrm{L}} = [1 \quad 0 \quad 0] \quad (10)$$

$$S_j = \begin{bmatrix} W_j & M_j & M_j \\ 0 & M_j & M_j \\ 0 & 0 & W_j \end{bmatrix} \quad (11)$$

and

$$T_{\mathrm{R}} = \begin{bmatrix} 0 \\ 0 \\ E_{36} \end{bmatrix} \quad (12)$$

E_{36} represents the 36-order identity matrix and each of the 0 entries in eqs 11 and 12 are matrices of all zeros of the correct dimensions to be commensurate. T_{L} is 1 × 3, S_1 is 3 × 12, S_2 is 12 × 36, S_3 is 36 × 108, each succeeding S_j is 108 × 108, and T_{R} is 108 × 36. Recall that $S_4 = S_6 = S_8 = ... = S_5{}^* = S_7{}^* = S_9{}^* = ...$ Therefore, we write

$$S(\mathbf{q}) = (N+1)^{-1} + 2(N+1)^{-2}Q^{-1}\,\mathscr{R}\, T_{\mathrm{L}}\cdot S_1\cdot S_2\cdot S_3\cdot (S\cdot S^*)^M\cdot T_{\mathrm{R}}\cdot J \quad (13)$$

where $S = S_4$ and S^* is its complex conjugate. Also, $3 + 2M = N$. By repetitive matrix squaring, this expression can be evaluated for large values of M rather easily.

5. Orientational Average

The above formulas only permit computation of $S(\mathbf{q})$. Usually, we require an average over all orientations:

$$S(q) = (4\pi)^{-1} \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \sin\theta \,\mathrm{d}\,\theta\, S(\mathbf{q}) \quad (14)$$

where $\mathbf{q} = q(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\varphi)$. Obviously, the average over orientations must be done numerically. (This represents the only source of approximation in this calculation.) For the diamond lattice, we expect each of the following symmetries: $S(q,\varphi,\theta) = S(q,\varphi,\pi-\theta)$; $S(q,\varphi,\theta) = S(q,\varphi+\pi/2, \theta)$; and $S(q,\varphi,\theta) = S(q,\varphi-\pi/2, \theta)$. This means we need only compute at θ and φ values in the intervals $[0, \pi/2]$ and $[0, \pi/4]$, respectively.

6. Results and Comments

Figure 1 displays results for the structure factor (in Kratky representation) computed using $E_t = 0$, $E_\sigma = 500$ cal/mol, $E_\omega = 2000$ cal/mol, $T = 413$ K, $M = 512$, and $N = 1027$. The double integral over orientations, eq 14, was performed by Simpson's rule with 10° intervals in both θ and φ. The curve compares quite favorably with that published by McCoy, et al.[7] Some differences exist beyond about $q = 8$, and these are attributable either to the difference in bond angle in the two calculations (112 *vs* 109.5°) or to integration errors incurred in the average over orientations.

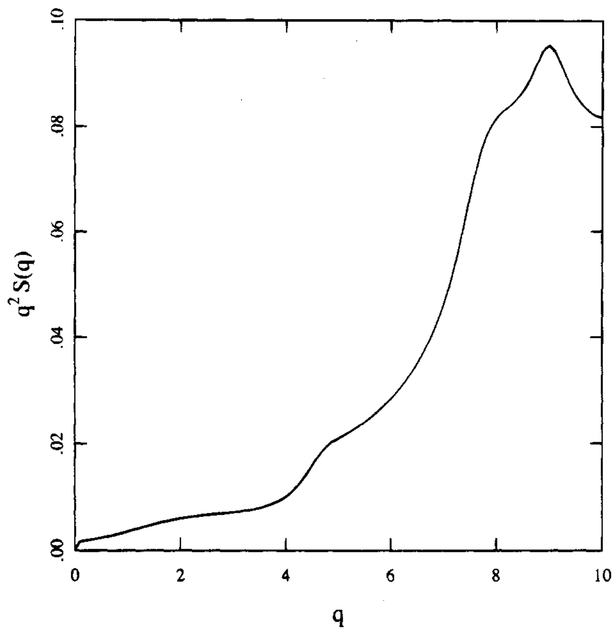

Figure 1. Single-chain structure factor, in Kratky representation, of a lattice model of polyethylene.

For these values of N, the computation of each $S(q)$ value, including the average over orientations, requires about 4 min on an IBM RS-6000. Presumably, it will run much more rapidly in vector arithmetic.

The main disadvantages of this approach relative to others[7] are the requirement of lattice embedding and the necessity to average numerically over orientations. The techniques explored by Fixman[2] and by Fixman and Skolnick[3] overcome both these disadvantages but at some cost; it becomes necessary to expand the transfer matrices in terms of spherical harmonics or some other basis set. This tends to complicate the computation and introduces another source of approximation, since the basis set expansions must inevitably be truncated.

In summary, it is possible to compute structure factors by transfer matrix techniques, but one must think in terms of sequences of oriented bonds, rather than in terms of sequences of bond rotations.

References and Notes

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