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On the Structural Non-Identifiability of Flexible Branched Polymers

Koh-hei Nitta

Division of Natural System, Institute of Science and Engineering, Kanazawa University, Kanazawa 920-1192, Japan; E-Mail: nitta@t.kanazawa-u.ac.jp

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Abstract: The dynamics and statics of flexible polymer chains are based on their conformational entropy, resulting in the properties of isolated polymer chains with any branching potentially being characterized by Gaussian chain models. According to the graph-theoretical approach, the dynamics and statics of Gaussian chains can be expressed as a set of eigenvalues of their Laplacian matrix. As such, the existence of Laplacian cospectral trees allows the structural nonidentifiability of any branched flexible polymer.

Keywords: Gaussian chain; branched polymer; graph theory; tree; cospectral graph; Laplacian matrix; Rouse matrix; Zimm matrix

1. Introduction

A polymer is a set of huge number of repeating units or atoms which are connected by chemical bonds. Modern polymerization techniques can produce various types of highly branched polymers with specific properties which cannot be achieved using linear polymers [1,2]. However, the discrimination of isomeric structures in branched polymers composed of the same repeating units becomes more difficult as the chain branching complexity increases.

The developments of experimental techniques and theoretical treatments for the identification of the structural architectures have become desirable as various polymerization techniques to produce the more complicated branched polymers are developed. While the specification of a linear polymer requires only one parameter, molecular weight or polymerization degree, additional key parameters based on the conformational properties are necessary for the specification of branched polymers [3]. Currently, there are two types of experimental techniques for structural identification which are based on the static and dynamic conformational properties of isolated molecules in a dilute solution. One is

the static methods by means of light scattering and viscometry for the non-draining polymer molecules, which allow the determination of the space size relating to the radius of gyration of polymers. The smaller expansion in the space of isolated branched molecules as compared with isolated linear molecules of the same molecular weight is the basis of such experimental methods. However, it is almost impossible for the static methods to analyze the branching architecture of polymers such as the branch length, the number of branches and the positions of the branching, even in the free-draining state. The other approach involves dynamic methods such as optical resonance frequency spectrometry and mechanical relaxation time. The former is based on the resonance oscillation modes of the repeat units in the short-time domain, whereas the later method is based on the molecular mobility of chain segments in the long-time domain. The data of dynamics include detailed information on branching architecture and the nature of the branching.

An important achievement of polymer physics is that any flexible polymer is expressed by a sequence of Hookean springs connecting point-like beads, which is termed as the Gaussian chain, in the ideal state of isolated polymers. The present work proves the existence of many pairs of Gaussian chains with different branched structures having the same relaxation and resonance spectra as well as the same radius of gyration. This would imply that the skeletal structure of any branched molecule cannot be uniquely determined on the basis of these experimental principles.

2. Specific Branched Chains

2.1. Ideal Chain Model

This article deals with the structural identification of tree-like chain molecules composed of the same repeat units without loops and rings like typical branched flexible homo-polymers. The dynamics and statics of isolated polymer molecules are usually examined in the equilibrium steady-state in order to identify their structural architecture. In the case of typical flexible vinyl polymers, a huge number of repeat units are connected by chemical single bonds. Although chemical bonds are fairly rigid with respect to stretching and bending of the valence angles between adjacent bonds, a single-polymer molecule has many internal degrees of rotational freedom about each actual bond in the molecule, resulting in the molecule adopting many different conformations, thereby necessitating the use of statistical mechanics. In the case of polyethylene, three types of micro-conformations, *i.e.*, one *trans* and two *gauche* states, occur every C–C bond.

As described above, a polymer chain can take many different conformations in a dilute solution. This corresponds to the micro-Brownian motion and the chains are rapidly converted into other conformations. Each conformation exists for only a very short time so that the resulting conformations are temporal averages over all actual bonds. This results in the polymer chain being expressed by random-flight chains composed of statistical bonds (effective bonds) joining beads of unit mass where an appropriate number of actual bonds are replaced by a single effective bond. According to the central limit theorem in statistical physics [4], the equilibrium distribution function of statistical bonds in random-flight chains is identical to the Gaussian distribution function. The distribution function $W(\mathbf{b}_i)$ of the effective vector \mathbf{b}_i between adjacent beads can be defined either as the time-averaged incidence

of \mathbf{b}_i within the specified range for a given molecule or as the average incidence for an ensemble of many identical units subject to identical conditions:

$$W(\mathbf{b}_{i}) = \left(\frac{3}{2\pi < \mathbf{b}^{2} >}\right)^{3/2} \exp\left(-\frac{3\mathbf{b}_{i}\mathbf{b}_{i}^{\mathrm{T}}}{2 < \mathbf{b}^{2} >}\right)$$
(1)

where $\langle \mathbf{b}^2 \rangle$ is the time-averaged square bond length, and the superscript T denotes the transpose of the vector and the matrix.

The probability distribution of the set of position vectors is given by the product of function $W(\mathbf{b}_i)$. The change in entropy of the bond distribution is derived from the relation $S = \sum k_B \ln W(\mathbf{b}_i)$ where k_B is the Boltzmann constant. Since all conformations may have the same internal energy in the isothermal state, the change in the free energy is $\Delta F = -T\Delta S$ where *T* is the absolute temperature so that we have $\Delta F = (\kappa/2)\Sigma \mathbf{b}^T \mathbf{b}$ where $\kappa = 3k_BT/\langle \mathbf{b}^2 \rangle$ and \mathbf{b} be a $3 \times (N-1)$ matrix whose rows contain the dimensional component of the *N*-1 bond vectors between adjacent beads. Consequently, each effective bond can be considered to be a Hookean oscillator with a spring constant of $\kappa = 3k_BT/\langle \mathbf{b}^2 \rangle$. It should be noted that the spring constant is proportional to the temperature of the system. This means that the Hookean spring is associated with the dynamic potential based on the changes in conformational entropy.

Let **r** be a 3 × *N* matrix whose rows contain the dimensional component of the *N* position vectors of beads. The equilibrium state of this chain is then described by a distribution function proportional to $\exp(-V/k_BT)$, where *V* corresponds to the potential energy [9], if we choose:

$$V = \frac{1}{2}\kappa \operatorname{Tr}\left[\mathbf{b} \cdot \mathbf{b}^{\mathrm{T}}\right] = \frac{1}{2}\kappa \operatorname{Tr}\left[\mathbf{r} \cdot \mathbf{Z} \cdot \mathbf{r}^{\mathrm{T}}\right]$$
(2)

where Tr denotes the trace of matrix, and Z is called the Zimm matrix in polymer dynamics [5]. The *ij*th element of matrix Z is -1 if the *i*th and *j*th beads are directly connected; otherwise it is zero, and the diagonal elements are equal to the sum of its non-diagonal elements in a given row taken with the negative sign. Z is the $N \times N$ connectivity matrix which is known as the Laplacian matrix L in graph theory.

2.2. Dynamics and Statistics of Gaussian Chains

If and only if the square root of $\langle \mathbf{b}^2 \rangle$ is identical with the effective bond length *b* of the randomflight chain model, the random-flight statistics of a flexible polymer can be described by a Gaussian distribution function where the effective bonds can be represented as entropy springs called the segment [6]. Rouse [7] and Bueche [8] demonstrated that the dynamics of a dilute solution of linear polymers can be characterized by considering a Gaussian chain suspended in a flowing viscous liquid. Subsequently, the extension of this model to any branched molecule was made by Ham [9]. To consider linear dynamics in the ideal state for such bead-spring systems, we assume that each bead experiences an external force φ , then the equation of motion becomes:

$$\mu \ddot{\mathbf{r}} + \zeta \dot{\mathbf{r}} = -\kappa \mathbf{Z} \cdot \mathbf{r} + \boldsymbol{\varphi} \tag{3}$$

This can be rewritten as follows using the bond vector b in place of the position vector r:

$$\mu \mathbf{b} + \zeta \mathbf{b} = -\kappa \, \mathbf{R} \cdot \mathbf{b} + \mathbf{\phi}' \tag{4}$$

where μ is the internal mass of each bead, ζ is the friction constant of each bead and the matrix **R** is $(N-1) \times (N-1)$ connectivity matrix which is called the Rouse matrix [7]. Denoting by $\Phi(\mathbf{Z}; \lambda)$ the characteristic polynomial $\text{Det}|\mathbf{Z} - \lambda \mathbf{I}|$ of matrix **Z**, where **I** is the identity matrix of the same order as **Z**, we can find the relation $\Phi(\mathbf{Z}; \lambda) = \lambda \Phi(\mathbf{R}; \lambda)$ [10]. It should be noted here that these equations are applicable only to the unentangled polymers.

The eigenvalues of Z contain one zero eigenvalue which represents the mode of chain transformation [11]. A set of resonant eigen-frequencies of such system is obtained as follows by introducing the normalized coordinate transformation of Equation 3 or 4:

$$\omega_p = \omega_0 \lambda_p^{-1/2}$$
 $p=1, 2, ..., N-1$ (5)

where λ_p is a set of the eigenvalues of **R** or non-zero eigenvalues of **Z** and ω_0 is the primary frequency given by $\omega_0 = \sqrt{\kappa/\mu}$. Each normal coordinate represents a mode of motion of the polymer chain. In addition, the relaxation time spectrum is written as:

$$\tau_p = \tau_0 / \lambda_p$$
 $p=1, 2, ..., N-1$ (6)

where $\tau_0 = \zeta/\kappa$. The relaxation times can be obtained by mechanical measurements in lower-frequency modes in which the inertial term in Equation 3 or 4 is neglected. In addition, the steady-state viscosity η in a dilute solution can be obtained from the total sum of relaxation times and is given by [12]:

$$\eta = \eta_s + c \frac{b^2 \zeta}{6N} \sum_{p=1}^{N-1} \frac{1}{\lambda_p}$$
(7)

where η_s is the viscosity of pure solvent and c is the concentration of beads per unit volume.

Forsman [13] showed that the square radius of gyration of any random-flight (or Gaussian) chain can be given by $S^2 = N^{-1}\mathbf{b}^{\mathrm{T}}\mathbf{R}^{-1}\mathbf{b}$. Consequently, the mean square of the radius of gyration can be expressed as:

$$< S^{2} >= \frac{b^{2}}{N} \operatorname{Tr}\left[\mathbf{R}^{-1}\right] = \frac{b^{2}}{N} \sum_{p=1}^{N-1} \frac{1}{\lambda_{p}}$$
(8)

It was found that not only the relaxation time and resonant frequency spectra but also the radius of gyration and steady-state viscosity of a single Gaussian chain with and without branching are entirely determined by a set of the eigenvalues of its Rouse matrix or the non-zero eigenvalues of its Zimm matrix. This means that the problem of identification of polymer chains is reduced to the problem of eigenvalues of the Rouse or Zimm matrix.

2.3. Graph-theoretical Approach

The mathematical representation of the graph theory is helpful in generalizing the statistics and dynamics of ideal chains to include in any type of branching [3,13-18]. In graph theory, points (atoms or beads) are generally referred to as *vertices* and lines (bonds or segments) are referred to as *edges*, and the functionality of the beads is called the "*vertex degree*". Here we may consider only tree graphs in which every vertex has at least one and no loops or multiple edges are involved. The random-flight chain can be regarded as a molecular graph composed of N - 1 statistical bonds (edges) of a length *b* joining *N* beads (vertices) of unit mass. Figure 1 shows a Gaussian chain and its corresponding molecular graph.

Figure 1. (a) An example of a branched Gaussian chain. (b) The corresponding molecular graph.



In graph theory, the algebraic expressions using several matrices reflecting the connectivity in a graph G [19] are important devices for identifying the topological structure of graphs, and the algebraic properties of the characteristic polynomials have been extensively examined. For any graph G, the adjacency matrix **A** is the most fundamental matrix for the representation of graphs [19] and it is defined as a square matrix in which *ij*th element of matrix **A** is 1 if the *i*th and *j*th beads are directly connected; otherwise it is zero.

The order of **A** is identical with the total number of vertices in *G*. The list of eigenvalues of a matrix calculated from the characteristic polynomial is called the spectrum of the matrix which includes a significant amount of quantitative information on the topological nature of the graphs. A secular determinant giving the Hückel molecular orbitals for the π electrons of an unsaturated hydrocarbon is reduced to the same form as the determinant of **A** of its corresponding graph [20–22]. In other words, the problem of the Hückel orbital energies can be completely reduced to the eigenvalue problem of **A**. Thus, the spectrum of the matrix **A** can be reduced to the energy levels of molecular orbitals.

A pair of graphs is said to be cospectral with respect to \mathbf{A} if they are non-isomorphic and their spectra are identical. A graph is said to be determined by the spectrum if there is no other non-

isomorphic graph with the same spectrum. It has been identified that there are many pairs of nonisomorphic graphs with the same eigenvalue spectrum of **A**. Theses pairs are considered to have the same energy levels under the Hückel approximation [23,24] but does not show always the identical photoelectron spectrum [25].

The matrix L defined as L = V - A, where V is the diagonal matrix with the degree of vertex, is called the Laplacian matrix which has also widely been studied for topological connectivities of various graphs [26]. The Laplace differential operator for a vibrating membrane can be transformed to the matrix L by discretizing the Laplace equation [27]. Immediately, we become aware that the Laplacian matrix is formally identical with the Zimm matrix; that is $\mathbf{L} = \mathbf{Z}$. In addition, the signless Laplacian matrix $L^+ = V + A$ has the entries which are the absolute values of the entries of L, and its polynomial equation is the same as that of **L**. Consequently, the non-zero eigenvalues of \mathbf{L}^+ or **L** are identical with those of the Rouse matrix **R**. Kirchhoff [28] introduced a connectivity matrix **K** for the calculation of currents in an electrical network and he found the relation $\mathbf{K} = \mathbf{A}_{L} + 2\mathbf{I}$ for tree-graph where A_L is the adjacency matrix for the line graph of the tree. The line graph of G is formed by replacing the edges of G by vertices in a manner such that the vertices in the line graph are connected whenever the corresponding edges in G are adjacent. It is interesting to note that the elements of the matrix **K** are the absolute values of the elements of **R** and we have $\Phi(\mathbf{K};\lambda) = \Phi(\mathbf{R};\lambda)$ [16]. Consequently, we have the relation $\Phi(\mathbf{R}; \lambda) = \Phi(\mathbf{A}_L; \lambda - 2)$ using the relation $\mathbf{K} = \mathbf{A}_L + 2\mathbf{I}$. The eigenvalues of K of a tree graph or R of a polymer chain can be obtained by adding 2 to the eigenvalues of A_L of its line graph.

The relations $\Phi(\mathbf{L};\lambda) = \lambda \Phi(\mathbf{R};\lambda)$ and $\Phi(\mathbf{R};\lambda) = \Phi(\mathbf{A}_L;\lambda-2)$ have a very important meaning for polymer physics. The multiset of eigenvalues of \mathbf{L} or \mathbf{A}_L is called the spectrum of \mathbf{L} or \mathbf{A}_L . McKay [29] found a mathematical technique for constructing a large number of pairs of Laplacian cospectral tree graphs or cospectral trees with cospectral line graphs. The probability that any tree graph is uniquely determined by its Laplacian spectrum goes to zero as the number of vertices approaches infinity [30]. This means that almost all tree graphs cannot be uniquely determined by their Laplacian spectrum or line graph spectrum.

Theorem 1. There are many tree-like Gaussian chains with different branched structures showing the same resonance frequency or relaxation time spectrum.

Proof. The resonance frequency and relaxation time spectra as well as the radius of gyration of treelike Gaussian chains were determined by a set of eigenvalues of the Rouse matrix or non-zero eigenvalues of the Zimm matrix. Since the Zimm matrix is identical to the Laplacian matrix, the resonance frequency and relaxation time spectra of the tree-like Gaussian chains can be determined by the Laplacian spectrum. There exist many Laplacian cospectral tree-graphs according to Mckay's theorem [29]. Consequently, there are many different tree-like Gaussian chains showing the same resonance frequency and relaxation time spectrum.

Theorem 1 has an important physical meaning. The proof shows that there are probably many pairs of different branched polymer chains showing the same relaxation time or resonance frequency spectra

as well as the same radius of gyration. In other words, we may say that the determination of whether two flexible polymer structures are, or are not, identical is impossible by both dynamics and statics methods in the case that the polymer chains are represented by the intramolecular entropic forces and segmental friction.

2.4. Example of the Laplacian Cospectral Trees

Here, we generalize McKay's approach for constructing a pair of Laplacian cospectral trees. Let T or U be a tree divided in two subgraphs T_1 and T_2 or U_1 and U_2 by a root *t* or *u* ($t \neq u$) with two degrees as shown in Figure 2. Here T = U and these subgraphs are different from each other. The coalescence S T of S and T is the tree formed by identifying the roots of S and T. Subsequently, S T \neq S U. The forest T_1 , T_2 formed by removing the root and its edges from T is denoted T* = T_1+T_2 and the incomplete tree formed by removing only the root of T is denoted T–*t* where the degree of vertices connected to the root is unchanged by removing the root. The V(T–*t*) is defined to be the diagonal matrix of the degree of the vertex, except the root in T (not T*) as defined by McKay [29].

Figure 2. Images of a tree graph T composed of subgraphs T_1 and T_2 connected by root *t* and its T* and T–t graph.



Let S be any rooted tree with two or more vertices. The necessary and sufficient condition that S T and S U are cospectral with respect to Laplacian matrix: $\Phi(\mathbf{L}(S T)) = \Phi(\mathbf{L}(S U))$ is $\Phi(\mathbf{A}(T^*) + \mathbf{V}(T - t)) = \Phi(\mathbf{A}(U^*) + \mathbf{V}(U - u))$. The mathematical details are skipped here. McKay [29] found an example for Laplacian cospectral graphs as shown in Figure 3.

Figure 3. (a) T_1 graph and T_2 graph; (b) U_1 graph and U_2 graph. Images of the coalescence process of S and T.



3. Final Remarks

Any real polymer system shows a distribution in the chain length, number and position of the branches that is dependent on the polymerization and/or fractionation; actual polymer systems may be a mixture of such isomers. The structural ambiguity due to such distributions and/or the deviation from the ideal state causes broad spectrum peaks and makes it difficult to identify complicated branched structures. Therefore, it has been thought that the limitation of the identification for highly branched structures may be overcome not only by resolution enhancement of experimental methods but also by the experimental innovation on isolation of single molecules without affecting thermodynamic interactions.

Let us here consider the analytical procedure of the structural characterization of these actual polymers. At first an extensive molecular weight fractionation is performed using some chromatographic process and the dynamics and statics of the dilute solution of each fraction are investigated in the equilibrium steady-state for reliability and validity of experimental data and tests. This means that such an analytical procedure requires actual polymers to be isolated in the equilibrium unperturbed state. Assuming that the molecular weight fractionation of the above polymer systems successfully reaches completion and each fraction attains the unperturbed ideal state, the spectrum peaks become sharp enough for discrimination of complicated structures. However, the present paper has clearly shown that the branching structure of isolated polymer chains in the ideal state cannot be uniquely determined by the spectrum peaks. This is due to the fact that every flexible polymer in the ideal unperturbed state can be coarse-grained to a Gaussian chain since its conformational statistics and dynamics are based on entropy where its free energy is minimized only by maximizing the conformational entropy. The present work showed the existence of many pairs of Gaussian chains with different branched structure having the same Rouse spectra, suggesting that the molecular structure of unknown branched flexible polymers cannot be always determined by both dynamics and statics methods.





In such circumstances, the following problem is raised: *Which trees are determined by their spectrum*? [31] This mathematical question will become a key problem for structural identification of branched flexible polymers. Omidi *et al.* [32] proved that star-like tree graphs are uniquely determined by the Laplacian spectrum. This suggests that the star-shaped polymers have intrinsic dynamic spectra

and can be identified on the basis of the present experimental principles. Godsil *et al.* [33] found that the order of the smallest pair of trees with a cospectral line graph is 11. Figure 4 shows the corresponding Gaussian chain pairs with the same eigenvalues of their Rouse matrices. This means that tree graphs or Gaussian chains with $N \le 10$ can be uniquely determined by Laplacian or Zimm spectrum and that branched polymers with lower molecular weights and/or higher levels of coarse-graining may possibly be identified.

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