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The largest eigenvalue method for stereo-regular vinyl chains

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We would like to dedicate this paper to Prof James E. Mark on the occasion of his 70th birthday.

Abstract

We derived the analytical solution of the eigenvalue problem for stereo-regular vinyl chains, such as stereo-regular polypropylene chains. The solution is applicable to all stereo-regular polymers of the type $(AB)_x$ which do not have symmetry between *gauche*$^+$ and *gauche*$^-$ states, and to polymers, such as polyoxymethylene or polydimethylsiloxane, for which symmetry between the *gauche*$^+$ and *gauche*$^-$ states does exist. For symmetric chains, the general solution of the eigenvalue problem is reduced to the known solution for polyoxymethylene chains. To illustrate the method the calculations have been performed for the three rotational states (*trans*, *gauche*$^+$ and *gauche*$^-$) model, but the general algebraic solution is applicable for any ν rotational states models of polymer chains. We used the analytical solution of the eigenvalue problem to calculate numerically elastic properties of stereo-regular polypropylene chains within the framework of Mark–Curro theory (J Chem Phys, 79, 5705, 1983).

Keywords: Eigenvalue; Mark–Curro theory; Rotational state

1. Introduction

The rotational isomeric state (RIS) model is one of the most important achievements in polymer science. It is based on rigorous statistical mechanics approach and it allows the calculations of various conformation-dependent macromolecular properties. Foundations of the rotational isomeric state model have been built by Flory in his classic monograph Statistical Mechanics of Macromolecules [1]. Important contributions to the early development of statistical mechanics of polymers were also done by Volkenstein [2]. The work on the rotational isomeric state model initiated by Flory [1] has been successfully continued by Mattice and Suter and presented in the seminal book Conformational Theory of Large Molecules [3] that shows the state of the art of the RIS theory. The major result of the RIS theory is the reduction of the continuous conformational space to a discrete space, based on the bond rotational potentials for polymer chains. Using this reduction, partition function calculations are treated as an algebraic problem, which is mathematically more tractable.

Another significant simplification (for sufficiently long chains) can be performed by applying matrix eigenvalue techniques for the derivation of chain statistics. The largest eigenvalue method is a very powerful tool, which provides the analytical solution of the RIS model in the limit of infinite chain length. The method has been previously applied to the solution of the RIS for simple symmetric polymer chains of type $(A)_n$, such as polymethylene chains [1,4], and to symmetric polymer chains of type $(AB)_x$ having symmetry between *gauche*$^+$ and *gauche*$^-$ states, such as polyoxymethylene (POM) [1] or polydimethylsiloxane (PDMS) [5]. We note that x is equal to $n/2$, where n is the number of bonds.

In the present paper we extend the largest eigenvalue method to asymmetric polymer chains of type $(AB)_x$. A well-known polymer of this type is polypropylene (PP). Here, we restrict our analysis to stereo-regular chains with periodically repeating dyad conformations, such as isotatic *d*, isotatic *l* or syndiotactic chains. Our analysis does not hold for atactic vinyl polymers.

The structure of the paper is as follows. We first present the foundations of the RIS for asymmetric $(AB)_x$ chains. In Section 2 we show in detail the solution of the eigenvalue

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problem for stereo-regular $(AB)_x$ chains. As a special case, we also include the known solution of the largest eigenvalue method for symmetric $(AB)_x$ chains, such as polyoxymethylene (POM). In the final part of the paper we apply the analytical solution of the eigenvalue problem to calculate the elastic properties of stereo-regular polypropylene chains within the framework of the Mark–Curro theory [6,7]. We also discuss possible future developments of the theory.

2. Statistical weight matrices for asymmetric polymer chains

In the rotational isomeric state (RIS) model of polymer chains, bond lengths and bond angles are kept fixed, and there is a limited set of allowed torsional angles. For example, in the simplest case of polymethylene chains the RIS model assumes that there are three torsional states: *trans* (*t*), *gauche*$^+$ (g^+) and *gauche*$^-$ (g^-). The chain conformation of a polymer is thus characterized by the set of torsional states of polymer bonds. This approach greatly simplifies the statistical mechanics of chain molecules by reducing it to a purely algebraic problem.

If $E_{\zeta\eta,i}$ denotes the energy associated with the bond i being state η, and the bond $i-1$ in being in state ζ, then the statistical weight $u_{\zeta\eta,i}$ is defined as [1]:

$$u_{\zeta\eta,i} = \exp\left(\frac{-E_{\zeta\eta,i}}{RT}\right) \tag{1}$$

The statistical weights then can be written as a statistical weight matrix $\mathbf{U}_i = [u_{\zeta\eta}]_i$.

For the case of polymethylene chains the statistical weight matrix can be written in the following form [1]

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \tag{2}$$

where $\sigma = \exp(-E_g/RT)$, E_g is the difference between energies of *gauche* and *trans* states, and ψ and ω are related to energies of g^+ and g^- pairs.

The RIS model is easily applicable to polymer chains of the type $(AB)_x$. For symmetric chains, instead of the single matrix $\mathbf{U}$, there are two types of statistical weight matrices: $\mathbf{U}_a$ and $\mathbf{U}_b$ with the subscript a referring to the A→B bond, and subscript b corresponding to the B→A bond [1].

$$\mathbf{U}_a = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi_a & \sigma\omega_a \\ 1 & \sigma\omega_a & \sigma\psi_a \end{bmatrix}; \quad \mathbf{U}_b = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi_b & \sigma\omega_b \\ 1 & \sigma\omega_b & \sigma\psi_b \end{bmatrix} \tag{3}$$

Symmetric polymer chains, such as polydimethylsiloxane (PDMS) or polyoxymethylene (POM) have symmetry between the *gauche*$^+$ and *gauche*$^-$ states.

The presence of an asymmetric center in a chain molecule distinguishes between the handedness of the rotations around skeletal bonds. Because of this handedness, frequencies of states corresponding to the left and right rotations differ.

For asymmetric vinyl chains $(\text{–CHR–CH}_2\text{–})_x$ such as polypropylene (with R being CH_3) there are two different statistical weight matrices corresponding to different stereochemical configurations. If R groups is located in the front of the plane formed by the skeletal bonds of the fully extended chain we name the corresponding carbon atoms *d* centers, while C atoms connected to R groups located behind this plane are named *l* centers [1]. Since any 180° rotation about the vertical axis of this plane changes *d* centers to *l* centers (and *l* centers to *d* centers) the stereochemical configuration of a given center is defined relative to its neighboring centers. Therefore, the pair *ll* is equivalent to *dd* due to symmetry, but differs from the pair *ld* (or *dl*), since such a symmetry operation cannot be applied. Such stereochemical neighbor pairs are called dyads.

For *dd* dyad the two statistical weight matrices are [1,8] $\mathbf{U}'_d$ corresponding to the $\text{CHR}\rightarrow\text{CH}_2$ bond, and $\mathbf{U}''_{dd}$, corresponding to the $\text{CH}_2\rightarrow\text{CHR}$ bond [1,8]:

$$\mathbf{U}'_d = \begin{bmatrix} \eta\tau^* & 1 & \tau \\ \eta & 1 & \tau\omega \\ \eta & \omega & \tau \end{bmatrix}; \quad \mathbf{U}''_{dd} = \begin{bmatrix} \eta\omega & \tau\omega & 1 \\ \eta & \tau\omega & \omega \\ \eta\omega & 0 & \omega \end{bmatrix} \tag{4}$$

The statistical weight matrices for *ll* dyad are [1,8]

$$\mathbf{U}'_l = \begin{bmatrix} \eta\tau^* & \tau & 1 \\ \eta & \tau & \omega \\ \eta & \tau\omega & 1 \end{bmatrix}; \quad \mathbf{U}''_{ll} = \begin{bmatrix} \eta\omega & 1 & \tau\omega \\ \eta\omega & \omega & 0 \\ \eta & \omega & \tau\omega \end{bmatrix} \tag{5}$$

i.e. matrices $\mathbf{U}'_l$ and $\mathbf{U}''_{ll}$ are equivalent to $(\mathbf{U}'_d)^T$ and $(\mathbf{U}''_{dd})^{\mathrm{T}}$, respectively, [1,8].

For the syndiotactic chains the following matrices are employed [1,8]

$$\mathbf{U}''_{dl} = \begin{bmatrix} \eta & \omega & \tau\omega \\ \eta\omega & 1 & \tau\omega \\ \eta\omega & \omega & 0 \end{bmatrix}; \quad \mathbf{U}''_{ld} = \begin{bmatrix} \eta & \tau\omega & \omega \\ \eta\omega & 0 & \omega \\ \eta\omega & \tau\omega & 1 \end{bmatrix} \tag{6}$$

The statistical weight factors η, 1 and τ in the first row (or the diagonal) of $\mathbf{U}'_d$ can be interpreted as resulting from the first order interactions associated with t, g^+ and g^- states about bond i. The second order interactions are associated with statistical weight factors ω and τ^*. A more detailed discussion of these statistical weight matrices and their relation to the bond rotational potentials is given in Ref. [1].

For the isotatic polypropylene these matrices repeat regularly in the form $(\mathbf{U}'_d\,\mathbf{U}''_{dd})_x$ where x is the number of dyads, so one may combine them into a single matrix [1,8]

$$\mathbf{U}^{(2)}_{\text{isotactic}} = \mathbf{U}'_d\mathbf{U}''_{dd} \tag{7}$$

The above equation applies to *dd* dyads, but for *ll* dyads corresponding equations have a similar form.

For simplicity we will use a shorter notation $\mathbf{U}_a$ and $\mathbf{U}_b$ and $\mathbf{U}^{(2)}$ which describes both *dd* and *ll* dyads with Ref. [1,8]

$$\mathbf{U}^{(2)} = \mathbf{U}_a\mathbf{U}_b \tag{8}$$

In the case of syndiotactic chains, however, matrix $\mathbf{U}^{(2)}$ equals: $\mathbf{U}'_d\,\mathbf{U}'_{dl}\mathbf{Q}$, where

$$\mathbf{Q} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

is the matrix that interchanges rows and columns corresponding to the states g^+ and g^- [1,8]. The isotactic *d* chain is composed of the sequence of preferred conformations $(g^+t)(g^+t)\ldots$ or $(tg^-)(tg^-)\ldots$, the isotactic *l* is composed of preferred sequences $(g^-t)(g^-t)\ldots$ or $(tg^+)(tg^+)\ldots$, while the syndiotactic chain is composed of preferred sequences $(g^+g^+)(tt)(g^+g^+)(tt)\ldots$ or $(tt)(g^-g^-)(tt)(g^-g^-)(tt)\ldots$, or all-*trans* $(tt)(tt)\ldots$ sequence [1,8].

The partition function of the chain within the rotational isomeric state model framework is [1,8]:

$$Z = \mathbf{J}^*[\mathbf{U}^{(2)}]^{x-1}\mathbf{J} \tag{9}$$

where $\mathbf{J}^*$ and $\mathbf{J}$ are vectors defined as

$$\mathbf{J}^* = \begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \tag{10}$$

and

$$\mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{11}$$

and x is the number of dyads in the chain.

3. The largest eigenvalue method

Before proceeding further with the analysis of polypropylene, let us first consider the largest eigenvalue method for the simplest, well-known case of polymethylene. This problem was first studied by Volkenstein [2], Birshtein and Ptitsyn [9] and the detailed analysis of the method was later presented by Flory [1]. Appendix A shows a variation of the detailed Volkenstein [2], Birshtein and Ptitsyn [9], Flory [1] solution of this problem, which might be useful to better understand the derivation of the similar solution for stereo regular vinyl chains.

The statistical weight matrix $\mathbf{U}$ for polymethylene can be diagonalized $\mathbf{BUA} = \mathbf{\Lambda}$ where $\mathbf{B}$ is the matrix inverse of $\mathbf{A}$, ($\mathbf{B} = \mathbf{A}^{-1}$). The probability of having bond $i-1$ in the ξ state and bond i in the η state for polymethylene is [1]

$$P_{i,\xi\eta} = \frac{1}{Z}\left(\mathbf{J}^*[\mathbf{U}^{(i-2)}\mathbf{U}'_{i,\xi\eta}\mathbf{U}^{(n-1-i)}]\mathbf{J}\right) \tag{12}$$

where $\mathbf{U}'_{i,\xi\eta}$ is the matrix obtained from $\mathbf{U}$ by striking out all elements except the element $u_{\xi\eta}$. It can be shown [1,9] that the largest eigenvalue method (for long chains) leads to a simple expression for $P_{\xi\eta}$: [1,9]

$$P_{\xi\eta} = B_{1\xi}u_{\xi\eta}A_{\eta 1}\lambda_1^{-1} \tag{13}$$

where λ_1 is the largest eigenvalue of $\mathbf{U}$, while $A_{\eta 1}$ and $B_{1\xi}$ are elements of matrices $\mathbf{A}$ and $\mathbf{B} = \mathbf{A}^{-1}$ that diagonalize the statistical weight matrix $\mathbf{U}$, and expressible through eigenvectors of $\mathbf{U}$ [1,9].

For polymethylene there is a single probability $P_{i,\xi\eta}$ of having bond $i-1$ in the ξ state and bond i in the η state. In the case of a vinyl chain there are two types of probabilities $P_{a_{i,\xi\eta}}$ and $P_{b_{i,\xi\eta}}$ with the subscript a referring to the CHR → CH_2 bond, and subscript b corresponding to the CH_2 → CHR bond [1]. These two kinds of probabilities $P_{a_{i,\xi\eta}}$ and $P_{b_{i,\xi\eta}}$ exist in general for any polymer of the type $(AB)_x$, in particular for the polyoxymethylene (POM), studied in detail the by the largest eigenvalue method by Flory [1] or for polydimethylsiloxane (PDMS) [5]. The symmetry between the *gauche*$^+$ and *gauche*$^-$ states for polyoxymethylene chains was used in these analyses. This symmetry is manifested in matrices $\mathbf{U}_a$ and $\mathbf{U}_b$ for POM chains (see Eq. (3)).

The use of this symmetry simplifies the solution of the eigenvalue problem. The partition function is [1]

$$Z = \mathbf{J}^*[\mathbf{U}^{(2)}]^{x-1}\mathbf{J} \tag{14}$$

where

$$\mathbf{U}^{(2)} = \mathbf{U}_a\mathbf{U}_b \tag{15}$$

By abolishing the distinction between the g^+ and g^- states the matrix $\mathbf{U}^{(2)}$ can be reduced to the 2×2 form: [1]

$$\mathbf{U}^{(2)} = \begin{bmatrix} 1+2\sigma & 2(\sigma+\sigma^2\beta) \\ 1+\sigma\alpha & 2\sigma+\sigma^2\alpha\beta \end{bmatrix} \tag{16}$$

with

$$\alpha = \psi_a + \omega_a \tag{17}$$

$$\beta = \psi_b + \omega_b \tag{18}$$

The eigenvalues of the matrix $\mathbf{U}^{(2)}$ are then given by relatively simple formula [1]

$$\lambda_{1,2}^{(2)} = \frac{1}{2}\left[(1+4\sigma+\sigma^2\alpha\beta) \pm \sqrt{(1-\sigma^2\alpha\beta)^2 + 8\sigma(1+\sigma\alpha)(1+\sigma\beta)}\right] \tag{19}$$

The first order a priori probabilities of gauche and trans states and the second order a priori probabilities for pairs of rotational states are then given in terms of algebraic equation containing the eigenvalues $\lambda_{1,2}^{(2)}$ and its various derivatives. These equations can be found in Flory's book [1] or (in reference to the PDMS chains) in the paper by Kloczkowski, Sharaf and Mark [5], where the analytical solution of the eigenvalue problem was used in the Monte-Carlo generation of long PDMS chains. The probabilities $P_{a_{i,\xi\eta}}$ and $P_{b_{i,\xi\eta}}$ are, however, not given in an explicit form but as a set of equations based on the symmetry between two gauche states.

In general, however, such a simplifying symmetry may not exist as in the case of the asymmetric vinyl chains. For polymers such as polypropylene, the corresponding matrices given by Eqs. (4)–(6) are clearly non-symmetric with respect to the elements g^+ and g^-. This non-symmetricalness requires the general solution of the eigenvalue problem without the symmetry simplification used for POM chains. Below we provide the exact analytical solution of this problem for stereo-regular polymer chains.

The probabilities $P_{a_{i,\xi\eta}}$ and $P_{b_{i,\xi\eta}}$ are given by the following formula:

$$P_{a_{i,\xi\eta}} = \frac{1}{Z}\left(\{\mathbf{J}^*[\mathbf{U}^{(2)}]^{(i-1)}\mathbf{U}'_{a_{i,\xi\eta}}\mathbf{U}_{b_i}[\mathbf{U}^{(2)}]^{(x-1-i)}\}\mathbf{J}\right) \tag{20}$$

and

$$P_{b_{i,\xi\eta}} = \frac{1}{Z}\left(\{\mathbf{J}^*[\mathbf{U}^{(2)}]^{(i-1)}\mathbf{U}_{a_i}\mathbf{U}'_{b_{i,\xi\eta}}[\mathbf{U}^{(2)}]^{(x-1-i)}\}\mathbf{J}\right) \tag{21}$$

where $\mathbf{U}'_{a_{i,\xi\eta}}$ and $\mathbf{U}'_{b_{i,\xi\eta}}$ denote the matrices $\mathbf{U}_a$ and $\mathbf{U}_b$, respectively, with all elements stricken out except the elements $u_{a,\xi\eta}$ (or $u_{b,\xi\eta}$), and $\mathbf{U}^{(2)}=\mathbf{U}_a\mathbf{U}_b$. The subscript i, which labels the position of the given dyad in the chain sequence, can be dropped off in the limit of the infinitely long chains when the largest eigenvalue method is applicable. If the matrix $\mathbf{U}^{(2)}$ is diagonalized

$$\mathbf{B}\mathbf{U}^{(2)}\mathbf{A} = \mathbf{\Lambda} \tag{22}$$

where $\mathbf{B}=\mathbf{A}^{-1}$ then the we can write the probabilities $P_{a_{i,\xi\eta}}$ and $P_{b_{i,\xi\eta}}$ as

$$P_{a,\xi\eta} = \frac{1}{Z}\left(\{\mathbf{J}^*\mathbf{A}\mathbf{\Lambda}^{(i-1)}\mathbf{B}\mathbf{U}'_{a,\xi\eta}\mathbf{U}_b\mathbf{A}\mathbf{\Lambda}^{(x-1-i)}\mathbf{B}\}\mathbf{J}\right) \tag{23}$$

and

$$P_{b,\xi\eta} = \frac{1}{Z}\left(\{\mathbf{J}^*\mathbf{A}\mathbf{\Lambda}^{(i-1)}\mathbf{B}\mathbf{U}_a\mathbf{U}'_{b,\xi\eta}\mathbf{A}\mathbf{\Lambda}^{(x-1-i)}\mathbf{B}\}\mathbf{J}\right) \tag{24}$$

It can be shown (see Appendix B for details) that by applying the largest eigenvalue method the probability $P_{a_{i,\xi\eta}}$ can be written as

$$P_{a,\xi\eta} = \frac{1}{\lambda_1}\left(B_{1\xi}u_{a,\xi\eta}[A_{11}u_{b,\eta1} + A_{21}u_{b,\eta2} + A_{31}u_{b,\eta3}]\right) \tag{25}$$

The equation for $P_{b,\xi\eta}$ (see Appendix B for details) becomes

$$P_{b,\xi\eta} = \frac{1}{\lambda_1}\left(u_{b,\xi\eta}A_{\eta1}[B_{11}u_{a,1\xi} + B_{12}u_{a,2\xi} + B_{13}u_{a,3\xi}]\right) \tag{26}$$

The above equation looks similar to Eq. (25) for $P_{a,\xi\eta}$. The difference between Eqs. (25) and (26) is due only to the replacement of elements of matrices $\mathbf{A}$ and $\mathbf{U}_a$ by the transposed elements of matrices $\mathbf{B}$ and $\mathbf{U}_b$, respectively. It can be proved that for symmetric polymer chains of the type $(AB)_n$ the solution given by Eqs. (25) and (26) is equivalent to the known solution of the largest eigenvalue problem for polyoxymethylene (POM) [1] or PDMS [5] given as a set of equations using the symmetry between two gauche states. Instead of a tedious analytical proof, it is straightforward to reproduce all numerical results obtained in reference [5] for PDMS using the probabilities given by Eqs. (25) and (26).

From the two-bond probabilities $P_{a,\xi\eta}$ and $P_{b,\xi\eta}$ we can calculate single-bond probabilities

$$P_{a,\eta} = \sum_{\xi=1}^{3} P_{a,\xi\eta} \tag{27}$$

and

$$P_{b,\eta} = \sum_{\xi=1}^{3} P_{b,\xi\eta} \tag{28}$$

and conditional probabilities

$$q_{a,\xi\eta} = \frac{P_{a,\xi\eta}}{P_{a,\xi}} \tag{29}$$

and

$$q_{b,\xi\eta} = \frac{P_{b,\xi\eta}}{P_{b,\xi}} \tag{30}$$

The conditional probabilities can be used for a very efficient Monte-Carlo generation of long polymer chains [4,5]. We have applied this method to calculate elastic properties of stereo regular polypropylene chains within the framework of the theory of Mark and Curro [6,7]. We should note that our model neglects all long range interactions, and, therefore, chains are almost phantom-like.

4. Calculation of elastic properties of polypropylene chains

To illustrate the application of the above analytical results we have performed the calculations of elastic properties of polypropylene chains. We have applied the method of Mark and Curro [6,7], based on the Monte-Carlo rotational isomeric state model, to calculate the polymer elastic properties from the distribution of the end-to-end vector of polymer chains. It has been shown [4,5] that this method is also applicable to filled polymers. In the Mark–Curro theory the distribution $P(r)$ of the end-to-end vector r obtained from Monte-Carlo simulations is directly related to the Helmholtz free energy $A(r)$ of a chain

$$A(r) = c - kT\ln P(r) \tag{31}$$

where c is a constant. The application of the three-chain model leads to the following expression for the elastic free energy change during the deformation of the network as a function of elongation ratio α

$$\Delta A = \frac{\nu}{3}([A(r_0\alpha) + A(r_0\alpha^{-1/2}) - 3A(r_0)]) \tag{32}$$

Here ν is the number chains in the network and r_0 is the root-mean-square end-to-end vector of network chains. The simplifying assumption of affine deformation of the network chains was used in the derivation of Eq. (32).

The nominal stress f^* defined as the elastic force at equilibrium per unit cross-sectional area of the sample in the undeformed state is

$$f^* = -T\left(\frac{\partial \Delta A}{\partial \alpha}\right)_T \tag{33}$$

and, therefore

$$f^* = -\frac{\nu k T r_0}{3}\left[G'(r_0\alpha) - \alpha^{-3/2}G'(r_0\alpha^{-1/2})\right] \tag{34}$$

where $G(r)=\ln P(r)$, and $G'(r)$ denotes the derivative $\mathrm{d}G/\mathrm{d}r$. In the past we have successfully used this methodology to calculate the elastic properties of both unfilled and filled polymethylene and polydimethylsiloxane materials [4,5]. Here we apply the same methodology to stereo-regular chains of polypropylene. We are especially interested in comparison of elastic properties of isotactic and syndiotactic chains.

There are several different rotational isomeric state models of polypropylene (PP) which differ in the number of rotational states assumed for PP chains [10–15]. The first PP model was proposed by Flory and co-workers was based on three rotational states [13]. There are also more accurate models of polypropylene involving five rotational states developed by Suter and Flory [8], or even nine states (Boyd and Breitling) [11]. The three-state model with proper parametrization [12] has been, however, successfully used for calculations of various properties of the polypropylene chains. In the present work we use the simplest three-state RIS model of PP chain proposed by Tonelli, Abe and Flory in 1970 [13]. In their model, the authors assumed the following values of the RIS parameters (in Eqs. (4)–(6)):

$$\eta = 1.0 \tag{35}$$

$$\tau = 0.5$$

$$\omega = 0\text{–}0.05$$

$$\tau^* = 1.0$$

The above values of rotational parameters for PP correspond to the temperature 481 K.

Bond length of C–C bonds was assumed to be 1.53 Å and the valence angles:

$$\text{C–CH}_2\text{–C} \quad 112^\circ \tag{36}$$

$$\text{CH}_2\text{–C–CH}_2 \quad 112^\circ$$

$$\text{C–C}^*\text{–H} \quad 106.8^\circ$$

$$\text{H–C–H} \quad 109^\circ$$

and torsion angles for different rotational states

$$t \quad 180^\circ - \Delta\phi \tag{37}$$

$$g^+ \quad 60^\circ - \Delta\phi$$

$$g^- \quad -60^\circ$$

with $\Delta\phi = 0$, 10 or 20°.

We have used the same values of RIS parameters for PP with $\Delta\phi=0$ and $\omega=0.05$.

We have generated 500,000 chains for each of the two cases (isotactic PP, syndiotactic PP) for varying lengths of the chains. We have studied PP chains of 100, 150 and 200 bonds long. The simulations of PP chains were based on bond probabilities and conditional probabilities obtained with the largest eigenvalue method from Eqs. (25)–(30).

Fig. 1 shows the end-to-end vector distribution functions for isotactic polypropylene. We note that the results for isotactic-D and isotactic-L polypropylene are indistinguishable from each other due to the chain symmetry. We have performed statistical analysis of errors in Monte-Carlo results by running simulations five times (2,500,000 generated chains) and calculating averages and variances (σ^2) for all points in Fig. 1. The calculated error bars were too small to show them in Fig. 1. For example, the largest value of σ (corresponding to the maximum of the curve for $n=150$) in Fig. 1 was 0.00065.

The similar plots for syndiotactic polypropylene are shown in Fig. 2. The end-to-end distance in Figs. 1 and 2 is normalized by nl, where n is the number of skeletal bonds and l is bond length.

The characteristic feature of both graphs is that with the increasing number of bonds the maximum of distribution curves moves towards smaller values of r/nl. Additionally, syndiotactic chains have a maximum in the end-to-end distribution function at larger values of r/nl than isotactic

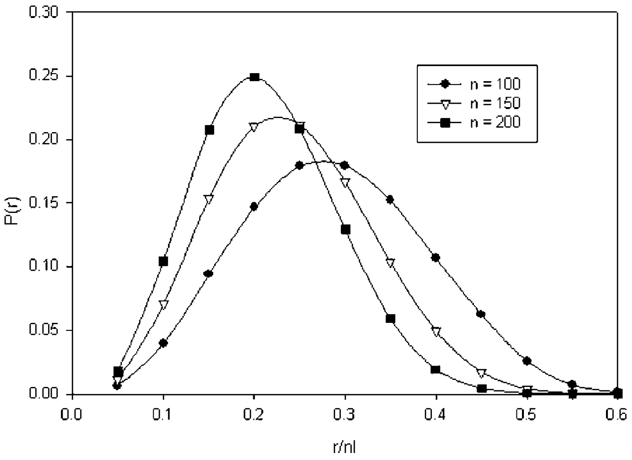

Fig. 1. The distribution function of the end-to-end vector for isotactic PP chains of length 100, 150, and 200 bonds.

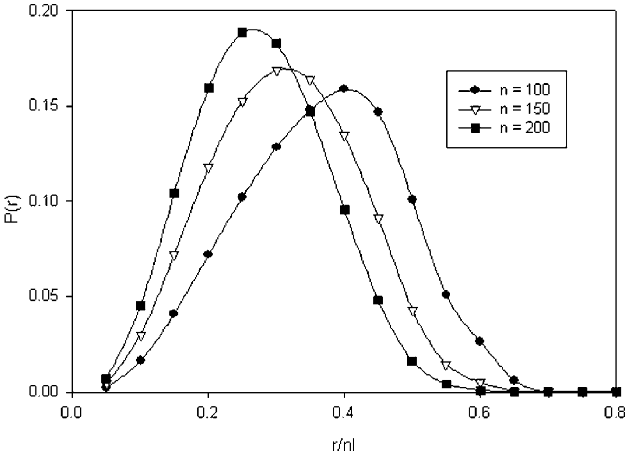

Fig. 2. The distribution function of the end-to-end vector for syndiotactic PP chains of length 100, 150, and 200 bonds.

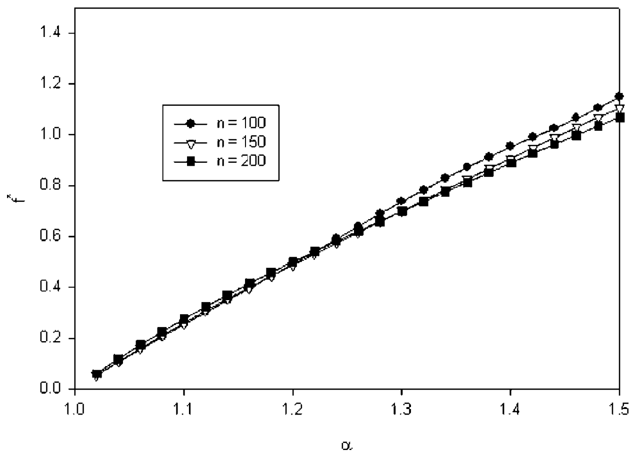

Fig. 4. Nominal stress f^* for isotactic PP chains as a function of the extension ratio α for chains of length 100, 150, and 200 bonds.

chains. This is clearly visible in Fig. 3 that compares distribution functions of isotactic and syndiotactic chains of 100 bonds.

This behavior of syndiotactic chains is easily explainable. The distribution function of syndiotactic PP is shifted towards larger values of *r*/*nl* than that of isotactic PP because the most extended all-*trans* conformations are preferred for syndiotactic polymers.

Figs. 4 and 5 show the nominal stress f^* calculated from Eq. (34) for isotactic and syndiotactic PP chains, respectively, as a function of the extension ratio α for varying length of chains. It is interesting that the nominal stress of syndiotactic PP chains shows significantly larger dependence on the length of the chain than that of isotactic PP.

Fig. 6 compares the variation of nominal stress f^* with extension ratio α of isotactic and syndiotactic chains composed of 100 bonds.

The significantly larger upward plot of the nominal stress for syndiotactic PP chains can be explained by the fact that syndiotactic conformations are already highly extended, and, therefore, the further elongation of such chains requires larger force than for isotactic chains.

Figs. 7 and 8 show Mooney–Rivlin plots of the reduced stress (modulus) $[f^*]$

$$[f^*] = \frac{f^*}{\alpha - \alpha^{-2}} \tag{38}$$

for isotactic and syndiotactic PP chains, respectively, as a function of reciprocal the extension ratio α for chains of length 100, 150, and 200 bonds.

Fig. 9 compares plots of the reduced stress $[f^*]$ as a function of α^{-1} for isotactic and syndiotactic PP chains of length 100 bonds. These results suggest that the Mooney–Rivlin semi-empirical formula

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{39}$$

where C_1 and C_2 are empirical constants independent of elongation α, is more applicable to isotactic PP chains in

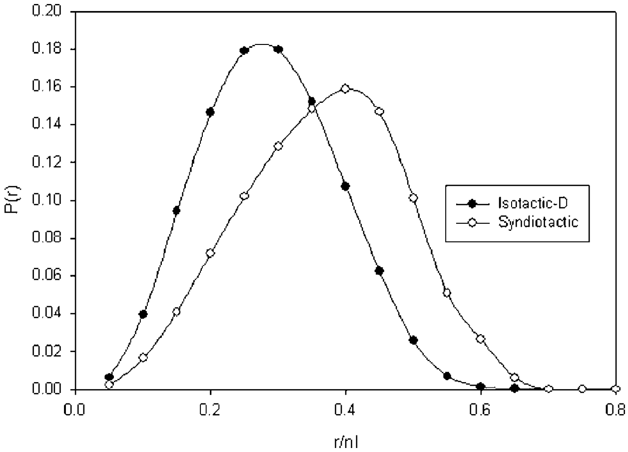

Fig. 3. The end-to-end vector distribution function of isotactic and syndiotactic PP chains of 100 bonds.

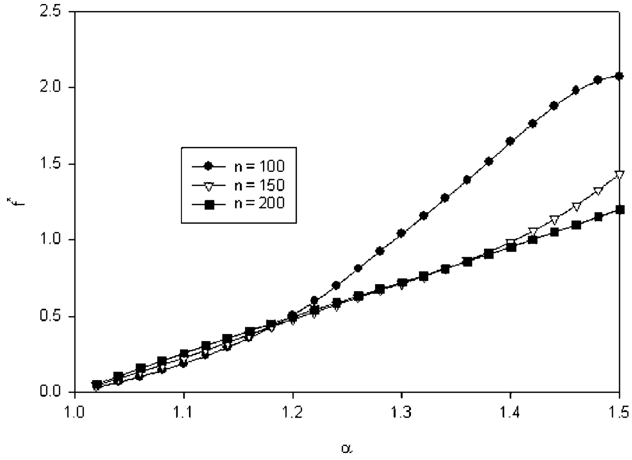

Fig. 5. Nominal stress f^* for syndiotactic PP chains as a function of the extension ratio α for chains of length 100, 150, and 200 bonds.

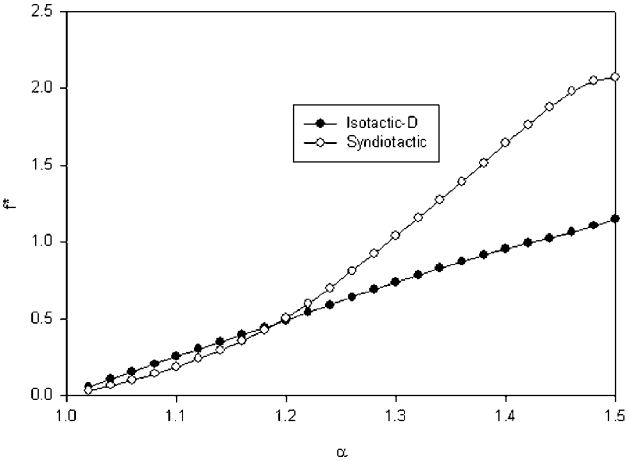

Fig. 6. Nominal stress f^* for isotactic and syndiotactic PP chains of length 100 bonds as a function of the extension ratio α.

Fig. 9 (for which the plot is almost linear) than to syndiotactic PP chains.

5. Discussion

The present study shows that the analytical solution of the largest eigenvalue problem for stereo regular chains is immediately applicable for theoretical studies of various properties of vinyl chains. We will continue to study this problem in the future. Our future work will concentrate on comparative analysis of elastic properties of different stereo-regular networks in filled rubbers and nanocomposites. The future research will be also focused on possible extension of the present approach to atactic vinyl chains and to RIS models with larger number of rotational states.

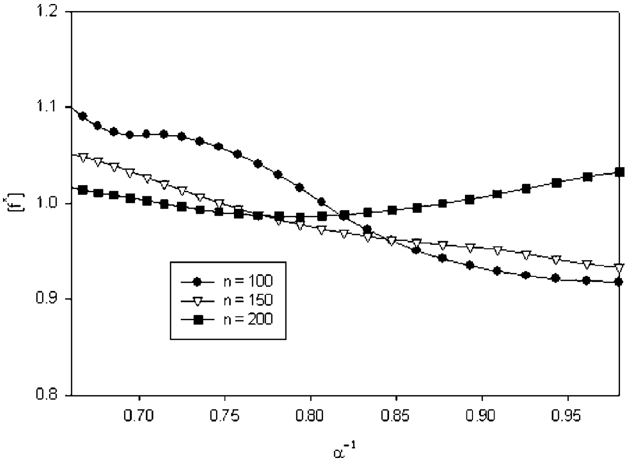

Fig. 7. The reduced stress $[f^*]$ as a function of α^{-1} for isotactic PP chains of length 100, 150, and 200 bonds.

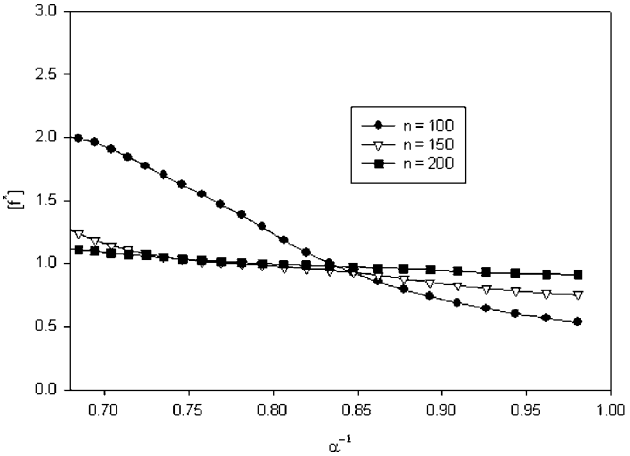

Fig. 8. The reduced stress $[f^*]$ as a function of α^{-1} for syndiotactic PP chains of length 100, 150, and 200 bonds.

Appendix A

The largest eigenvalue method for polymethylene

The equation for the partition function for a simple chain composed of identical units, such as polymethylene is

$$Z = \mathbf{J}^*[\mathbf{U}]^{n-2}\mathbf{J} \tag{A1}$$

where n is the number of monomer units. The matrix $\mathbf{U}$ in Eq. (9) can be diagonalized

$$\mathbf{BUA} = \mathbf{\Lambda} \tag{A2}$$

where $\mathbf{B}$ is the matrix inverse of $\mathbf{A}$

$$\mathbf{B} = \mathbf{A}^{-1} \tag{A3}$$

and $\mathbf{\Lambda}$ is the matrix containing eigenvalues on the diagonal. In the case of three rotational states (in general we may have ν rotational states),

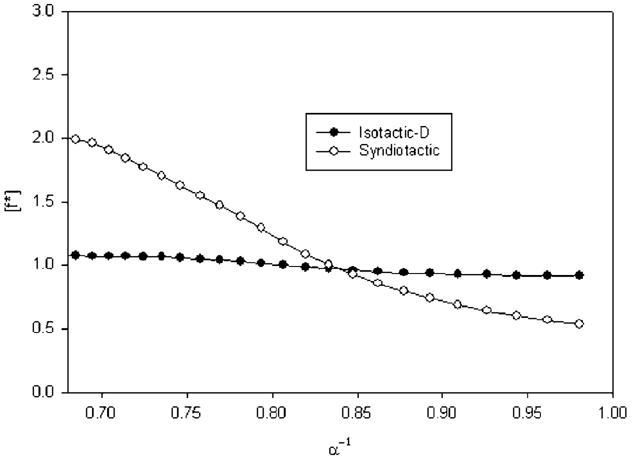

Fig. 9. The reduced stress $[f^*]$ as a function of α^{-1} for isotactic and syndiotactic PP chains of length 100 bonds.

$$\mathbf{\Lambda} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix} \tag{A4}$$

In order to understand the more complicated case of polypropylene it is worth looking into the detailed algebraic calculation of the partition function for polymethylene. The partition function in this case becomes:

$$Z = \mathbf{J}^*\mathbf{A}\mathbf{\Lambda}^{n-2}\mathbf{B}J \tag{A5}$$

The term $\mathbf{J}^*\mathbf{A}\mathbf{\Lambda}^{n-2}$ can be written

$$\begin{aligned} \mathbf{J}^*\mathbf{A}\mathbf{\Lambda}^{n-2} &= \begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \begin{bmatrix} \lambda_1^{n-2} & 0 & 0 \\ 0 & \lambda_2^{n-2} & 0 \\ 0 & 0 & \lambda_3^{n-2} \end{bmatrix} \\ &= \begin{bmatrix} A_{11} & A_{12} & A_{13} \end{bmatrix} \begin{bmatrix} \lambda_1^{n-2} & 0 & 0 \\ 0 & \lambda_2^{n-2} & 0 \\ 0 & 0 & \lambda_3^{n-2} \end{bmatrix} \\ &= \begin{bmatrix} A_{11}\lambda_1^{n-2} & A_{12}\lambda_2^{n-2} & A_{13}\lambda_3^{n-2} \end{bmatrix} \end{aligned} \tag{A6}$$

The term $\mathbf{BJ}$ on the other hand is

$$\mathbf{B}J = \begin{bmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} \sum_{\eta=1}^{3} B_{1\eta} \\ \sum_{\eta=1}^{3} B_{2\eta} \\ \sum_{\eta=1}^{3} B_{3\eta} \end{bmatrix} \tag{A7}$$

The product of the two vectors given in Eqs. (A6) and (A7) (which can be easily generalized to ν rotational states) leads to the following expression for the partition function of the polymethylene chain [1]

$$Z = \sum_{\xi=1}^{\nu} A_{1\xi} \sum_{\eta=1}^{\nu} B_{\xi\eta}\lambda_\xi \tag{A8}$$

For long chains in the limit $n \to \infty$ the largest eigenvalue λ_1 gives the major contribution to the above summation and the partition function can be approximated by

$$Z = A_{11} \sum_{\eta=1}^{\nu} B_{1\eta}\lambda_1 \tag{A9}$$

The probability of having bond $i-1$ in the ξ state and bond i in the η state for polymethylene is [1]

$$P_{i,\xi\eta} = \frac{1}{Z}\left(\mathbf{J}^*[\mathbf{U}^{(i-2)}\mathbf{U}'_{i,\xi\eta}\mathbf{U}^{(n-1-i)}]\mathbf{J}\right) \tag{A10}$$

where $\mathbf{U}'_{i,\xi\eta}$ is the matrix obtained from $\mathbf{U}$ by striking out all elements except the element $u_{\xi\eta}$. The dummy subscript i in $\mathbf{U}'_{i,\xi\eta}$ indicating the position of the bond in the chain will be neglected in the further analysis. Eq. (A10) can be rewritten in terms of matrices $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{\Lambda}$ as

$$P_{i,\xi\eta} = \frac{1}{Z}\left(\mathbf{J}^*[\mathbf{A}\mathbf{\Lambda}^{(i-2)}\mathbf{B}\mathbf{U}'_{\xi\eta}\mathbf{A}\mathbf{\Lambda}^{(n-1-i)}\mathbf{B}]\mathbf{J}\right) \tag{A11}$$

In the above product the term on the left $\mathbf{J}^*\mathbf{A}\mathbf{\Lambda}^{i-2}$ is similar to that calculated in Eq. (A6), while the last product on the right $\mathbf{BJ}$ was calculated earlier in Eq. (A7). The only difference between Eqs. (A11) and (A5) is (besides the factor 1/*Z*) the product of matrices $\mathbf{B}\mathbf{U}'_{\xi\eta}\mathbf{A}\mathbf{\Lambda}^{(n-1-i)}$ in the middle.

The product $\mathbf{B}\mathbf{U}'_{\xi\eta}$ is given by the matrix composed of the vector

$$\begin{bmatrix} B_{1\xi}u_{\xi\eta} \\ B_{2\xi}u_{\xi\eta} \\ B_{3\xi}u_{\xi\eta} \end{bmatrix}$$

in the η-th column and vectors

$$\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

in all other columns. This can be checked directly, for example

$$\begin{aligned} &\begin{bmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{bmatrix} \begin{bmatrix} 0 & u_{12} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \\ &= \begin{bmatrix} 0 & B_{11}u_{12} & 0 \\ 0 & B_{21}u_{12} & 0 \\ 0 & B_{31}u_{12} & 0 \end{bmatrix} \end{aligned} \tag{A12}$$

The product $\mathbf{A}\mathbf{\Lambda}^N$, where the abbreviation

$$N = n - 1 - i \tag{A13}$$

is introduced to simplify the notation becomes:

$$\begin{aligned} \mathbf{A}\mathbf{\Lambda}^N &= \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \begin{bmatrix} \lambda_1^N & 0 & 0 \\ 0 & \lambda_2^N & 0 \\ 0 & 0 & \lambda_3^N \end{bmatrix} \\ &= \begin{bmatrix} A_{11}\lambda_1^N & A_{12}\lambda_2^N & A_{13}\lambda_3^N \\ A_{21}\lambda_1^N & A_{22}\lambda_2^N & A_{23}\lambda_3^N \\ A_{31}\lambda_1^N & A_{32}\lambda_2^N & A_{33}\lambda_3^N \end{bmatrix} \end{aligned} \tag{A14}$$

If the largest eigenvalue is λ_1, then eigenvalues λ_2 and λ_3 can be set to zero in the limit $n \to \infty$ to simplify calculations.

With this simplification

$$\mathbf{A\Lambda}^N = \begin{bmatrix} A_{11}\lambda_1^N & 0 & 0 \\ A_{21}\lambda_1^N & 0 & 0 \\ A_{31}\lambda_1^N & 0 & 0 \end{bmatrix} \tag{A15}$$

and the product $\mathbf{BU}'_{\xi\eta}\mathbf{A\Lambda}^N$ becomes:

$$\mathbf{BU}'_{\xi\eta}\mathbf{A\Lambda}^N = \begin{bmatrix} B_{1\xi}u_{\xi\eta}A_{\eta1}\lambda_1^N & 0 & 0 \\ B_{2\xi}u_{\xi\eta}A_{\eta1}\lambda_1^N & 0 & 0 \\ B_{3\xi}u_{\xi\eta}A_{\eta1}\lambda_1^N & 0 & 0 \end{bmatrix} \tag{A16}$$

Additionally if eigenvalues λ_2 and λ_3 are set to zero we have

$$\mathbf{J}^*\mathbf{A\Lambda}^{(i-2)} = \begin{bmatrix} A_{11}\lambda_1^{i-2} & 0 & 0 \end{bmatrix} \tag{A17}$$

and the expression the probability $P_{\xi\eta}$ becomes

$$\begin{aligned} P_{\xi\eta} &= \frac{1}{Z}\left(\mathbf{J}^*[\mathbf{A\Lambda}^{(i-2)}\mathbf{BU}'_{\xi\eta}\mathbf{A\Lambda}^{n-1-i}\mathbf{B}]\mathbf{J}\right) \\ &= \frac{1}{Z}\left(\begin{bmatrix} A_{11}\lambda_1^{i-2} & 0 & 0 \end{bmatrix}\begin{bmatrix} B_{1\xi}u_{\xi\eta}A_{\eta1}\lambda_1^{n-1-i} & 0 & 0 \\ B_{2\xi}u_{\xi\eta}A_{\eta1}\lambda_1^{n-1-i} & 0 & 0 \\ B_{3\xi}u_{\xi\eta}A_{\eta1}\lambda_1^{n-1-i} & 0 & 0 \end{bmatrix}\begin{bmatrix} \sum_{\eta=1}^{3} B_{1\eta} \\ \sum_{\eta=1}^{3} B_{2\eta} \\ \sum_{\eta=1}^{3} B_{3\eta} \end{bmatrix}\right) \\ &= \frac{1}{Z}\left[A_{11}B_{1\xi}u_{\xi\eta}A_{\eta1}\lambda_1^{n-3}\sum_{\eta=1}^{3} B_{1\eta}\right] \end{aligned} \tag{A18}$$

Substituting Z by expression given in Eq. (A5) leads finally to [1,9]:

$$P_{\xi\eta} = B_{1\xi}u_{\xi\eta}A_{\eta1}\lambda_1^{-1} \tag{A19}$$

Appendix B

The solution of the eigenvalue problem for stereo-regular vinyl chains

The diagonalization of the matrix $\mathbf{U}^{(2)}$ leads to

$$\mathbf{BU}^{(2)}\mathbf{A} = \mathbf{\Lambda} \tag{B1}$$

where $\mathbf{B} = \mathbf{A}^{-1}$ and $\mathbf{\Lambda}$ is the matrix containing eigenvalues on the diagonal and zeros off-diagonal. The probabilities $P_{a_{i,\xi\eta}}$ and $P_{b_{i,\xi\eta}}$ are defined as

$$P_{a,\xi\eta} = \frac{1}{Z}\left(\mathbf{J}^*\mathbf{A\Lambda}^{(i-1)}\mathbf{BU}'_{a,\xi\eta}\mathbf{U}_b\mathbf{A\Lambda}^{(x-1-i)}\mathbf{B}\}\mathbf{J}\right) \tag{B2}$$

and

$$P_{b,\xi\eta} = \frac{1}{Z}\left(\{\mathbf{J}^*\mathbf{A\Lambda}^{(i-1)}\mathbf{BU}_a\mathbf{U}'_{b,\xi\eta}\mathbf{A\Lambda}^{(x-1-i)}\mathbf{B}\}\mathbf{J}\right) \tag{B3}$$

The part of the product $\mathbf{J}^*\mathbf{A\Lambda}^{(i-1)}$ is similar to that derived for the polymethylene chain (in Appendix A), if we neglect and set to zero eigenvalues λ_2 and λ_3 which are smaller than λ_1.

$$\mathbf{J}^*\mathbf{A\Lambda}^{(i-1)} = \begin{bmatrix} A_{11}\lambda_1^{(i-1)} & 0 & 0 \end{bmatrix} \tag{B4}$$

Similarly as in Appendix A the product $\mathbf{BJ}$ is given by Eq. (A7). We additionally have to compute the product $\mathbf{BU}'_{a,\xi\eta}\mathbf{U}_{b,\xi\eta}\mathbf{A\Lambda}^{(x-1-i)}$ (and $\mathbf{BU}'_{a,\xi\eta}\mathbf{U}'_{b,\xi\eta}\mathbf{A\Lambda}^{(x-1-i)}$). Neglecting eigenvalues λ_2 and λ_3, smaller than λ_1 we have

$$\mathbf{A\Lambda}^{(x-1-i)} = \begin{bmatrix} A_{11}\lambda_1^{(x-1-i)} & 0 & 0 \\ A_{21}\lambda_1^{(x-1-i)} & 0 & 0 \\ A_{31}\lambda_1^{(x-1-i)} & 0 & 0 \end{bmatrix} \tag{B5}$$

The product $\mathbf{BU}'_{a,\xi\eta}$, where $\mathbf{BU}'_{a,\xi\eta}$ is the matrix with all elements of U_a set to zero, except the $u_{a,\xi\eta}$ element is similar to that derived for the polymethylene chain (Appendix A) and it is a matrix composed of the vector

$$\begin{bmatrix} B_{1\xi}u_{a,\xi\eta} \\ B_{2\xi}u_{a,\xi\eta} \\ B_{3\xi}u_{a,\xi\eta} \end{bmatrix}$$

in the η-th column and vectors

$$\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

in two other columns. The only difference between the case of the polymethylene and stereo-regular polypropylene is an additional factor $\mathbf{U}_b$ on the right in the product of matrices.

We also have to calculate the product $\mathbf{BU}'_{a,\xi\eta}\mathbf{U}_{b,\xi\eta}$. It can be shown that

$$\mathbf{BU}'_{a,\xi\eta}\mathbf{U}_{b,\xi\eta} = \begin{bmatrix} B_{1\xi}u_{a,\xi\eta}u_{b,\eta1} & B_{1\xi}u_{a,\xi\eta}u_{b,\eta2} & B_{1\xi}u_{a,\xi\eta}u_{b,\eta3} \\ B_{2\xi}u_{a,\xi\eta}u_{b,\eta1} & B_{2\xi}u_{a,\xi\eta}u_{b,\eta2} & B_{2\xi}u_{a,\xi\eta}u_{b,\eta3} \\ B_{3\xi}u_{a,\xi\eta}u_{b,\eta1} & B_{3\xi}u_{a,\xi\eta}u_{b,\eta2} & B_{3\xi}u_{a,\xi\eta}u_{b,\eta3} \end{bmatrix} \tag{B6}$$

We can use this result to calculate

$$\mathbf{J}^*\mathbf{A}\boldsymbol{\Lambda}^{(i-1)}\mathbf{B}\mathbf{U}'_{a,\xi\eta}\mathbf{U}_{b,\xi\eta}=\begin{bmatrix}A_{11}\lambda_1^{(i-1)} & 0 & 0\end{bmatrix}\begin{bmatrix}B_{1\xi}u_{a,\xi\eta}u_{b,\eta 1} & B_{1\xi}u_{a,\xi\eta}u_{b,\eta 2} & B_{1\xi}u_{a,\xi\eta}u_{b,\eta 3}\\ B_{2\xi}u_{a,\xi\eta}u_{b,\eta 1} & B_{2\xi}u_{a,\xi\eta}u_{b,\eta 2} & B_{2\xi}u_{a,\xi\eta}u_{b,\eta 3}\\ B_{3\xi}u_{a,\xi\eta}u_{b,\eta 1} & B_{3\xi}u_{a,\xi\eta}u_{b,\eta 2} & B_{3\xi}u_{a,\xi\eta}u_{b,\eta 3}\end{bmatrix}$$

$$=\begin{bmatrix}A_{11}\lambda_1^{(i-1)}B_{1\xi}u_{a,\xi\eta}u_{b,\eta 1} & A_{11}\lambda_1^{(i-1)}B_{1\xi}u_{a,\xi\eta}u_{b,\eta 2} & A_{11}\lambda_1^{(i-1)}B_{1\xi}u_{a,\xi\eta}u_{b,\eta 3}\end{bmatrix}$$

$$=A_{11}\lambda_1^{(i-1)}B_{1\xi}u_{a,\xi\eta}\begin{bmatrix}u_{b,\eta 1} & u_{b,\eta 2} & u_{b,\eta 3}\end{bmatrix} \tag{B7}$$

The expression for the probability $P_{a_{i,\xi\eta}}$ is now:

$$P_{a,\xi\eta}=\frac{1}{Z}\left\{A_{11}\lambda_1^{(i-1)}B_{1\xi}u_{a,\xi\eta}\begin{bmatrix}u_{b,\eta 1} & u_{b,\eta 2} & u_{b,\eta 3}\end{bmatrix}\begin{bmatrix}A_{11}\lambda_1^{(x-1-i)} & 0 & 0\\ A_{21}\lambda_1^{(x-1-i)} & 0 & 0\\ A_{31}\lambda_1^{(x-1-i)} & 0 & 0\end{bmatrix}\begin{bmatrix}\sum_{\eta=1}^{3}B_{1\eta}\\ \sum_{\eta=1}^{3}B_{2\eta}\\ \sum_{\eta=1}^{3}B_{3\eta}\end{bmatrix}\right\}$$

$$=\frac{1}{Z}\left\{A_{11}\lambda_1^{(x-2)}B_{1\xi}u_{a,\xi\eta}(A_{11}u_{b,\eta 1}+A_{21}u_{b,\eta 2}+A_{31}u_{b,\eta 3})\sum_{\eta=1}^{3}B_{1\eta}\right\} \tag{B8}$$

Because the partition function Z is equal to:

$$Z=A_{11}\lambda_1^{(x-1)}\sum_{\eta=1}^{3}B_{1\eta} \tag{B9}$$

the final expression for the probability $P_{a_{i,\xi\eta}}$ is

$$P_{a,\xi\eta}=\frac{1}{\lambda_1}\left(B_{1\xi}u_{a,\xi\eta}[A_{11}u_{b,\eta 1}+A_{21}u_{b,\eta 2}+A_{31}u_{b,\eta 3}]\right) \tag{B10}$$

The equation for $P_{b,\xi\eta}$ can be derived in a similar way. We start from the definition:

$$P_{b_{i,\xi\eta}}=\frac{1}{Z}\left(\{\mathbf{J}^*[\mathbf{U}^{(2)}]^{(i-1)}\mathbf{U}_{a_i}\mathbf{U}'_{b_{i,\xi\eta}}[\mathbf{U}^{(2)}]^{(x-1-i)}\}\mathbf{J}\right) \tag{B11}$$

when written in terms of matrices **A** and **B**, it becomes:

$$P_{b,\xi\eta}=\frac{1}{Z}\left(\{\mathbf{J}^*\mathbf{A}\boldsymbol{\Lambda}^{(i-1)}\mathbf{B}\mathbf{U}_a\mathbf{U}'_{b,\xi\eta}\mathbf{A}\boldsymbol{\Lambda}^{(x-1-i)}\mathbf{B}\}\mathbf{J}\right) \tag{B12}$$

Similarly as before (Eq. (B4))

$$\mathbf{J}^*\mathbf{A}\boldsymbol{\Lambda}^{(i-1)}=[A_{11}\lambda_1^{(i-1)}\quad 0\quad 0]$$

if the eigenvalues λ_2 and λ_3, smaller than λ_1 are neglected. Now we introduce a new matrix **C** defined as a product

$$\mathbf{C}=\mathbf{B}\mathbf{U}_a \tag{B13}$$

Instead of the product $\mathbf{B}\mathbf{U}'_{a,\xi\eta}$ (which we calculated in the derivation of $P_{a,\xi\eta}$) we have a similar product $\mathbf{C}\mathbf{U}'_{b,\xi\eta}$. Similarly as before this matrix product gives a matrix which has in the η-th column the vector

$$\begin{bmatrix}C_{1\xi}u_{b,\xi\eta}\\ C_{2\xi}u_{b,\xi\eta}\\ C_{3\xi}u_{b,\xi\eta}\end{bmatrix}$$

and vectors

$$\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

in two other columns.

By multiplying this matrix $\mathbf{CU}'_{b,\xi\eta}$ by $\mathbf{A\Lambda}^{(x-i-1)}$ and neglecting eigenvalues λ_2 and λ_3, smaller than λ_1 we obtain

$$\mathbf{CU}'_{b,\xi\eta}\mathbf{A\Lambda}^{(x-1-i)} = \begin{bmatrix} C_{1\xi}u_{b,\xi\eta}A_{\eta 1}\lambda_1^{(x-1-i)} & 0 & 0 \\ C_{2\xi}u_{b,\xi\eta}A_{\eta 1}\lambda_1^{(x-1-i)} & 0 & 0 \\ C_{3\xi}u_{b,\xi\eta}A_{\eta 1}\lambda_1^{(x-1-i)} & 0 & 0 \end{bmatrix} \tag{B14}$$

The formula for $P_{b,\xi\eta}$ then becomes:

$$P_{a,\xi\eta} = \frac{1}{Z}\left\{ \begin{bmatrix} A_{11}\lambda_1^{(i-1)} & 0 & 0 \end{bmatrix} \begin{bmatrix} C_{1\xi}u_{b,\xi\eta}A_{\eta 1}\lambda_1 & 0 & 0 \\ C_{2\xi}u_{b,\xi\eta}A_{\eta 1}\lambda_1 & 0 & 0 \\ C_{3\xi}u_{b,\xi\eta}A_{\eta 1}\lambda_1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \sum_{\eta=1}^{3} B_{1\eta} \\ \sum_{\eta=1}^{3} B_{2\eta} \\ \sum_{\eta=1}^{3} B_{3\eta} \end{bmatrix} \right\}$$
$$= \frac{1}{Z}\left\{ A_{11}\lambda_1^{(x-2)}C_{1\xi}u_{b,\xi\eta}A_{\eta 1}\left[\sum_{\eta=1}^{3} B_{1\eta}\right] \right\} \tag{B15}$$

Since Z is given by Eq. (B9) the final equation for $P_{b,\xi\eta}$ becomes

$$P_{b,\xi\eta} = \frac{1}{\lambda_1}(C_{1\xi}u_{b,\xi\eta}A_{\eta 1}) \tag{B16}$$

By using the definition of $\mathbf{C}=\mathbf{BU}_a$, i.e.

$$C_{1\xi} = B_{11}u_{a,1\xi} + B_{12}u_{a,2\xi} + B_{13}u_{a,3\xi} \tag{B17}$$

we finally obtain

$$P_{b,\xi\eta} = \frac{1}{\lambda_1}(u_{b,\xi\eta}A_{\eta 1}[B_{11}u_{a,1\xi} + B_{12}u_{a,2\xi} + B_{13}u_{a,3\xi}]) \tag{B18}$$

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