Exact evaluation of the mean square radius of gyration for Gaussian topological polymer chains

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Abstract:

Various polymers with nontrivial molecular structures expressed by graphs have recently been synthesized in experiments. We call them topological polymers for the graphs. We consider a set of Gaussian chains describing an ideal topological polymer or ideal polymer network for a given graph and call it topologically constrained random walks (TCRW) of the graph. In this chapter we show an exact evaluation of the mean square radius of gyration for the TCRW of complete graphs. We first review fundamental aspects of the novel method for constructing TCRW through the boundary operator of homology theory, as given in Ref. [5]. Then we rigorously derive the average size of the TCRW for complete graphs. By making use of the asymptotic formula [6] we exactly derive the mean square radius of gyration for the subdivided topological polymers consisting of Gaussian chains or the subdivided TCRW for a given graph in the large subdivision degree limit. That is, in the limit of sending the number of subdivided segments in each branch to infinity. Throughout the chapter we emphasize the key point of the TCRW method that the probability distribution function of the edge displacements or bond vectors of the TCRW for a connected graph is directly derived from the normal distribution with unit variance. For instance, thanks to it we can rapidly generate conformations of the Gaussian network of a given graph where external forces are applied at the surfaces so that it has a nonzero finite volume in equilibrium.

1. Introduction

Polymer architecture is an important feature in polymeric materials. It represents the chemical connectivity among the monomers or sub-chains, and characterizes most of the physical quantities of the polymers such as the mean square radius of gyration and the scattering functions. There are various types of polymer architecture: linear, cyclic (ring), star-branched, comb-like, randomly branched, and multi-cyclic polymers. Moreover, polymer networks have complex polymer architectures. Recently, polymers of nontrivial architectures have been designed and synthesized in chemical experiments [1,2,3]. We call them topological polymers. In a given polymer network such as rubbers and gels, there exist a huge number of cross-links, each of which is connected to subchains with a fixed functionality, and all the cross-links and subchains lead to a large number of topological constraints corresponding to many loops in the polymer network. It is therefore nontrivial to calculate the statistical average of a physical quantity over all conformations of the polymer satisfying the topological constraints. Thus, it is often suggested that a straightforward theoretical or numerical study on topological polymers or polymer networks should be quite intricate and perhaps nontrivial. For polymer networks, almost all theoretical studies on the macroscopic behavior so far are performed under phenomenological assumptions such as affine deformation [4].

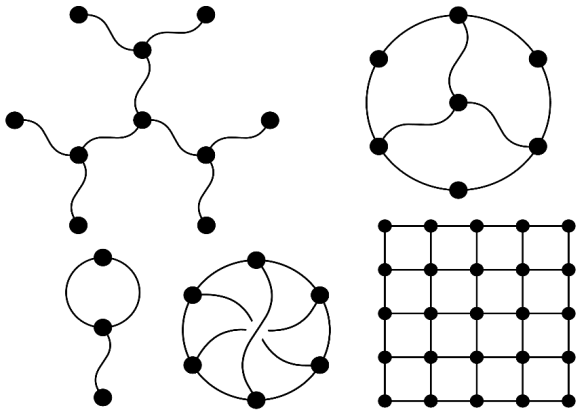


Fig. 1: Various topological architectures: Branched tree, alpha graph, in the upper level from the left; tadpole graph, $K_{3,3}$ bipartite graph, and square lattice network, in the lower level from the left.

For an illustration, let us consider a cyclic polymer chain, which forms a cycle or loop (Fig. 2). It has such a constraint that the sum of all bond vectors between pairs of adjacent monomers is equal to zero. Thus, in order to construct conformations of the cyclic polymer, as a direct method we may generate randomly many sequences of bond vectors and select only conformations in which the sum of the bond vectors is given by zero. Of course, the probability of having such a set of bond vectors satisfy the constraint is very small and hence the direct

method is not practically useful. Here we assume that a sequence of the position vectors of vertices or that of the bond vectors in a cyclic polymer determines a polymer conformation. There can be many topological constraints in topological polymers with complex architectures, since their number is equal to that of independent loops. We call the constraints on the bond vectors associated with loops *topological constraints*. As the conformation of a linear polymer chain is given by a random walk, that of a topological polymer or polymer network is expressed by a complex of several random walks satisfying all the topological constraints. We call such a set of the positions of vertices connected by the bond vectors *topologically constrained random walks* (TCRW) or *Gaussian random embeddings of multigraphs* [5]. Hereafter, we call the bond vectors the edge displacements, in the manuscript.

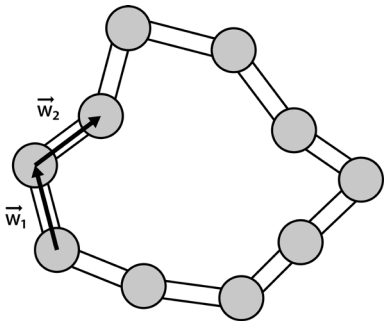


Fig 2: Cyclic polymer imposes on its bond vectors the loop constraint:

$\vec{w}_1 + \vec{w}_2 + \cdots + \vec{w}_{10} = 0.$

It should be nontrivial to generate non-biased random walks satisfying all the topological constraints, i.e., TCRW: Even for a cyclic polymer, we hardly obtain it if we simply generate a random walk step by step, as argued in the above. However, in the present manuscript we demonstrate that by the method of Gaussian random embeddings of multigraphs [5] we can systematically evaluate the statistical average of any physical quantity for a given topological polymer or polymer network where we take into account all the topological constraints. All the topological constraints are taken into account in terms of the boundary operator in graph theory or homology theory. Furthermore, the method is practically useful even if the polymer architecture is quite complex [5, 6]. As an illustration, we evaluate the mean square radius of gyration for topological polymers of complete graphs. In this manuscript we first review the method presented in Ref. [5] and then show the applied result.

One of the most important properties in the method of TCRW (or Gaussian random embeddings of multigraphs) is that for any given topological polymer or polymer network consisting of Gaussian chains the probability distribution function of the edge displacements is directly constructed from the normal distributions with unit variance [5]. By taking advantage of this key property, we can easily generate non-biased random walks satisfying all the topological constraints, i.e., TCRW. Most importantly, we can generate samples of conformations for the polymer by making use of it. Thus, the method is practically useful in

evaluating statistical expectation values by taking the average over generated samples.

The key property is consistent with physical requirements in statistical physics. A polymer in solution or melt is exposed to incessant thermal collisions due to solvent molecules or monomers and changes its conformation in time evolution. We can show that the statistical ensemble derived in the method of TCRW is consistent with the Rouse dynamics of the polymer in solution or melt. Furthermore, we can also show that the normal distributions of the edge displacements (i.e., the bond vectors) are transformed into the Boltzmann distributions of the position vectors of vertices where the elastic potentials are assigned on them and the center of mass in each network conformation is always located at the origin. We thus obtain a special regularized version of the Gaussian phantom networks [7, 8, 9, 10]. In the standard regularization of the phantom networks, however, the position vectors of selected vertices in the networks are fixed [7, 8, 9, 10,11,12]. Hereafter, if the center of mass is located at the origin in a polymer conformation, we call it *centered*. Thus, if we regard TCRW as a model of polymer networks, the normal distributions of the edge displacements due to thermal noises correspond to the Boltzmann distributions of the centered network conformations (i.e., the sets of vertex position vectors with the center of mass fixed at the origin). In fact, most of polymer networks are of bulk size, so that the center of mass does not fluctuate thermally.

There are two different methods for deriving statistical properties of TCRWs: one method is that we generate a large number of independent TCRWs, and numerically evaluate the average of some physical quantity over them; another method is that we derive an explicit form of the probability distribution of TCRWs and analytically evaluate the expectation value of some physical quantity. In this article, we employ the second method.

Here we present an introductory review on fundamental aspects of the method of TCRW [5,6]. In particular, we elaborate the key property of TCRW found recently and addressed in Ref. [5] in sections 2 and 3. As an application of the method of TCRW we show an exact evaluation of the mean square radius of gyration for TCRW of topological polymers associated with an n-subdivided complete graph of a finite number of vertices in sections 4 and 5. Here, the n-subdivided complete graph is derived from a complete graph by replacing each edge (or branch) in the graph with a linear chain of n edges (or n bonds). It should be a realistic model of topological polymers synthesized in experiments, since each branch is given by a linear polymer chain consisting of a sequence of monomers for most of topological polymers.

2. Elements of graph theory

We express the architecture of a polymer by a graph. Let us introduce useful tools in graph theory. A graph consists of a set of vertices also called nodes and a set of edges also called links or lines. An edge has a pair of vertices at the ends called the endpoints, i.e., it links its two endpoints. A graph represents the way how some objects denoted as vertices or nodes are connected to each other with edges or lines. For an illustration, let us consider a railway map. It is a graph in which a vertex corresponds to a station. Distances between vertices are not always proportional to those of corresponding stations, and the shapes of railway tracks are simplified to straight lines since a passenger often desires just to find which train to take for transfer. For a polymer, a graph represents the structure of the chemical connectivity. A subchain (or a Kuhn segment in polymer physics, i.e., a subchain with the Kuhn length (see Ref. [4])) corresponds to an edge in the graph, while a chemical cross-link or an end point of the Kuhn segment to a vertex.

2.1 Boundary matrix

We express the set of vertices of a graph G by $\{v_1, v_2, \ldots, v_V\}$ where the number of the vertices is denoted as $V(G)$ or simply by V, and the set of edges by $\{e_1, e_2, \ldots, e_\epsilon\}$ where the number of the edges is denoted as $\mathcal{E}(G)$ or $\mathcal{E}$. The number of edges which link to vertex v_i, namely the vertex degree or the valence of vertex v_i is denoted by d_i. Here we remark that the sum is equal to $2\mathcal{E}$. If there are plural edges between a pair of vertices, they are called multiple edges or a multi-edge. If an edge links a vertex to itself, it is called a loop. If vertices v_i and v_j are connected by a finite sequence of edges, we say that there is a path between the pair of the vertices or the two vertices are connected. If all pairs of vertices in a graph are connected, we say that the graph is connected.

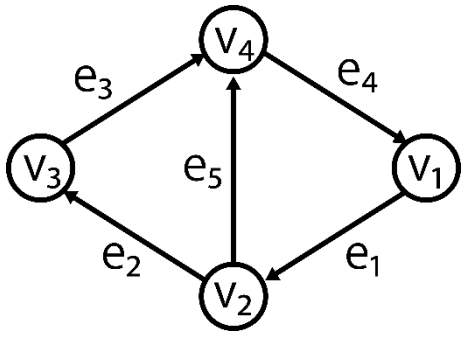


Fig. 3: A directed graph with four vertices and five edges

Let us consider graphs with directions, i.e., directed graphs. A directed graph is exhibited in Fig. 2. All edges in the graph have directions: edge e_1 is a directed edge from v_1 to v_2. A graph is said to be directed if all the edges have directions. In a polymer graph, the directions do not have any chemical meaning. They are simply an organizational device, and can be

assigned in any way which is convenient.

The boundary matrix B of a directed graph shows both the connectivity at the vertices and the directions of the edges in the graph. We define the (i, j) entry of B by

$$B_{ij} = \begin{cases} +1 & if\ v_i\ is\ the\ head\ vertex\ of\ e_j \\ -1 & if\ v_i\ is\ the\ tail\ vertex\ of\ e_j \\ 0 & otherwise \end{cases} \quad (1)$$

For example, the boundary matrix of the graph of Figure 3 is given by the following matrix:

$$B = \begin{pmatrix} -1 & 0 & 0 & 1 & 0 \\ 1 & -1 & 0 & 0 & -1 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 1 \end{pmatrix} \quad (2)$$

Here the nonzero matrix elements of the j-th row of matrix B correspond to the endpoints of the j-th edge.

2.2 The space of paths

Let us introduce the space of paths for a given graph. We assume that edges $\{e_1, e_2, \dots, e_\epsilon\}$ in the graph correspond to the unit vectors $\vec{e}_j$ for $j = 1,2, \dots, \mathcal{E}$, in the $\mathcal{E}$-dimensional Euclidean space $R^{\mathcal{E}}$, respectively. We call it the space of paths in the graph. Any path in the graph can be expressed as a linear combination of the basis vectors. For instance, the path from vertex v_1 to v_3 via v_2 shown in Figure 3 is given by $\vec{e}_1 + \vec{e}_2$.

The boundary matrix acts on the vector space of paths $R^{\mathcal{E}}$. If we apply it to a path p, the product Bp leads to the difference of the two end points of the path p. For instance, we have $B(\vec{e}_1 + \vec{e}_2) = \vec{v}_1 - \vec{v}_3$. Here we recall that the boundary matrix acting on an edge leads to the difference of the two end points of the edge. We have $B\vec{e}_1 = \vec{v}_1 - \vec{v}_2$.

The boundary matrix B of a graph characterizes the topological constraints associated with loops in the graph: It annihilates any loop in the graph, and hence every loop in the graph is an element of $\ker B$. For instance, it is easy to show that we have $B(\vec{e}_1 + \vec{e}_4 + \vec{e}_5) = 0$, where path $\vec{e}_1 + \vec{e}_4 + \vec{e}_5$ gives a loop in the graph of Figure 3. Here we recall that the symbol $\ker B$ denotes such a subspace of $R^{\mathcal{E}}$ on which the action of B vanishes, I.e., the null space.

Similarly for edges, we introduce the space of vertices in a given graph by assuming that vertices in $\{v_1, v_2, \dots, v_\mathcal{V}\}$ correspond to the unit vectors $\vec{v}_j$ for $j = 1, 2, \dots, \mathcal{V}$ in the $\mathcal{V}$-

dimensional Euclidean space $R^{\mathcal{V}}$. Therefore, the boundary matrix B is a linear map from the space of paths $R^{\mathcal{E}}$ to the space of vertices $R^{\mathcal{V}}$.

We define the graph Laplacian L for a given graph by the product between the boundary matrix B and its transpose B^T:

$$L = BB^T \tag{3}$$

For instance, the graph Laplacian of the graph in Fig. 3 is given as follows:

$$L = \begin{pmatrix} 2 & -1 & 0 & -1 \\ -1 & 3 & -1 & -1 \\ 0 & -1 & 2 & -1 \\ -1 & -1 & -1 & 3 \end{pmatrix}$$

The diagonals of L are positive integer numbers since B is an integer matrix. Off-diagonal element L_{ij} is the product of -1 and the number of the edges that link v_i and v_j.

$$L_{ij} = \begin{cases} d_i & if\ i = j \\ -1 & if\ i\ and\ j\ are\ adjacent \\ 0 & otherwise \end{cases} \tag{4}$$

We remark that the sum of all elements in each row of L is given by zero. The sum of all the elements of a row of L is equal to the product of the row with the vector in which all components are equal to 1:

$$\vec{1} = (1,1,\ldots,1)^T \tag{5}$$

Therefore, the vector $\vec{1}$ is in the kernel of L.

2.3 Singular value decomposition of boundary matrix *B*

We first recall that the boundary matrix B is a linear map from the space of paths $R^{\mathcal{E}}$ to that of vertices $R^{\mathcal{V}}$. We can express it in terms of singular value decomposition as follows.

$$B = USV^T \tag{6}$$

Here the matrix S is pseudo-diagonal where all off-diagonal matrix elements are equal to zero, and the matrices U and V are $\mathcal{V}$-dimensional and $\mathcal{E}$-dimensional orthogonal matrices, respectively. We recall that V^T denotes the transpose of the matrix V.

Since the graph Laplacian L is real and symmetric, we can diagonalize it by an orthogonal matrix U:

$$L = U\Lambda U^T \tag{7}$$

Here the diagonal matrix Λ is given by $\Lambda = SS^T$. We denote the eigenvalues of the graph Laplacian L by λ_j for j =1, 2, ⋯, $\mathcal{V}$. We remark that the orthogonal matrix U has appeared in the singular value decomposition of boundary matrix B of eq. (6).

Let us introduce the Moore-Penrose inverse A^+ for a given square or rectangular matrix A. It satisfies the defining relations.

$$AA^+A = A, \qquad A^+AA^+ = A^+ \tag{8}$$

$$(A^+A)^\dagger = \mathrm{A}^+A, \qquad (\mathrm{AA}^+)^\dagger = AA^+$$

Here the symbol $A^\dagger$ denotes the conjugate of the matrix A. It is associated with the inner products in the vector spaces as the domain or the range of the linear transformation A. We can show the following properties.

$$(A^+)^+ = A, \qquad (\mathrm{A}^T)^+ = (\mathrm{A}^+)^T$$

Hereafter we call the Moore-Penrose inverse also the pseudo-inverse of the matrix A.

It is now easy to show that the pseudo-inverse of the boundary matrix B is given by

$$B^+ = (USV^T)^+ = VS^+U^T \tag{9}$$

We remark that for an $m \times n$ pseudo-diagonal matrix S its pseudo-inverse S^+ is given by an $n \times m$ matrix in which each nonzero diagonal element is given by the reciprocal of the corresponding nonzero diagonal element of S and all other matrix elements are given by zero.

3. Graph embeddings

We now explain the method for embedding a graph in space [5]. We assign a set of values to the x-, y-, or z- coordinates of the vertices in a connected graph G. Let the symbol x_i denote the x-coordinate of vertex v_i for each i and w_i that of the edge displacement (i.e., the bond vector) of edge e_i for each i. The vector $\vec{x}$ denotes the collection of the coordinates x_i for all vertices of graph G, and the vector $\vec{w}$ the collection of the edge displacements w_i for all edges of G.

3.1 Direct sum decomposition of the space of paths

We first recall that the boundary matrix B is a linear map from the space of paths $R^{\mathcal{E}}$ to the space of the *x*-coordinates of vertices $R^{\mathcal{V}}$ in the graph *G*. We decompose the space of paths as a direct sum as follows (See, Definition 4 in Ref. [5]).

$$R^{\mathcal{E}} = \ker B \oplus \mathrm{im} B^T \tag{10}$$

The space $\mathrm{im}\, B^T$ is the orthogonal complement of $\ker B$, and hence it gives the configuration space of paths under all the loop constraints: $\mathrm{im}\, B^T = R^{\mathcal{E}}/\ker B$. Here we have introduced equivalence classes under $\ker B$: If given two paths are different only with respect to some additional loops, we say that they are equivalent to each other. We expect that by generating random configurations of paths uniformly in the space $\mathrm{im}\, B^T$we can numerically evaluate the statistical average of any physical quantity for the polymer with a given nontrivial architecture.

In order to generate Gaussian random numbers uniformly in the space $\mathrm{im}\, B^T$, we take an orthonormal basis for the ($\mathcal{V}$-1)-dimensional space $\mathrm{im}\, B^T : \vec{V}_1, \vec{V}_2, \ldots \vec{V}_{\mathcal{V}-1}$. Since the number of independent loops is given by $\mathcal{E} - \mathcal{V} + 1$, the space $\ker B$ has $\mathcal{E} - \mathcal{V} + 1$ dimensions. Therefore, $\mathrm{im}\, B^T$ has $\mathcal{V} - 1$ dimensions: $\mathcal{E} - (\mathcal{E} - \mathcal{V} + 1) = \mathcal{V} - 1$. Here we can construct the basis of the space $\mathrm{im}\, B^T$ by applying the Gram-Schmidt orthogonalization to the row vectors of the matrix B^T. Let us denote by $\vec{\alpha}$ a sequence of $\mathcal{V} - 1$ random numbers which follow the normal distributions with unit variance. Thus, we construct the vector $\vec{w}$ of edge displacements (the x-coordinates of the bond vectors) by

$$\vec{w} = \sum_{j=1}^{V-1} \vec{V}_j \, \alpha_j \tag{11}$$

We have called it the key property in Introduction. It gives explicitly edge displacements $\vec{w}$.

We can show that the vector $\vec{x}$ of the x-coordinates of vertices v_j is related to the vector $\vec{w}$ of edge displacements by the following:

$$\vec{w} = B^T \vec{x} \tag{12}$$

Let us derive eq. (12). First, we note that there are only two nonzero matrix elements 1 and -1 in each column of boundary matrix *B*, as shown in eq. (2) for the graph of Figure 3. It follows that each *j*-th entry of $B^T \vec{x}$ is given by the difference between the x-coordinates of the two end points of the *j*-th edge, which is equal to the *j*-th edge displacement w_j. We thus obtain

eq. (12).

3.2 Centered conformations

Let us now consider only centered conformations for the polymer. Hereafter we assume that the center of mass is always located at the origin for them. Or, we may assume that after all the displacements are given, we shift all the vertices in space together so that the center of mass is equal to zero.

For the centered conformations, by making use of the singular value decomposition of boundary matrix B in eqs. (6) and (9), we express the vector $\vec{x}$ of the x-coordinates of vertices v_j in terms of the vector $\vec{w}$ of edge displacements from eq. (12) as follows.

$$\vec{x} = B^{T+}\vec{w} \tag{13}$$

It is easy to show that the probability distribution function of $\vec{x}$ for centered conformations is given by the following Gaussian form:

$$P(\vec{x}) \propto \exp\left[-\frac{1}{2}\vec{x}^T L\vec{x}\right]\ \delta(x_1 + \cdots + x_v) \tag{14}$$

Thus, the probability distribution of the coordinates $\vec{x}$ is given by the Boltzmann distribution for the Gaussian polymer network. Here we remark that the delta functional factor in eq. (14) corresponds to the constraint that the center of mass is fixed at the origin. The probability distribution for three-dimensional conformations is given by the product of the three one-dimensional distributions with respect to the x, y, and z coordinates, respectively, since in the phantom chains the x, y and z coordinates are independent of each other.

In order to illustrate the usefulness of the key property in the distribution of edge displacements, i.e., eq. (11), let us consider the Gaussian network of a cubic lattice. In Figure 4 each lattice edge of the cubic lattice consists of five bridges (or subchains) between crosslinking vertices (or cross-links), where each bridge has fifty edges or bonds. By applying external forces on the three opposite pairs of surfaces of the cubic lattice in the opposite directions, respectively, such as with respect to the x-, y-, and z-axis, we keep the volume of the network nonzero and finite even in equilibrium. We have generated conformations of the Gaussian network of the 5 x 5 x 5 cubic lattice by making use of the key property of the TCRW method: We have constructed an ensemble of the edge displacements by applying the normal distribution with unit variance to them through eq. (11). Such an ensemble of random

conformations of the Gaussian network should be useful when we study statistical properties of the polymer network by evaluating the expectation values of a physical quantity in interest.

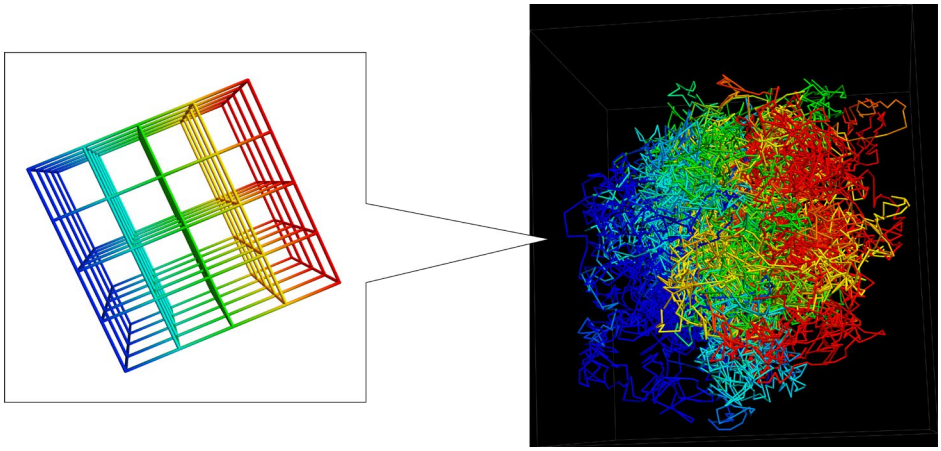


Fig. 4: The network of the $5\times5\times5$ cubic lattice where each branch has 50 edges in the left-hand side has three-dimensional conformations such as depicted in the right-hand side where external forces are applied at the vertices in the opposite pairs of surfaces in the opposite directions for the three directions. The corresponding edges are depicted with the same colors in the left-hand side and the right-hand side.

3.3 Diagonalization of the graph Laplacian in terms of eigenmodes

The graph Laplacian L is real and symmetric, and we can diagonalize it by an orthogonal matrix U: $L = U\Lambda U^T$. Here we recall that U is given by the same matrix that has appeared in the singular value decomposition of matrix B: $B = USV^T$, if we arrange the order of the basis vectors. Thus, through the transformation: $\vec{X} \equiv U^T\vec{x}$, we express the probability distribution function of the x-coordinates in terms of normal mode coordinates X_i as follows.

$$\exp\left[-\frac{1}{2}\vec{x}^T U\Lambda U^T\vec{x}\right]\delta(x_1+\cdots+x_v) \propto \exp\left[-\frac{1}{2}\vec{X}^T\Lambda\vec{X}\right]\delta(X_V) = \delta(X_V)\prod_i^{v-1}\exp\left[-\frac{1}{2}\lambda_i X_i^2\right] \quad (15)$$

Here we remark that the diagonal matrix Λ has a zero eigenvalue. i.e., a zero mode. We thus arrange the eigenvalues of Λ in descending order, so that the last eigenvalue λ_V is given by the zero eigenvalue:

$$\Lambda = \mathrm{diag}(\lambda_1, \ldots, \lambda_{v-1}, 0) \quad (16)$$

We now calculate the Moore-Penrose inverse L^+ of the graph Laplacian L. Here we recall that L is not invertible. By making use of eqs. (3), (6) and (9) we have

$$L^+ = (BB^T)^+ = (B^+)^T B^+ = US^+V^T VS^+U^T = U\Lambda^+U^T \tag{17}$$

We also recall that the pseudo-inverse of a diagonal matrix is given by such a diagonal matrix in which each of the nonzero element of the former is reciprocal to the corresponding non-zero diagonal element of the latter and all other elements are given by zero (see also eq. (9)).

$$\Lambda^+ = \mathrm{diag}(1/\lambda_1, 1/\lambda_2, \ldots, 1/\lambda_{v-1}, 0) \tag{18}$$

The normal mode coordinates $\{X_1, X_2, \ldots, X_{v-1}\}$ are independent of each other as random variables, since the probability distribution function is diagonalized with respect to them, as shown in eq. (15). Making use of the distribution function (15) we can show

$$\langle x_i x_j \rangle = \langle \sum_{k=1}^{v-1} U_{ik} X_k \sum_{l=1}^{v-1} U_{jl} X_l \rangle = \sum_{k=1}^{v-1} \sum_{l=1}^{v-1} U_{ik} U_{jl} \langle X_k X_l \rangle = \sum_{k=1}^{v} \sum_{l=1}^{v} U_{ik} U_{jl} \Lambda^+_{kl} = L^+_{ij} \tag{19}$$

We have thus shown that the two-point correlation functions for the position coordinates of a given pair of vertices are given by the corresponding matrix elements of the pseudo-inverse matrix L^+ of the graph Laplacian.

3.4 Mean square radius of gyration

By making use of eq. (19) we derive the following relations.

$$\langle (x_i - x_j)^2 \rangle = \langle x_i^2 \rangle - 2\langle x_i x_j \rangle + \langle x_j^2 \rangle = L^+_{ii} - 2L^+_{ij} + L^+_{jj} \tag{20}$$

That is, the mean square of the difference between the coordinates of a given pair of vertices is expressed in terms of the corresponding matrix elements of the pseudo-inverse of the graph Laplacian. As shown in Ref. [5], it follows from eq. (20) that the mean square radius of gyration for any given connected (multi-)graph is calculated as follows.

$$\langle R_g^2 \rangle = \frac{1}{2v^2} \sum_{i,j}^{v} \langle (r_i - r_j)^2 \rangle = \frac{1}{2v^2} \sum_{i,j}^{v} \left(L^+_{ii} - 2L^+_{ij} + L^+_{jj} \right) = \frac{1}{2v} \left(2 \,\mathrm{tr}\, L^+ - \frac{2}{v} \sum_{i,j}^{v} L^+_{ij} \right) \tag{21}$$

We thus obtain the following formula.

$$\langle R_g^2 \rangle = \frac{1}{v} \mathrm{tr}\, L^+ \tag{22}$$

Here we have made use of the fact that L is symmetric and hence the following equations hold.

$$\sum_{i=1}^{v} L_{ij}^{+} = 0 \tag{23}$$

In order to derive eq. (23), we remark that the kernel space of L coincides with that of L^{+}, since the graph Laplacian L is a symmetric matrix. Therefore, if an element is in ker L, then it is also in $\ker L^{+}$: $\vec{1} \in \ker L = \ker L^{+}$ (See also eqs. (28) and (29) in section 4).

We can evaluate the mean square radius of gyration for TCRW with any given connected graph rigorously by making use of eq. (22), as we shall explicitly demonstrate in section 4 for some graphs such as a subdivided theta graph and subdivided complete graphs. For an illustration, the exact values of the mean square radius of gyration for the ring TCRW with some small values of the number of vertices $\mathcal{V}$ are listed in Table 1.

We can show that the mean square radius of gyration for the ring TCRW with the number of vertices $\mathcal{V}$ is exactly given by $(\mathcal{V}^2 - 1)/(12\mathcal{V})$. For instance, it is shown in Ref. [5]. Thus, the well-known approximation $\mathcal{V}/12$ as the mean square radius of gyration for the ring polymer becomes close to the exact value as the number of vertices $\mathcal{V}$ increases.

Table 1. Exact values of the mean-square radius of gyration of a ring TCRW for small values of $\mathcal{V}$ and the estimates of formula $\mathcal{V}/12$.

V	tr L+/V	V/12
4	5/16 =0.3125	0.3333...
8	21/32 =0.65625	0.6666...
12	143/144 =0.993056	1.
16	85/64 =1.32813	1.333...
20	133/80 =1.6625	1.666...
24	575/288 =1.99653	2.
28	261/112 =2.33036	2.333...
32	341/128 =2.66406	2.666...

We remark that the mean square radius of gyration has explicitly been evaluated for several topological polymers such as those associated with double-ring chain, cyclic multiple-ring chains and long chain branch polymer chains [13, 14].

4. Exact dependence of the mean square radius of gyration on polymerization degree

4.1 Subdivision

When we study the topological polymer of a given graph synthesized in experiments, it is often important to evaluate the mean square radius of gyration for the TCRW of such a graph that is obtained by replacing each edge of the original graph with n edges or n monomers for some large n. Here we remark that the number n is proportional to the degree of polymerization. We thus consider subdividing a graph G by replacing each edge with n edges, as shown in Fig. 5. The subdivided graph is denoted by G_n. We call each sequence of n edges in G_n, i.e., each subdivided edge, a branch or an arc of G_n, if it corresponds to an edge of G.

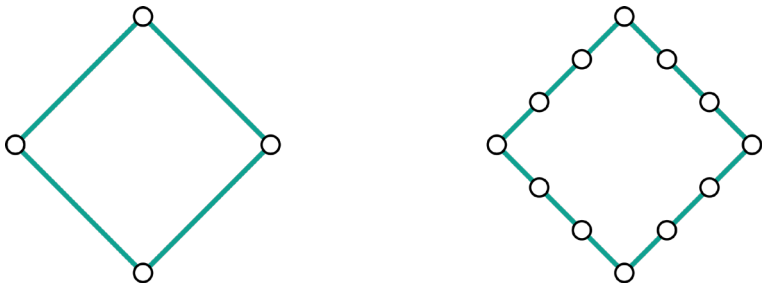


Fig 5. Graph in the right-hand side is the 3-subdivided graph of the left one.

We shall derive the exact formula of the mean square radius of gyration as a function of the number of all vertices $\mathcal{V}$ for the topological polymer of an n-subdivided complete graph for an arbitrary integer n.

4.2 Resistance distances in electrical circuits

Let us regard a graph as an electric circuit where each edge is a 1 ohm resistor. Then, the resistance between a given pair of vertices v_i and v_j in the circuit is denoted by r_{ij}. We also call it resistance distance r_{ij}. Suppose that the electric potential denoted by $\vec{\phi}_{ij}$ appears in

the electric circuit when the unit electric current flows in at the vertex v_i and flows out at the vertex v_j. The resistance distance r_{ij} is equal to the difference between the value of the electric potential $\vec{\phi}_{ij}$ at v_i and that of v_j. Here we remark that the k-th component of vector $\vec{\phi}_{ij}$ denotes the value of the electric potential at the k-th vertex v_k for each k.

In order to derive the electric potential $\vec{\phi}_{ij}$ we introduce vector $\vec{\phi}$. Then, the k-th component of product $B^T\vec{\phi}$ is given by the difference between the electric potentials at the two ends of edge e_k, respectively, for each k. It is equal to the current J_k flowing via edge e_k if the resistance of edge e_k is equal to 1. The current denoted as $\vec{J}$ is therefore given by

$$B^T\vec{\phi} = B^T\begin{pmatrix}\phi_1\\ \phi_2\\ \vdots\\ \phi_v\end{pmatrix} = \vec{J} \tag{24}$$

The j-th component of product $B\vec{J}$ is equal to the sum of electric currents flowing in at the j-th vertex v_j. We therefore have

$$B\vec{J} = L\vec{\phi} \tag{25}$$

Thus, the electric potential in the case when the unit electric current flows in at v_i and flows out at v_j is derived from the system of equations expressed by L as follows.

$$L\vec{\phi}_{ij} = \vec{v}_i - \vec{v}_j = \begin{pmatrix}\vdots\\ 0\\ 1\ (i)\\ 0\\ \vdots\\ 0\\ -1\ (j)\\ 0\\ \vdots\end{pmatrix} \tag{26}$$

Here we recall that $\vec{v}_i$ denotes the unit vector in which the i-th component is given by 1 and the other components by zero.

We apply the pseudo-inverse L^+ to the above equation. Then, we have

$$L^+L\vec{\phi}_{ij} = L^+\left(\vec{v}_i - \vec{v}_j\right) \tag{27}$$

Here we remark that we have

$$L^+L = U\Lambda^+U^TU\Lambda U^T = U\Lambda^+\Lambda U^T = U\ diag(1,\dots,1,0)\ U^T = U(I - E_{vv})U^T \equiv I - P_0 \tag{28}$$

where E_{vv} denotes the unit matrix whose only nonzero element 1 is located at entry $(\mathcal{V},\ \mathcal{V})$

and P_0 denotes the projection operator as follows.

$$UE_{vv}U^T = (\vec{u}_1, \dots, \vec{u}_v)\, diag(0, \dots, 0, 1) \begin{pmatrix} \vec{u}_1^T \\ \vdots \\ \vec{u}_v^T \end{pmatrix} = \frac{1}{v} \vec{1}\vec{1}^T \equiv P_0 \tag{29}$$

We now choose the zero point of potential $\vec{\phi}$ so that we have $(I - P_0)\vec{\phi} = \vec{\phi}$. We thus solve the above equation as follows.

$$\vec{\phi}_{ij} = L^+(\vec{v}_i - \vec{v}_j) \tag{30}$$

Since the electric potential $\vec{\phi}_{ij}$ at vertex v_j denoted as $\vec{\phi}_{ij}(\vec{v}_j)$ is given by

$$\vec{\phi}_{ij}(\vec{v}_j) = \vec{v}_j^T \vec{\phi}_{ij}$$

we obtain the expression of resistance distance in terms of the pseudo-inverse of the graph Laplacian as follows.

$$r_{ij} = \vec{\phi}_{ij}(\vec{v}_i) - \vec{\phi}_{ij}(\vec{v}_j) = (\vec{v}_i - \vec{v}_j)^T L^+(\vec{v}_i - \vec{v}_j) = L_{ii}^+ + L_{jj}^+ - 2L_{ij}^+ \tag{31}$$

Therefore, resistance distance r_{ij} is equal to the mean squared difference of the *x*-coordinates of vertices v_i and v_j .

$$r_{ij} = \langle (x_i - x_j)^2 \rangle \tag{32}$$

4.3 Derivation of an exact formula for the *n*-subdivided theta graph

We now calculate the mean square radius of gyration for an *n*-subdivided connected graph. It is given by the sum of the resistance distances between two vertices in the subdivided graph over all the pairs of vertices. We take advantage of the analogy to electric circuits. We remark that the resistance of *n* unit resistances in a series circuit is equal to *n*. We also recall that the resistance distance is inversely proportional to the matrix elements of the graph Laplacian.

For a given graph G and its subdivided graph G_n we introduce a reduced graph and its weighted reduced graph Laplacian. We remark that its matrix size is much smaller than that of the subdivided graph Laplacian $L(G_n)$. We define the weighted reduced graph Laplacian as follows. Suppose that ρ_{ij} denotes the resistance between a given pair of vertices v_i and v_j in G_n. We assign the value $-1/\rho_{ij}$ to the off-diagonal matrix element L_{ij} of the weighted

reduced graph Laplacian: $L_{ij} = -1/\rho_{ij}$, while we assign the value $L_{ii} = -\sum_{j\neq i} L_{ij}$ to each diagonal element L_{ii} in the weighted reduced graph Laplacian.

Here we remark that replacing an edge of unit resistance in the graph G with a set of ρ_{ij} consecutive edges of unit resistance in the subdivided graph G_n should correspond to replacing it with an edge of resistance ρ_{ij} in the reduced graph.

We distinguish interior and exterior vertices in the subdivided graph G_n. We call the vertices added by subdivision *interior* and the original vertices before subdivision *exterior*. Here we remark that the number of interior vertices is given by $\mathcal{E}(G)(n-1)$. We consider the following four cases among all the pairs of vertices in the subdivided graph G_n : (i) pairs between interior-interior vertices on different branches; (ii) pairs between interior-interior vertices on the same branch, (iii) pairs between exterior-interior vertices, (iv) pairs between exterior-exterior vertices.

For an illustration, we consider the n-subdivided theta graph. We give numbers 1, 2 and 3 to the three branches, respectively. The two branching points (or vertices) in the original theta graph before subdivision are denoted by 1 and 2, respectively, in Fig. 6.

(i) Interior-interior vertex pairs on different branches.

Let us consider the resistance distance r_{jk} between the k-th vertex of branch 1 and the j-th vertex of branch 2. We replace branch 1 by the two edges with weights k and $n-k$, respectively, and add a new vertex called vertex k; we replace branch 2 by the two edges with weights j and $n-j$, respectively, and add a new vertex called vertex j; we replace branch 3 by an edge of weight n, as shown in Fig. 4. Here we remark that integers k, j and n satisfy $0 < k, j < n$.

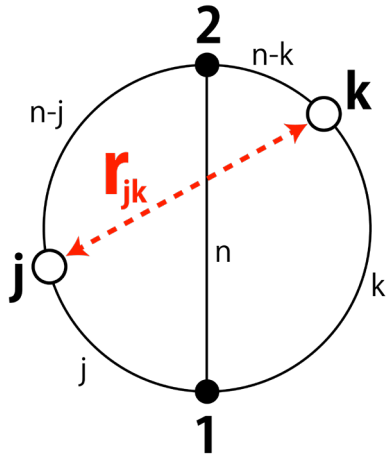


Fig. 6: Reduced graph with weights on edges for calculating the resistance distance between the type-(i) pair vertex j and vertex k.

Let $G(n,1,k,2,j)$ denotes the reduced graph in Fig. 4, with vertices k and j in branches 1 and 2, respectively. It has four vertices 1, k, 2, and j counterclockwise along the outer circle from vertex 1, and five edges: edges with weights k and n-k on branch 1, those of weights n-j

and j on branch 2, and the vertical edge of weight n which connects vertices 1 and 2.

We derive the weighted reduced graph Laplacian of $G(n,1,k,2,j)$ as follows.

$$L(G(n,1,k,2,j)) = \begin{pmatrix} \frac{1}{n}+\frac{1}{k}+\frac{1}{j} & -\frac{1}{n} & -\frac{1}{k} & -\frac{1}{j} \\ -\frac{1}{n} & \frac{1}{n}+\frac{1}{n-k}+\frac{1}{n-j} & -\frac{1}{n-k} & -\frac{1}{n-j} \\ -\frac{1}{k} & -\frac{1}{n-k} & \frac{1}{k}+\frac{1}{n-k} & 0 \\ -\frac{1}{j} & -\frac{1}{n-j} & 0 & \frac{1}{j}+\frac{1}{n-j} \end{pmatrix}$$

Here we have assumed that the vertex 1, 2, k, j of the reduced graph $G(n,1,k,2,j)$ correspond to the vertex 1, 2, 3 and 4 in $L(G(n,1,k,2,j))$: The third column and row correspond to vertex k and the 4-th ones to vertex j, where the matrix elements of (3,4) and (4,3) are given by zero since there is no edge between vertices j and k. The resistance distance between vertices k and j is derived from the pseudo-inverse matrix $L^{+}(G(n,1,k,2,j))$.

We make use of the Bapat-Gutman-Xiao theorem to calculate the resistance distance [15]:

$$r_{ij} = \frac{\mathrm{Det}\, L(i,j)}{\mathrm{Det}\, L(i)} \tag{33}$$

where $L(i,j)$ denotes the partial matrix obtained from L by deleting the ith and jth columns and the ith and jth rows, and $L(i)$ that of deleting the ith column and the ith row. We thus avoid calculating the pseudo-inverse matrix directly. Here we remark that it might take a long computational time to calculate a matrix element of the pseudo-inverse matrix.

Thus, we obtain the resistance distance between vertices k and j as follows:

$$r_{kj} = \frac{1}{3n}(2j^2 + 2k^2 + 2jk - 3jn - 3kn)$$

The contribution from the type-(i) pairs between branches 1 and 2 to the mean square radius of gyration is therefore given by

$$RII_{12} = \sum_{k=1}^{n-1}\sum_{j=1}^{n-1} r_{kj} = \frac{7n^3 - 10n^2 - n + 4}{18} \tag{34}$$

We have the same contribution from the type-(i) pairs between branches 2 and 3 and that of the type-(i) pairs between branches 1 and 3. It is because the theta graph is symmetric with respect to the three branches 1, 2 and 3.

Here we remark that according to Ref. [16] the same formula as Bapat's formula is addressed in the Ph. D thesis of den Nijs (1979) (See, e.g., eq. (4.34) of Ref. [16]).

(ii) Interior-interior vertex pair on a branch

We consider the resistance distance between the *j*-th and *j+k*-th vertices on branch 1, where integers *j*, *k* and *n* satisfy $0 < j, k < n$. We replace branch 1 by three edges with weights $j, k, n-j-k$, respectively, and add vertices *j* and *k*, and replace branches 2 and 3 by two parallel edges of weight n. The reduced graph is denoted by $G(n,1,j,1,k)$. We obtain the graph Laplacian of $G(n,1,j,1,k)$ as follows.

$$L(G(n,1,j,1,k)) = \begin{pmatrix} \frac{2}{n}+\frac{1}{j} & -\frac{2}{n} & -\frac{1}{j} & 0 \\ -\frac{2}{n} & \frac{2}{n}+\frac{1}{n-j-k} & 0 & -\frac{1}{n-j-k} \\ -\frac{1}{j} & 0 & \frac{1}{j}+\frac{1}{k} & -\frac{1}{k} \\ 0 & -\frac{1}{n-j-k} & -\frac{1}{k} & \frac{1}{k}+\frac{1}{n-j-k} \end{pmatrix}$$

Note that the third column and row correspond to vertex *j*, and the 4-th ones to vertex *k*. We obtain the resistance distance by making use of the Bapat formula:

$$r_{kj} = k - \frac{2k^2}{3n}$$

The contribution of the type-(ii) pairs on branch 1 to the mean square radius of gyration is given by

$$RII_1 = \sum_{j=1}^{n-2} \sum_{k=1}^{n-j-1} r_{kj} = \frac{1}{18}(2n^3 - 5n^2 + n + 2) \tag{35}$$

We remark that the contributions from branches 2 and 3 are the same as RII_1.

(iii) Exterior-interior vertex pairs

We consider the resistance distance between the *k*-th vertex on branch 1 and an exterior vertex, i.e., a vertex of the original graph G. We replace branch 1 by two edges with weights k and $n-k$, respectively, and add a new vertex called vertex *k*, and replace branches 2 and 3 by two

edges of weight n. Here we recall $0 < k < n$. The reduced graph is denoted as $G(n,1,k)$. We obtain the graph Laplacian of $G(n,1,k)$ as follows.

$$L\big(G(n,1,k)\big) = \begin{pmatrix} \frac{2}{n}+\frac{1}{n-k} & -\frac{2}{n} & -\frac{1}{n-k} \\ -\frac{2}{n} & \frac{2}{n}+\frac{1}{k} & -\frac{1}{k} \\ -\frac{1}{n-k} & -\frac{1}{k} & \frac{1}{k}+\frac{1}{n-k} \end{pmatrix}$$

The resistance distance between vertices 1 and k is given by

$$r_{1k} = \frac{(n-k)(n+2k)}{3n}$$

The contribution from all the pairs between vertex 1 and interior vertices on edge 1 is

$$REI_1 = \sum_{k=1}^{n-1} r_{1k} = \frac{1}{18}(5n^2 - 3n - 2) \tag{36}$$

The total contribution from all the branches and the original vertices are equal to $6REI_1$.

(iv) Exterior-exterior vertex pair

The theta graph has an exterior-exterior pair, i.e., vertices 1 and 2, and the three branches are replaced with three edges of weight n. We have the weighted reduced graph Laplacian

$$L(G) = \begin{pmatrix} \frac{3}{n} & -\frac{3}{n} \\ -\frac{3}{n} & \frac{3}{n} \end{pmatrix}$$

and the contribution of the type-(iv) pairs is given by

$$REE_{12} = \frac{1}{\mathrm{Det}\frac{3}{n}} = \frac{n}{3} \tag{37}$$

We now take the sum of the contributions from all the pairs such as eqs. (34), (35), (36) and (37), and divide it by the square of the number of vertices

$$\mathcal{V}^2(G_n) = \big(\mathcal{V}(G) + (n-1)\mathcal{E}(G)\big)^2 = (3n-1)^2 \tag{38}$$

and we have

$$\frac{3RII_{12}+3RII_1+6REI_1+REE_{12}}{(3n-1)^2}=\frac{9n^3-5n^2-4n+2}{6(3n-1)^2}$$
$$=\frac{3\mathcal{V}^3+4\mathcal{V}^2-13\mathcal{V}+4}{54\mathcal{V}^2} \tag{39}$$

Thus, we obtain an exact expression of the mean-square radius of the *n*-subdivided theta graph expressed as a function of the total number of vertices $\mathcal{V}=\mathcal{V}(G_n)$ as follows.

$$\langle R_g^2\rangle=\frac{3\mathcal{V}^3+4\mathcal{V}^2-13\mathcal{V}+4}{54\mathcal{V}^2} \tag{40}$$

If the number of vertices $\mathcal{V}$ is very large, we have the following approximation

$$\langle R_g^2\rangle\cong\frac{\mathcal{V}}{18} \tag{41}$$

It should be emphasized that the expression of eq. (40) gives the exact value of the mean square radius of gyration for the n-subdivided theta graph in terms of the total number of vertices $\mathcal{V}(G_n)$. It can also be expressed in terms of the degree *n* of subdivision, since we have $\mathcal{V}(G_n)=3n-1$, as seen in eq. (38). There is no approximation made. The expression of eq. (41) gives its asymptotic value for $\mathcal{V}\gg 1$. When *n* is large, the number $\mathcal{V}$ of all the vertices in the *n*-subdivided theta graph is approximately equal to 3*n*. We therefore have the asymptotic value of the mean square radius of gyration for the *n*-subdivided theta graph as follows.

$$\langle R_g^2\rangle\cong\frac{\mathcal{V}}{18}=\frac{n}{6} \tag{42}$$

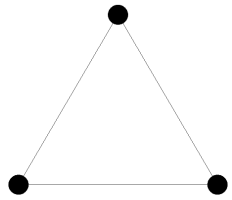
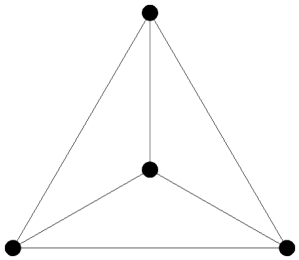
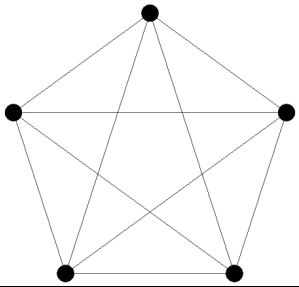
Thus, the mean square radius of gyration is the same as that of the corresponding linear chain with the same number of vertices as that of each branch of the *n*-subdivided theta graph [17].

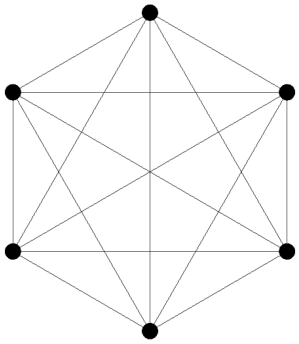
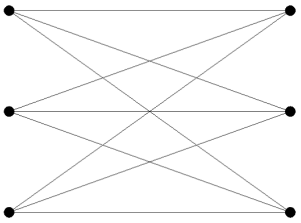
4.4 Exact expressions of the mean square radius of gyration for the *n*-subdivided complete graphs

In the TCRW of the *n*-subdivided complete graphs with the number of exterior vertices (cross-links) m for $m=3,4,5,and\ 6,$ and that of the *n*-subdivided bipartite complete graph with $m+m=3+3$ exterior vertices (cross-links) (i.e., m =3) we present the exact expressions of the mean square radius of gyration as a function of the total number of vertices $\mathcal{V}$. They are listed in Table 2.

We emphasize that the expressions are exact and valid for the TCRW with any finite number of vertices $\mathcal{V}(G_n)$. Here we recall $\mathcal{V}(G_n) = \mathcal{V}(G) + (n-1)\mathcal{E}(G)$. For complete graphs we have $\mathcal{V}(G_n) = m + (n-1)m(m-1)/2$. Here and hereafter, we abbreviate $\mathcal{V}(G_n)$ by $\mathcal{V}$ for simplicity. We remark that in the n-subdivided graphs we also call exterior vertices cross-links, at which some subchains with length n are connected in the polymer.

Table 2. Exact expressions of the mean square radius of gyration for TCRW of complete graphs and a bipartite graph with a finite number of vertices $\mathcal{V}$.

G	$\langle R_g^2(\mathcal{V})\rangle$	Note
	$-\frac{1}{12V}+\frac{V}{12}$	Complete graph K_3 (Circle)
	$\frac{5}{48}+\frac{4}{27V^2}-\frac{7}{18V}+\frac{37V}{864}$	Complete graph K_4 6 edges 4 vertices
	$\frac{67}{400}+\frac{5}{16V^2}-\frac{35}{48V}+\frac{151V}{6000}$	Complete graph K_5 10 edges 5 vertices

	$\frac{31}{150}+\frac{12}{25V^2}-\frac{161}{150V}+\frac{11V}{675}$	Complete graph K_6 15 edges 6 vertices
	$\frac{10}{81}+\frac{2}{9V^2}-\frac{29}{54V}+\frac{17V}{486}$	Complete bipartite graph $K_{3,3}$ 9 edges 3+3 vertices

It is straightforward to calculate the mean square radius of gyration for the Gaussian topological polymer simply associated with complete graph K_m. That is, we consider the case of n=1. The graph Laplacian is given by $L = m(I - \frac{1}{m}\vec{1}\vec{1}^T)$, where the symbol $\vec{1}$ denotes the vector with m elements where all of them are equal to 1, as shown in eq. (5). Since its pseudo-inverse is given by $L^+ = m^{-1}(I - \frac{1}{m}\vec{1}\vec{1}^T)$, it follows from eq. (22) that the mean square radius of gyration of TCRW with complete graph K_m is given by

$$\langle R_g^2 \rangle = m^{-1}(1 - m^{-1}) \tag{43}$$

Here we have considered only the one-dimensional contribution to the mean square radius of gyration. The expression (43) is much simpler than any expression listed in Table 2.

Thus, we conclude that the mean square radius of gyration for the Gaussian topological polymers associated with the n-subdivided complete graph K_m is quite different from that of complete graph K_m. The former is much more complex than the latter. However, one can probably synthesize topological polymers of n-subdivided graphs more often in experiments.

5. Asymptotic value of the mean square radius of

gyration for an arbitrary complete graph

Let us recall that in the study of a topological polymer with a graph synthesized in experiments, it is often significant to evaluate the mean square radius of gyration for the polymer of an n-subdivided graph with large n. Here we remark that a method for reducing the graph Laplacian of the Gaussian topological polymer of an n-subdivided graph for large n has been derived [18]. Furthermore, we can derive even the exact asymptotic value of the mean square radius of gyration for TCRW of the n-subdivided graph in the large n limit [6].

It has been rigorously shown in Ref. [6] that the ratio between the mean square radius of gyration and the number of vertices in the subdivided graph is given by the following formula.

$$\lim_{n\to\infty}\frac{\langle R_g^2(G_n)\rangle}{\mathcal{V}(G_n)}=\frac{1}{2\mathcal{E}^2(G)}\left(\mathrm{tr}\,\mathcal{L}^+(G)+\frac{1}{3}\mathrm{Loops}(G)-\frac{1}{6}\right) \tag{44}$$

Here $\mathcal{L}$ denotes the normalized graph Laplacian. It is defined as follows:

$$\mathcal{L}_{ij}=\begin{cases}1 & if\ i=j\\ -1/\sqrt{d_i d_j} & if\ i\ and\ j\ are\ adjacent\\ 0 & otherwise\end{cases}$$

For example, the normalized graph Laplacian and its pseudo-inverse for the 3-complete graph, i.e., a ring, is given by

$$\mathcal{L}=\begin{pmatrix}1 & -1/2 & -1/2\\ -1/2 & 1 & -1/2\\ -1/2 & -1/2 & 1\end{pmatrix},\qquad \mathcal{L}^+=\frac{1}{9}\begin{pmatrix}4 & -2 & -2\\ -2 & 4 & -2\\ -2 & -2 & 4\end{pmatrix}$$

Thus, we confirm by taking the trace of $\mathcal{L}^+$ that the asymptotic value of the ratio of the mean square radius of gyration to the number of vertices for a ring is given by $1/12$.

(i) Complete graph

For the complete graph with m vertices, the normalized graph Laplacian is given by

$$\mathcal{L}=\begin{pmatrix}1 & -1/(m-1) & -1/(m-1) & \cdots\\ -1/(m-1) & 1 & -1/(m-1) & \cdots\\ -1/(m-1) & -1/(m-1) & 1 & \\ \vdots & \vdots & & \ddots\end{pmatrix}=\frac{1}{m-1}\left(mI-\vec{1}\vec{1}^T\right)$$

and its pseudo-inverse matrix is given by

$$\mathcal{L}^{+}=\begin{pmatrix}(m-1)^2/m^2 & -(m-1)/m^2 & \cdots\\ -(m-1)/m^2 & (m-1)^2/m^2 & \\ -(m-1)/m^2 & -(m-1)/m^2 & \\ \vdots & \vdots & \end{pmatrix}=\frac{m-1}{m^2}\left(mI-\vec{1}\vec{1}^{T}\right)$$

We recall $\vec{1}\vec{1}^{T}$ denotes such a matrix in which all the matrix elements are given by 1. We remark that its square is given by m times itself: $\left(\vec{1}\vec{1}^{T}\right)^2=m\vec{1}\vec{1}^{T}$. We confirm that it leads to the pseudo-inverse of $\mathcal{L}$:

$$\mathcal{L}\mathcal{L}^{+}\mathcal{L}=\frac{1}{m-1}\left(mI-\vec{1}\vec{1}^{T}\right)\frac{m-1}{m^2}\left(mI-\vec{1}\vec{1}^{T}\right)\frac{1}{m-1}\left(mI-\vec{1}\vec{1}^{T}\right)=\frac{1}{m(m-1)}\left(m^2I-m\vec{1}\vec{1}^{T}\right)$$
$$=\mathcal{L}$$

We obtain from eq . (44) the asymptotic value of the mean square radius of gyration by calculating the trace: $\mathrm{tr}\,\mathcal{L}^{+}=(m-1)^2/m$, the number of edges $\mathcal{E}(G)=m(m-1)/2$ and the number of loops $\mathrm{Loop}(G)=\mathcal{E}(G)-v(G)+1=m(m-1)/2-m+1$ as follows.

$$\frac{1}{2\mathcal{E}^2(G)}\left(\mathrm{tr}\,\mathcal{L}^{+}(G)+\frac{1}{3}\mathrm{Loops}(G)-\frac{1}{6}\right)=\frac{2}{m^2(m-1)^2}\left(\frac{(m-1)^2}{m}+\frac{1}{3}\left(\frac{m(m-1)}{2}-m+1\right)-\frac{1}{6}\right)$$
$$=\frac{6-11m+3m^2+m^3}{3(m-1)^2m^3}$$

Thus, the average size of an n-subdivided complete graph with m exterior vertices (cross-links) is much smaller than that of the corresponding linear chain with the same number of vertices. Furthermore, if m is large enough, the ratio of the sizes is approximately given by $1/3m^2$. Here we remark that the ratio is different from that of the case of n=1.

(ii) Complete bipartite graph

The normalized graph Laplacian and its pseudo-inverse of the complete bipartite graph with $m+m$ exterior vertices (cross-links), respectively, are expressed in terms of block matrices as follows.

$$\mathcal{L}=\begin{pmatrix} I & -\frac{\vec{1}\vec{1}^{T}}{m}\\ -\frac{\vec{1}\vec{1}^{T}}{m} & I\end{pmatrix},\qquad \mathcal{L}^{+}=\frac{1}{4m}\begin{pmatrix}4mI-3\vec{1}\vec{1}^{T} & -\vec{1}\vec{1}^{T}\\ -\vec{1}\vec{1}^{T} & 4mI-3\vec{1}\vec{1}^{T}\end{pmatrix}$$

We thus obtain from eq. (44) the asymptotic value of the mean square radius of gyration by calculating the trace of the pseudo-inverse of the normalized graph Laplacian as $\mathrm{tr}\,\mathcal{L}^{+} = (4m-3)/2$, the number of the edges $\mathcal{E}(G) = m^2$ and the number of the loops: $\mathrm{Loop}(G) = \mathcal{E}(G) - v(G) + 1 = m^2 - 2m + 1$, as follows.

$$\frac{1}{2\mathcal{E}^2(G)}\left(\mathrm{tr}\,\mathcal{L}^{+}(G) + \frac{1}{3}\mathrm{Loops}(G) - \frac{1}{6}\right) = \frac{1}{2m^4}\left(\frac{4m-3}{2} + \frac{1}{3}(m^2 - 2m + 1) - \frac{1}{6}\right) = \frac{m^2 + 4m - 4}{6m^4}$$

The average size of an n-subdivided complete bipartite graph with $m+m$ exterior vertices (cross-links) is much smaller than that of the corresponding linear chain with the same number of vertices. Furthermore, if the number of cross-links m is large enough, the ratio of the sizes is approximately given by $1/6m^2$. Here we also remark that the ratio is different from that of the case of n=1.

6. Perspectives on Gaussian networks

There are two important physical aspects in polymer networks: The molecular size of a polymer network is very large, and the volume of the region in space occupied by the polymer network is nonzero and finite-valued. Thus, the polymer network has a finite density. Furthermore, the center of mass of the network is fixed at the origin since the mass of the network is of a bulk quantity and hence is asymptotically large such as Avogadro's number.

In the method for constructing TCRW, we can make the volume of the system nonzero finite by applying external forces at the vertices located on the surfaces of the network. Let us consider the cubic lattice network depicted in Fig. 7. By adding external forces at the opposite or antipodal faces of the cubic lattice in opposite directions, respectively, we can keep the volume of the network nonzero finite in equilibrium. Here we remark that in the phantom network model, it is often assumed that the vertices on the surface of the network are fixed at some points of the boundary walls or containers.

We recall the Gaussian TCRW for the $5\times5\times5$ cubic lattice depicted in Fig. 7. Here each lattice edge of the cubic lattice consists of five branches while each branch has fifty edges or bond vectors. When we elongate the network in one direction, we increase the external forces acting on the two opposite faces of the cubic lattice network in opposite directions which are

parallel to the elongation direction, while we decrease the corresponding forces in two other directions properly, so that the total volume of the network is kept constant under elongation of the network.

Furthermore, we can easily generate conformations of the Gaussian network elongated due to an external force. Here we make use of the construction of the edge displacements through the normal distribution with unit variance again.

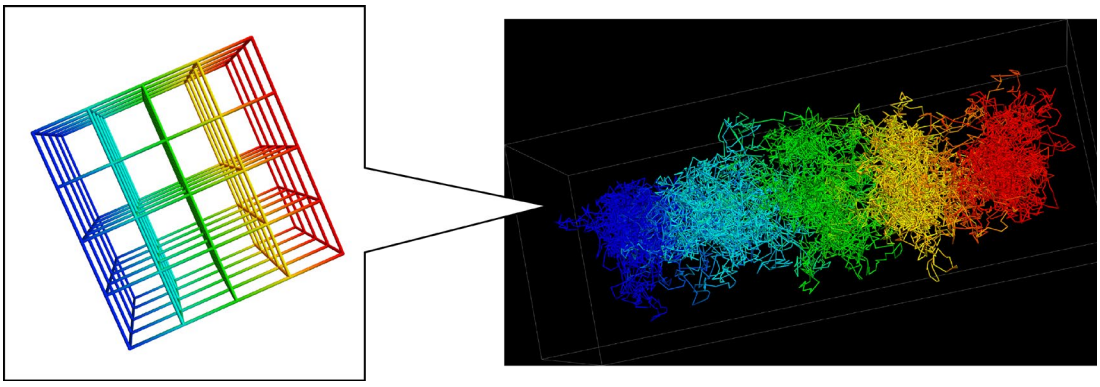


Fig. 7. The $5 \times 5 \times 5$ cubic lattice where each branch has 50 edges is elongated by 5 times in one direction due to the force applied at the opposite faces in opposite directions as shown in the three-dimensional conformation in the right-hand side. It is compressed by about $\sqrt{5}$ times in other two directions perpendicular to it. The corresponding edges in the network are depicted by the same colors.

7. Concluding remarks

By making use of the method of TCRW we can derive exact expressions for most of the statistical quantities of TCRW with any given graph.

We have presented the exact expressions of the mean square radius of gyration for Gaussian topological polymers with the n-subdivided complete graphs in Table 2. They are valid for any given finite number of vertices. We have also derived the exact asymptotic values for the

mean square radius of gyration for the Gaussian topological polymers of the n-subdivided complete graphs. The result should be useful in future researches on topological polymers in experiments.

Through the method of TCRW we can investigate systematically statistical properties of Gaussian polymer networks. In order to assign the bulk behavior of the Gaussian network of a given graph, i.e., in order to let the TCRW of the graph have some finite volume, we can apply external fields on the surface vertices of the network, as was briefly shown in section 6. The results of the systematic study will be reported in subsequent publications.

Making use of the key property shown in eq. (11) we can explicitly and exactly evaluate almost any physical quantities of the Gaussian networks such as the shear modulus elasticity without making any macroscopic assumptions. In particular, we do not assume the affine deformation of cross-linking chains under network deformation. Details will be reported elsewhere.

The simple method for generating edge displacements, i.e., the key property shown in eq. (11), plays a central role in constructing the topologically constrained random walks (TCRW). This viewpoint can be extended and then applied not only to the Gaussian topological polymers with elastic potentials but also to almost arbitrary polymer models with general potentials on edge displacements [19]. Details will be presented in subsequent reports.

We expect that by making use of the method of TCRW many fundamental aspects on the statistical properties of topological polymers and polymer networks will be explicitly and quantitatively studied. Therefore, we expect that they should indeed be clarified in the near future.

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