Bead–Spring Model Predictions of Solution Dynamics for Flexible Homopolymers Incorporating Long-Chain Branches and/or Rings

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ABSTRACT: A generalization of the model of Zimm is presented which predicts solution dynamics for chains composed of any assortment of identical spherical beads connected by identical Hookean springs. The model is formulated in a coordinate system that translates with the chain to ensure that the predicted dynamic properties may be computed, regardless of chain size or degree of hydrodynamic interaction, with the efficient eigenvalue algorithm applied by Lodge and Wu to linear chains. Several new block-diagonal matrices, which further improve the computation efficiency for linear, ring, and regular H structures, also arise from this formulation. All three features enable new quantitative predictions of the effects of long-chain branches, combinations of rings and branches, chain size, and hydrodynamic interaction on dilute-solution, low-shear-rate, dynamic properties of flexible homopolymers. Numerical results for selected chain geometries will be presented in a subsequent paper.

I. Introduction

Over the last 30 years the predictions of bead–spring models have been indispensable for interpreting equilibrium and low-shear-rate dynamical properties of flexible macromolecules in dilute solution. Of these numerous models only an important subset of bead–spring models[1-8] are of interest here; these models describe homopolymers with chains composed of identical beads and springs, incorporate springs with Hookean force laws, use the "preaveraging" treatment of the hydrodynamic interaction, employ Gaussian statistics, and ignore interchain interactions and sample polydispersity. Collectively this subset of models will be referred to as the bead–spring model (BSM).

Although the BSM description of homopolymers in dilute solution is simplistic in certain respects, this model has been very successful in three important ways. It is mathematically tractable for a variety of bead–spring structures, properties can be computed exactly for chains of finite size regardless of the chain geometry or degree of hydrodynamic interaction, and predicted properties correspond quantitatively to measured linear viscoelastic (VE)[9-15] and oscillatory flow birefringence (OFB)[16-19] properties of long-chain homopolymers when extrapolated to infinite dilution and the solvating medium contributions are properly accounted for. This excellent agreement is observed for a wide range of shearing frequencies, for homopolymers dissolved under Θ and non-Θ conditions, and for homopolymers of linear, star, and comb geometries. Quantitative predictions of such properties which reflect chain dynamics are essential to studies evaluating the polymer characterization potential of these experiments. It is clear from the limited number of existing theoretical and experimental comparisons that changes in chain topology give rise to modifications of the relaxation time spectrum; some types of branching give rise to substantial, easily detected spectral modifications, while other structural changes give rise to subtle differences. An evaluation of the characterization potential of such dynamics experiments will require extensive experimental studies together with theoretical predictions for different and frequently more complicated chain structures than have been studied to date; comparisons of measured properties and theoretical predictions for the frequency dependence of OFB and VE properties are essential for determination of the chain topology involved as well as an assessment of the characterization potential of chain dynamics for various types of structural modification. With this in mind, a general bead–spring model has been developed and is presented here that enables predictions of the dynamic properties of bead–spring chains with any arbitrary chain geometry. In addition, special attention has been paid to making the numerical computation of the relaxation spectra of these idealized chains as efficient as possible so that the properties of large chains can be predicted. The efficiencies arise from (1) use of normal coordinates that are constructed from a set that translates with the chain which happens to guarantee that each spectrum will depend on the eigenvalues of a symmetric matrix and (2) finding of equivalent, but more concise, block-diagonal forms of these symmetric matrices for chains of linear, regular star, regular H, and ring geometries. These features make this an excellent model for predicting the effects of chain structure, chain size, and hydrodynamic interaction on low-shear-rate dynamic properties.

II. BSM Formalism for Arbitrary Chain Geometries

The dynamic properties to be modeled are the VE and OFB properties of a dilute solution of identical homopolymers subjected to a homogeneous shear flow. The solvent throughout the solution is modeled as an incompressible Newtonian fluid with a uniform viscosity η_s. Recognizing that the solvent viscosity may vary in the neighborhood of real chains in solution, the η_s used for this idealized fluid represents the average environmental viscosity of the dilute homopolymer solution; in the past it has been approximated by that measured for the pure solvent or by the product of the viscosity of pure solvent and the volume fraction of solvent. Recent evidence suggests that these are frequently poor approximations.[19] The homopolymer is modeled as an assortment of N_b spherical beads connected by N_s Hookean springs. All beads are identical in radius a, mass m, and friction coefficient ζ. Each massless spring is under tension which is directed along the line connecting the ends of the spring and is proportional to the distance separating these ends. The Hookean proportionality constant H is the same $(3kT/b^2)$ for all springs (k is the Boltzmann constant, T the absolute temperature, and b^2 the mean-square distance between connected beads in a nonflowing solution). The size of the bead–spring chain elements is sufficiently small that fluctuating random forces associated with thermal motions cannot be neglected. These randomizing forces

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oppose the orienting action of the hydrodynamic and spring forces and are approximated with a smoothed-out Brownian motion force.

At this point we turn to the BSM formulation of Bird et al.,[7] rather than that of Zimm,[2] to generalize from linear chains to arbitrary chain geometry.[20] This equivalent formulation reported in DPL[7] is a natural choice since its normal coordinates are constructed from a set that translates with the chain. Throughout this generalization the forms of the DPL matrix equations describing the chain configuration, motion, and dynamic properties is found to apply to all chain structures; only the elements (and eigenvalues) of the matrices appearing in these equations vary with chain structure. This enables us to bypass the derivations of such equations and concentrate on the generalization of the $\bar{\mathbf{B}}$, $\mathbf{H}$, and $\mathbf{L}$ matrices.

A. The Elements of $\bar{\mathbf{B}}$, H, and L. The $N_s \times N_b$ matrix $\bar{\mathbf{B}}$ summarizes the following transformation between the set of laboratory $\{\mathbf{r}_\nu\}$ and connector $\{\mathbf{Q}_i\}$ coordinate systems.

$$\mathbf{Q}_k = \sum_\nu \bar{B}_{k\nu}\mathbf{r}_\nu \tag{1}$$

Here Σ_ν indicates a sum over all beads. The generalized form for the elements of this matrix is

$$\bar{B}_{k\nu} = \delta_{\gamma_k\nu} - \delta_{\mu_k\nu} \tag{2}$$

with δ_{ij} the Kronecker δ and indices γ_k and μ_k defined such that connector vector $\mathbf{Q}_k$ points from bead γ_k to bead μ_k. The particular values of these indices, of course, depend on the schemes used to number the beads and connector vectors and are discussed in more detail in Section III.

The elements of the $N_b \times N_b$ hydrodynamic interaction matrix $\mathbf{H}$ arise from preaveraging the tensor $\boldsymbol{\Omega}_{\nu\mu}$.

$$\boldsymbol{\Omega}_{\nu\mu} = \frac{(1-\delta_{\nu\mu})}{8\pi\eta_s r_{\nu\mu}}\left(\delta + \frac{\mathbf{r}_{\nu\mu}\mathbf{r}_{\nu\mu}}{r_{\nu\mu}^2}\right) + \frac{a^2(1-\delta_{\nu\mu})}{4\pi\eta_s r_{\nu\mu}^3}\left(\frac{1}{3}\delta - \frac{\mathbf{r}_{\nu\mu}\mathbf{r}_{\nu\mu}}{r_{\nu\mu}^2}\right) \tag{3}$$

This tensor describes the hydrodynamic interaction between beads ν and μ and is expressed in terms of the unit tensor δ and $\mathbf{r}_{\nu\mu} = \mathbf{r}_\nu - \mathbf{r}_\mu$, the vector representing the separation of these beads. Its form is actually that given by Oseen[21] to which the first-order correction term of Rotne and Prager[22] or that of Yamakawa[23] has been added. This correction term, proportional to a^2 and not found in DPL, is included here because the original Oseen tensor has the physically unrealistic property of not being positive definite when the beads are close together. The average of this tensor is determined with the Gaussian distribution function which characterizes the chain in a nonflowing system. First, after performing the polar and azimuthal integrations, one obtains the important result

$$\langle \boldsymbol{\Omega}_{\nu\mu}\rangle_{eq} = \frac{1}{6\pi\eta_s}\langle r_{\nu\mu}^{-1}\rangle_{eq}\delta \tag{4}$$

Here, $\langle r_{\nu\mu}^{-1}\rangle_{eq}$ is the mean inverse distance between beads ν and μ. This is, of course, the same result found for the average of the Oseen tensor alone; the correction term vanishes because of radial symmetry of the distribution function. Hence, in the equilibrium-average limit, the first-order correction to the Oseen tensor for these flexible Gaussian chains is not important regardless of the chain geometry. The remaining radial integrations are straightforward for Gaussian chains:

$$\langle r_{\nu\mu}^{-1}\rangle_{eq} = \left(\frac{6}{\pi b^2 n_{\nu\mu}}\right)^{1/2} \tag{5}$$

The factor $n_{\nu\mu}$ is the equivalent number of springs in the chain between beads μ and ν. After performing such integrations for a wide variety of chains with combinations of branches and/or rings, we found that $n_{\nu\mu}$ may be evaluated in a manner analogous to that used to determine the equivalent resistance between two points in an electrical circuit. In this analogy the configuration of the beads attached by springs represents the electrical circuit; the beads are considered to be ideal conductors and the springs ideal resistors of unit resistance. There are, however, more elegant ways[24,25] to deduce this analogy for Gaussian chains. Expressions for $n_{\nu\mu}$ are given in Table II for selected chain geometries.

Combining these results with the usual construction of $\mathbf{H}$ yields

$$H_{\nu\mu} = \delta_{\nu\mu} + (1-\delta_{\nu\mu})h^*(2/n_{\nu\mu})^{1/2} \tag{6}$$

with h^* the hydrodynamic interaction parameter of Thurston and Peterlin:[26]

$$h^* = \frac{\zeta}{\eta_s}\left(\frac{1}{12\pi^3 b^2}\right)^{1/2} \tag{7}$$

We define the elements of the $N_s \times N_s$ symmetric matrix $\mathbf{L}$ as

$$L_{ij} = \sum_\nu\sum_\mu \bar{B}_{i\nu}H_{\nu\mu}\bar{B}_{j\mu} \tag{8}$$

In DPL, which is restricted to linear chains, this matrix is denoted $\tilde{\mathbf{A}}$ and called the "modified" Rouse matrix; it is modified from that of Rouse in that it includes hydrodynamic interaction effects. In contrast, the $\mathbf{L}$ matrix is more extensively modified since it is applicable to chains having any geometry. The symmetry of the real and dimensionless $\mathbf{L}$ matrix is very important. First, it guarantees that all its eigenvalues exist and that they are real. This feature is used to construct the normal coordinates required to decouple the diffusion equation and to find its equilibrium configurational distribution function. Second, it is important because efficient numerical algorithms exist to compute accurately all of the eigenvalues of symmetric matrices. Calculation of these eigenvalues is essential to predict dynamic properties, and in general, properties computed for chains of finite size with exact eigenvalues fit OFB and VE data better than those evaluated with various eigenvalue approximation schemes.

B. Small-Amplitude Oscillatory Flow Properties. A special class of dynamical properties is the one dealing with properties of solutions undergoing small-amplitude oscillatory shear flow. Such flow properties have been characterized by the complex mechano-optic coefficient S^* in OFB experiments and the complex viscosity coefficient η^* or the dynamic shear modulus G^* in VE studies and are predicted by the BSM only for very dilute solutions of flexible homopolymers experiencing low shear rates. The form of the equations predicting S^*, η^*, and G^* are found to be independent of chain structure:

$$S^* = q'nb^2\sum_p \frac{\tau_p}{1+i\omega\tau_p} + S_s \tag{9}$$

$$\eta^* = nkT\sum_p \frac{\tau_p}{1+i\omega\tau_p} + \eta_s \tag{10}$$

$$G^* = nkT\sum_p \frac{i\omega\tau_p}{1+i\omega\tau_p} + i\omega\eta_s \tag{11}$$

Here q' is an optical factor; n is the number density of chains in the suspension; ω is the angular shearing frequency; τ_p is the relaxation time for the pth normal mode of internal motion; S_s and η_s represent the frequency in-

dependent contribution of the chain environment to S^* and η^* and, in general, will differ from those of the bulk solvent; $\sum_p$ indicates a sum over all N normal modes; $N = N_s - N_c$ or the number of positive eigenvalues in the matrix $\mathbf{L}$; N_c is the number of cyclic structures within the chain; and $i = (-1)^{1/2}$. For the special case of an isorefractive homopolymer/solvent system, the optical factor is related to the index of refraction n_s of the solvent and the intrinsic optical anisotropy $(\alpha_1 - \alpha_2)$ of the Kuhn statistical segment by

$$q' = \frac{4\pi}{45} \frac{(n_s^2 + 2)^2}{n_s} \frac{\alpha_1 - \alpha_2}{b^2} \tag{12}$$

In general, each relaxation time τ_p is inversely proportional to one of the N positive (and possibly degenerate) eigenvalues of the $\mathbf{L}$ matrix:

$$\tau_p = \frac{b^2\zeta}{6kT\lambda_p} \tag{13}$$

The relaxation times are customarily assembled in decreasing order, $\tau_1 \geq \tau_2 \geq \ldots \tau_N$, and τ_1 is called the longest relaxation time. The spacings of the relaxation times can be dramatically affected by chain size, chain geometry, and to a lesser extent the degree of hydrodynamic interaction; the number of relaxation times is only affected by chain size. The ways to compute accurately all of the λ_p are limited. This limitation becomes particularly acute as the complexity of the chain structure increases, as well as when intermediate degrees of hydrodynamic interaction or chains of finite size are involved. In these cases the spectrum of eigenvalues is best computed with a numerical algorithm on a digital computer.

III. L Matrix for Special Chain Geometries

Explicit forms of the $\mathbf{L}$ matrix must be known before its eigenvalues are computed and used to predict dynamic properties with eq 9–13. These forms are developed here for only two broad classes of chain structure: chains with comb geometry and chains which have what we term cyclic-comb geometry. The restriction arises only from our desire here to use simple, rather than completely general, schemes to number the beads and springs.

Chains with comb or cyclic-comb geometry encompass such a wide variety of chain structures that more complicated bead–spring numbering schemes will seldom be needed. In particular, chains with comb geometry are defined as those with straight-chain branches attached to any bead on a straight-chain backbone; chains with cyclic-comb geometry differ from those with comb geometry only in that the backbone is constrained to form a ring. Hence included in these two broad geometries are several important simple chain geometries such as linear, regular star, regular H, regular comb, ring, and regular cyclic-comb geometries. Also included are many irregular chain structures which could represent polydispersity components in real samples of these simple chain structures.

To concisely represent the wide variety of possible bead–spring structures available to chains of comb or cyclic-comb geometry, a set of chain structure parameters is introduced. This particular set has been designed to be applicable to both geometries. These parameters are NBB, the number of beads in the backbone; NBR, the number of branches attached to the backbone; NBPB(I), the number of the backbone bead to which branch I is attached; and NBEAD(I), the number of beads in branch I. Branch index I varies from 1 to NBR and hence the structure of any comb or cyclic comb is completely specified with 2(NBR + 1) parameters. Note that comb and cyclic-comb structures defined by the same parameters contain the same number of beads but differ in the number of springs; the cyclic-comb structure has an additional ring-closing spring. These parameters are also immensely helpful when introducing the bead–spring numbering schemes and the elements of the $\mathbf{L}$ matrix.

A. Bead–Spring Numbering Schemes. The scheme used to number the beads in combs or cyclic combs is the same. The backbone beads are numbered consecutively along the chain contour from 1 to NBB. The beads of each branch are also numbered consecutively; the bead closest to the backbone on branch I is number

$$1 + \mathrm{NBB} + \sum_{m_b=1}^{I-1} \mathrm{NBEAD}(m_b)$$

and the last bead on branch I is number

$$\mathrm{NBB} + \sum_{m_b=1}^{I} \mathrm{NBEAD}(m_b)$$

The schemes used to number the springs in combs and cyclic combs are slightly different. For combs, the backbone springs are numbered consecutively along the chain contour from 1 to NBB – 1. Likewise the springs along branch I are also numbered consecutively, but the spring attached to the backbone is number

$$\mathrm{NBB} + \sum_{m_b=1}^{I-1} \mathrm{NBEAD}(m_b)$$

and the last spring of branch I is number

$$\mathrm{NBB} - 1 + \sum_{m_b=1}^{I} \mathrm{NBEAD}(m_b)$$

A cyclic comb having the same chain structure parameters as a comb requires a different spring numbering scheme due to the "extra" ring-closing spring in the backbone of cyclic combs. To include this extra spring the backbone springs are numbered from 1 to NBB. This displaces the numbering of the branch springs by one relative to that of combs.

Finally, with the introduction of a specific bead numbering scheme, the connector vector direction is made unique by simply requiring that $\mu_i < \gamma_i$. However, we choose to make a single exception for cyclic combs; the "extra" vector $\mathbf{Q}_{\mathrm{NBB}}$ points from bead NBB to bead 1.

B. Comb and Cyclic-Comb Geometries. In general, the $\mathbf{L}$ matrix only depends on the chain structure and degree of hydrodynamic interaction. Its construction, as prescribed by its general form (eq 8), indicates that first the $\bar{\mathbf{B}}$ and $\mathbf{H}$ matrices are to be assembled followed by two matrix multiplications. However, recognizing that each row of $\bar{\mathbf{B}}$ has at most two nonzero elements, it is convenient to combine eq 2 and 8 and to evaluate the required summations. As a result each element of $\mathbf{L}$ is always found to be a sum (weighted by ± 1) of four elements of $\mathbf{H}$:

$$L_{ij} = H_{\gamma_i,\gamma_j} + H_{\mu_i,\mu_j} - H_{\gamma_i,\mu_j} - H_{\mu_i,\gamma_j} \tag{14}$$

The hydrodynamic interaction elements in this sum represent the four possible interactions occurring between the two beads attached to the ends of submolecules (connector vectors) i and j. Thus besides providing a more concise general form of $\mathbf{L}$, eq 14 suggests that the element L_{ij} represents the hydrodynamic interaction between submolecules i and j.

The use of eq 14 to generate $\mathbf{L}$ for any chain still requires two nontrivial steps: the identification of the indices γ_i and μ_i for each i and the determination of $H_{\nu\mu}$ for any ν and μ. For comb and cyclic-comb structures, both steps

Table I
Summary of γ_i and μ_i for Combs and Cyclic Combs[a]

index	$\mathbf{Q}_i$ location	combs	cyclic combs
γ_i	backbone	$i + 1$	1 + mod (i, NBB)[b]
	any branch	$i + 1$	i
μ_i	backbone	i	i
	connects backbone to branch I	NBPB(I)	NBPB(I)
	all other $\mathbf{Q}_i$	i	$i - 1$

[a] Assumes that connector vector $\mathbf{Q}_i$ points from bead μ_i to bead γ_i and that the bead and spring numbering schemes of section III.A are employed. [b] mod $(i,j) = i - j$ Integer (i/j).

Table II
Expressions of $n_{\nu\mu}$ for Combs and Cyclic Combs[a]

ν location	μ location	combs[b]	cyclic combs[b]
backbone	backbone	n	$n(1 - n/\mathrm{NBB})$
branch I	backbone	$n_1 + n_L$	$n_1 + n_L(1 - n_L/\mathrm{NBB})$
backbone	branch J	$n_2 + n_L$	$n_2 + n'_L(1 - n'_L/\mathrm{NBB})$
branch I	branch J		
$I = J$		n	n
$I \neq J$		$n_1 + n_2 + n''_L$	$n_1 + n_2 + n''_L(1 - n''_L/\mathrm{NBB})$

[a] Assumes that the bead–spring numbering schemes of section III.A are employed. [b] $n = |\mu - \nu|$; $n_1 = (\nu - \mathrm{NBB}) - \sum_{m_b=1}^{I-1}\mathrm{NBEAD}(m_b)$; $n_2 = (\mu - \mathrm{NBB}) - \sum_{m_b=1}^{I-1}\mathrm{NBEAD}(m_b)$; $n_L = |\mathrm{NBPB}(I) - \mu|$; $n'_L = |\mathrm{NBPB}(I) - \nu|$; $n''_L = |\mathrm{NBPB}(I) - \mathrm{NBPB}(J)|$.

are straightforward with the bead–spring numbering schemes introduced in section III.A. The first step is summarized in Table I. Note that these tabulated relations, which identify the beads attached to the ends of each connector vector, depend on whether the vector is located on the backbone or a branch and whether the chain has comb or cyclic-comb geometry. Similarly, Table II summarizes the expressions for $n_{\nu\mu}$ required to evaluate the elements $H_{\nu\mu}$ with eq 6. From both sets of expressions it is clear that generating **L** for large or irregular chains can be laborious. FORTRAN software has recently been reported[27] that uses these expressions to generate and compute the eigenvalues of **L** for any comb or cyclic comb.

In the remaining parts of section III, explicit forms of **L** are presented for six special classes of combs or cyclic combs. Each of these classes has simple, or at least highly regular, chain geometries. The forms are all based on eq 14 and Tables I and II. For convenience, these matrices are expressed in terms of one or more of four types of submatrices. The first type of submatrix represents all of the hydrodynamic interactions occurring between two submolecules on the backbone. These submatrices are square and symmetric and are found in **L** for every chain containing one or more backbone submolecules; they are always denoted with an uppercase A. The second type of submatrix represents all of the hydrodynamic interactions occurring between a submolecule on the backbone and a submolecule on a particular branch. These submatrices are never symmetric and usually are not square; they are always denoted with an uppercase V. The third type of submatrix represents all of the hydrodynamic interactions occurring between two submolecules on the same branch. These submatrices are square and symmetric and are denoted with an uppercase U. The last type of submatrix represents all of the hydrodynamic interactions occurring between submolecules on different branches. These submatrices, denoted with a uppercase W, are square and symmetric.

C. Linear Chains. Linear chains are a particularly simple special case of combs. Their structure can be summarized in terms of a simple comb parameter NBB; the remaining comb parameters, NBR, NBPB(I), and NBEAD(I), are either zero or undefined. Alternatively, these chains could be represented by any parameter indicating the chain length such as the total number of springs in the chain N_s. In this section N_s is preferred since it also happens to equal N, the number of normal modes of internal motion. The two parameters only differ by 1: NBB = $N_s + 1$. The **L** matrix for linear chains only needs to have two parameters (N_s and h^*) assigned to make its elements unique. From the prescriptions of section III.B for these special combs, eq 14 is found to have a single form.

$$L_{ij} = H_{i+1,j+1} + H_{i,j} - H_{i+1,j} - H_{i,j+1} \tag{15}$$

After evaluating the required hydrodynamic interaction elements with eq 6 and the expressions for $n_{\nu\mu}$ in Table II, the elements of **L** may be compactly represented as

$$L_{ij} = a(|i - j| + 1) \qquad i, j = 1, 2, 3, ..., N_s \tag{16}$$

with

$$\begin{aligned} a(i) &= 2[h(0) - h(1)] && i = 1 \\ &= 2h(i - 1) - h(i) - h(i - 2) && i = 2, 3, 4, ..., N_s \end{aligned} \tag{17}$$

and

$$\begin{aligned} h(n) &= 1 && n = 0 \\ &= h^*(2/n)^{1/2} && n = 1, 2, 3, ..., N_s \end{aligned} \tag{18}$$

The elements of **L** and its N_s eigenvalues are identical with those of the **B** matrix originally reported by Lodge and Wu[5] even though a different bead numbering scheme has been used here. These eigenvalues are nondegenerate and vary between 0 and 4 as long as h^* is within its free-draining and non-free-draining limits of about 0.00 and 0.25, respectively. Closed-form expressions for these eigenvalues are only known for small chains or for free-draining chains; these expressions are listed in Table III.

D. Regular Stars. A regular star, first described by Zimm and Kilb,[3] is a chain composed of f arms attached to a central bead with each arm made up of n_b beads. The total numbers of beads, springs, and normal modes in such a chain are $fn_b + 1$, fn_b, an fn_b, respectively. Since these highly symmetric chains are also a special class of combs (NBB = 1, NBR = f, NBPB(I) = 1, and NBEAD(I) = n_b with $I = 1, 2, ..., f$), the prescriptions of section III.B can be used to show that the $N_s \times N_s$ **L** matrix for regular stars is

$$\mathbf{L} = \begin{bmatrix} \mathbf{U} & \mathbf{W} & \mathbf{W} & \dots & \mathbf{W} \\ \mathbf{W} & \mathbf{U} & \mathbf{W} & \dots & \mathbf{W} \\ \mathbf{W} & \mathbf{W} & \mathbf{U} & \dots & \mathbf{W} \\ \vdots & & & & \\ \mathbf{W} & & & & \mathbf{U} \end{bmatrix} \tag{19}$$

Each row or column in the above expression contains f symmetric submatrices each of order n_b. The elements of the **U** and **W** submatrices are defined as

$$U_{ij} = a(|i - j| + 1) \qquad i, j = 1, 2, 3, ..., n_b \tag{20}$$

$$W_{ij} = -a(i + j) \qquad i, j = 1, 2, 3, ..., n_b \tag{21}$$

In general, the fn_b eigenvalues of **L** are identical with the nonzero eigenvalues of the Zimm–Kilb **HA** matrix. As shown in section IV.B, n_b of these eigenvalues are nondegenerate and depend on f, n_b, and h^*; the remaining eigenvalues are $(f - 1)$-fold degenerate and only depend on n_b and h^*. All but the largest of these eigenvalues vary between 0 and 4 for the usual values of h^* between 0.00 and 0.25; the upper bound of this largest eigenvalue is $f + 1$. Closed-form expressions for the eigenvalues of se-

Table III
Closed-Form Eigenvalue Expressions for Selected Linear Chains

eigenvalue expression	restriction
$\lambda_p = 4 \sin^2 [\pi p/[2(N_s + 1)]]$	$h^* = 0$ and $p = 1, 2, 3, ..., N_s$
$\lambda_1 = 2 - 2(2)^{1/2}h^*$	$N_s = 1$
$\lambda_1 = 1 - h^*$ $\lambda_2 = 3 - [4(2)^{1/2} - 1]h^*$	$N_s = 2$
$\lambda_1 = 2 + [1 - (5/2)2^{1/2} - (1/2)(2/3)^{1/2}]h^* - [2 - x_1h^* + x_2(h^*)^2]^{1/2}$ $\lambda_2 = 2 + [(2/3)^{1/2} - 2^{1/2} - 2]h^*$ $\lambda_3 = 2 + [1 - (5/2)2^{1/2} - (1/2)(2/3)^{1/2}]h^* + [2 - x_1h^* + x_2(h^*)^2]^{1/2}$ $x_1 = 4(2(2)^{1/2} - 1)$ $x_2 = 59/3 - 9(2)^{1/2} + 1/3^{1/2} - (2/3)^{1/2}$	$N_s = 3$
$\lambda_1 = 3/2 - x_1h^* - [5/4 + x_2h^* + x_3(h^*)^2]^{1/2}$ $\lambda_2 = 5/2 + x_4h^* - [5/4 + x_5h^* + x_6(h^*)^2]^{1/2}$ $\lambda_3 = 3/2 - x_1h^* + [5/4 + x_2h^* + x_3(h^*)^2]^{1/2}$ $\lambda_4 = 5/2 + x_4h^* + [5/4 + x_5h^* + x_6(h^*)^2]^{1/2}$ $x_1 = 1 + 2^{1/2}[5/4 - 1/3^{1/2}]$ $x_2 = 6^{1/2} - (13/4)2^{1/2} - 2$ $x_3 = 179/24 + 2(2)^{1/2} - 2(2/3)^{1/2} - 3(3)^{1/2}$ $x_4 = 1 - 2^{1/2}[11/4 + 1/3^{1/2}]$ $x_5 = 6 - (29/4)2^{1/2} - (2/3)^{1/2}$ $x_6 = 755/24 - 18(2)^{1/2} - 6(2/3)^{1/2} + 7/3^{1/2}$	$N_s = 4$

Table IV
Closed-Form Eigenvalue Expressions[a] for Selected Regular Stars

eigenvalue expression	restriction
$\lambda_p = 4 \sin^2 [\pi p/[2(2n_b + 1)]]$	$h^* = 0$ and $p = 1, 3, 5, ..., 2n_b - 1$
$\lambda_1 = 1 - h^*$ $\lambda_2 = (1 + f) - [2f(2)^{1/2} - (f - 1)]h^*$	$n_b = 1$
$\lambda_1 = 3/2 - x_1h^* - [5/4 + x_2h^* + x_3(h^*)^2]^{1/2}$ $\lambda_2 = (f + 3)/2 + x_4h^* - [(f^2 - 2f + 5)/4 + x_5h^* + x_6(h^*)^2]^{1/2}$ $\lambda_3 = 3/2 - x_1h^* + [5/4 + x_2h^* + x_3(h^*)^2]^{1/2}$ $\lambda_4 = (f + 3)/2 + x_4h^* + [(f^2 - 2f + 5)/4 + x_5h^* + x_6(h^*)^2]^{1/2}$	$n_b = 2$

[a] The eigenvalues with odd indices are $(f - 1)$-fold degenerate; $x_1 = 1 + 2^{1/2}[5/4 - 1/(3)^{1/2}]$; $x_2 = 6^{1/2} - (13/4)2^{1/2} - 2$; $x_3 = 179/24 + 2(2)^{1/2} - 2(2/3)^{1/2} - 3(3^{1/2})$; $x_4 = f - 1 - (3f + 5)2^{1/2}/4 - (f - 1)(2/3)^{1/2}$; $x_5 = [(2/3)^{1/2} - (5/4)2^{1/2}]f^2 + [4 + 2^{1/2}/2 - 4(2/3)^{1/2}]f + [3(2/3)^{1/2} - (13/4)2^{1/2} - 2]$; $x_6 = [251/24 - 1/3^{1/2} - 4(2^{1/2})(1 + 1/3^{1/2})]f^2 + [-107/12 + 10/3^{1/2} + 6(2/3)^{1/2} - 2(2)^{1/2}]f + [179/24 - 9/3^{1/2} + 2(2^{1/2})(1 - 1/3^{1/2})]$.

lected regular stars are collected in Table IV. The eigenvalues listed there having odd indices are $(f - 1)$-fold degenerate; these eigenvalues are also the same as the odd-indexed eigenvalues of a linear chain composed of $2n_b$ springs when computed at the same degree of hydrodynamic interaction.

E. Regular H Chains. A regular H chain has two equal-length, straight-chain branches attached to each end of a straight-chain backbone. Its structure can be summarized in terms of two parameters: n_b, the number of beads in each of the four arms, and n_0, the number of beads in the backbone (excluding the two end beads attached to the arms). The total number of beads, springs, and normal modes of motion in these regular H chains are $n_0 + 2 + 4n_b$, $n_0 + 1 + 4n_b$, and $n_0 + 1 + 4n_b$, respectively. Alternatively, the structure of these special combs can also be represented by NBB = $n_0 + 2$, NBR = 4, NBPB(1) = NBPB(2) = 1, NBPB(3) = NBPB(4) = $n_0 + 2$, and NBEAD(I) = n_b for all I. Using the prescription for combs of section III.B, the **L** matrix of regular H chains is

$$\mathbf{L} = \begin{bmatrix} \mathbf{A} & \mathbf{V}_1 & \mathbf{V}_1 & \mathbf{V}_2 & \mathbf{V}_2 \\ \mathbf{V}_1^T & \mathbf{U} & \mathbf{W} & \mathbf{W}_1 & \mathbf{W}_1 \\ \mathbf{V}_1^T & \mathbf{W} & \mathbf{U} & \mathbf{W}_1 & \mathbf{W}_1 \\ \mathbf{V}_2^T & \mathbf{W}_1 & \mathbf{W}_1 & \mathbf{U} & \mathbf{W} \\ \mathbf{V}_2^T & \mathbf{W}_1 & \mathbf{W}_1 & \mathbf{W} & \mathbf{U} \end{bmatrix} \quad (22)$$

Most of the submatrices in the above expression are square and symmetric; only submatrices $\mathbf{V}_1$, $\mathbf{V}_2$, and their transposes are not. The **A** submatrix, of order $n_0 + 1$, represents the hydrodynamic interaction occurring between submolecules on the backbone; its elements are identical with those of **L** for a linear chain (eq 16) composed of $n_0 + 1$ springs:

$$A_{ij} = a(|i - j| + 1) \qquad i, j = 1, 2, 3, ..., n_0 + 1 \quad (23)$$

The **U** matrix, appearing four times along the diagonal of **L**, is of order n_b and its elements are again given by eq 20. Submatrices $\mathbf{V}_1$ and $\mathbf{V}_2$, each appearing twice in the top row of **L**, each have dimensions of $(n_0 + 1) \times n_b$ with elements defined by

$$V_1(i,j) = -a(i + j) \qquad i = 1, 2, 3, ..., n_0 + 1 \quad (24)$$

$$V_2(i,j) = +a(-i + j + n_0 + 2) \qquad i = 1, 2, 3, ..., n_0 + 1 \quad (25)$$

Column index j varies from 1 to n_b. Submatrices **W** and $\mathbf{W}_1$ are both of order n_b. The elements of the former are again given by eq 21 and those of the latter are defined by

$$W_1(i,j) = -a(i + j + n_0 + 1) \qquad i, j = 1, 2, 3, ..., n_b \quad (26)$$

The N_s eigenvalues of **L** for these regular H chains vary between 0 and 5 for values of h^* within 0.00 and 0.25. As shown in section IV.C, n_b eigenvalues are doubly degenerate; the remaining are nondegenerate. The degenerate eigenvalues are independent of n_0 and are the same as the odd-indexed eigenvalues in a linear chain composed of $2n_b$ springs when computed at the same degree of hydrodynamic interaction. As an example of these eigenvalues, closed-form expressions for those of a particularly small chain are reported in Table V.

F. Regular Combs. A regular comb is a comb with equal length arms attached at regular intervals to the

Table V
Closed-Form Eigenvalue Expressions for Simple H, Comb, and Cyclic Comb Chains[a]

Regular H Chain: $n_b = 1$, $n_0 = 0$

define

$s_1 = -3a(1) + 2a(2)$

$s_2 = +3a(1)^2 - 4a(1)a(2) - 3a(2)^2 - 4a(3)^2$

$s_3 = -a(1)^3 + 2a(1)^2a(2) + 3a(1)a(2)^2 - 8a(2)^2a(3) - 4a(2)^3 + 4a(1)a(3)^2$

$a = s_2 - s_1^2/3$

$b = (2s_1^3 - 9s_1s_2 + 27s_3)/27$

$r = (-a/3)^{1/2}$

$\phi = (1/3)[\pi + \tan^{-1}[(-1 - 4a^3/[27b^2])^{1/2}]]$

eigenvalues

$\lambda_1 = -r(\cos\phi + 3^{1/2}\sin\phi) - s_1/3$

$\lambda_2 = 1 - h^*$

$\lambda_3 = 1 - h^*$

$\lambda_4 = 2r\cos\phi - s_1/3$

$\lambda_5 = -r(\cos\phi - 3^{1/2}\sin\phi) - s_1/3$

Regular Comb: $f = 3$, $n_b = 1$, $n_0 = 0$

define

$x_1 = 1 + 2^{1/2}[5/4 - 1/3^{1/2}]$

$x_2 = 6^{1/2} - (13/4)2^{1/2} - 2$

$x_3 = 179/24 + 2(2)^{1/2} - 2(2/3)^{1/2} - 3(3)^{1/2}$

$s_1 = a(2) + a(4) - 3a(1)$

$s_2 = 3[a(1)^2 - a(2)^2 - a(3)^2] - 2[a(1)a(2) + a(1)a(4) - a(2)a(3)] + a(2)a(4)$

$s_3 = [a(1) - a(2)][2a(3)^2 - a(1)[a(1) - a(4)]] + [a(2) - a(3)][a(1)[a(2) - a(3)] - 4a(2)a(3)] + 2a(2)^2[a(1) - a(4)]$

$a = s_2 - s_1^2/3$

$b = (2s_1^3 - 9s_1s_2 + 27s_3)/27$

$r = (-a/3)^{1/2}$

$\phi = (1/3)[\pi + \tan^{-1}[(-1 - 4a^3/[27b^2])^{1/2}]]$

eigenvalues

$\lambda_1 = 3/2 - x_1h^* - [5/4 + x_2h^* + x_3(h^*)^2]^{1/2}$

$\lambda_2 = -r(\cos\phi + 3^{1/2}\sin\phi) - s_1/3$

$\lambda_3 = -r(\cos\phi - 3^{1/2}\sin\phi) - s_1/3$

$\lambda_4 = 3/2 - x_1h^* + [5/4 + x_2h^* + x_3(h^*)^2]^{1/2}$

$\lambda_5 = 2r\cos\phi - s_1/3$

Regular Cyclic Comb: $f = 3$, $n_b = 1$, $n_0 = 0$

define

$a = 3(1 - 3^{1/2}h^*)$

$b = 2 - h^*[2(2)^{1/2} + 3^{1/2} + (3/4)^{1/2} - 2(6/5)^{1/2}]$

$c = h^*(3 + 6^{1/2} - 3(2/5)^{1/2}) - 3^{1/2}$

nonzero eigenvalues

$\lambda_1 = (a + b)/2 - [(a - b)^2 + 4c^2]^{1/2}/2$

$\lambda_2 = (a + b)/2 - [(a - b)^2 + 4c^2]^{1/2}/2$

$\lambda_3 = 2 + 2h^*[3^{1/2} + (3/4)^{1/2} - 2^{1/2} - 2(6/5)^{1/2}]$

$\lambda_4 = (a + b)/2 + [(a - b)^2 + 4c^2]^{1/2}/2$

$\lambda_5 = (a + b)/2 + [(a - b)^2 + 4c^2]^{1/2}/2$

[a] Note: use eq 17 to evaluate $a(i)$; angle 3ϕ is in quadrant III for $0 < h^* < 0.36$.

backbone. Its structure can be summarized in terms of three parameters: f, the number of arms; n_b, the number of beads per arm; and n_0, the number of backbone beads between the arms. The total number of beads, springs, and normal modes of motion are $f(n_0 + n_b + 1) + n_0$, $f(n_0 + n_b + 1) + n_0 - 1$, and $f(n_0 + n_b + 1) + n_0 - 1$, respectively. Alternatively, a regular comb could also have been characterized by NBB = $n_0 + f(n_0 + 1)$, NBR = f, NBPB(I) = $I(n_0 + 1)$, and NBEAD(I) = n_b with $I = 1, 2, 3, \ldots, f$. Using the prescription for combs of section III.B, the **L** matrix for a regular comb is

$$\mathbf{L} = \begin{bmatrix} \mathbf{A} & \mathbf{V}_1 & \mathbf{V}_2 & \mathbf{V}_3 & \cdots & \mathbf{V}_{f-1} & \mathbf{V}_f \\ \mathbf{V}_1^T & \mathbf{U} & \mathbf{W}_1 & \mathbf{W}_2 & \cdots & \mathbf{W}_{f-2} & \mathbf{W}_{f-1} \\ \mathbf{V}_2^T & \mathbf{W}_1 & \mathbf{U} & \mathbf{W}_1 & \cdots & \mathbf{W}_{f-3} & \mathbf{W}_{f-2} \\ \mathbf{V}_3^T & \mathbf{W}_2 & \mathbf{W}_1 & \mathbf{U} & \cdots & & \\ \cdot & \cdot & \cdot & & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \ddots & \cdot & \cdot \\ \cdot & \cdot & \cdot & & & \cdot & \cdot \\ \mathbf{V}_{f-1}^T & \mathbf{W}_{f-2} & & & \cdots & \mathbf{U} & \mathbf{W}_1 \\ \mathbf{V}_f^T & \mathbf{W}_{f-1} & & & \cdots & \mathbf{W}_1 & \mathbf{U} \end{bmatrix} \quad (27)$$

Most of the submatrices in the above expression are square and symmetric; only the f submatrices $\mathbf{V}_I$ and their transposes are not. The **A** submatrix is of order $f(n_0 + 1) + n_0 - 1$ and its elements are

$$A_{ij} = a(|i - j| + 1) \qquad i, j = 1, 2, 3, \ldots, f(n_0 + 1) + n_0 - 1 \quad (28)$$

The elements of the **U** submatrix are again give by eq 20; it is of order n_b. The f submatrices $\mathbf{V}_I$, found only in the top row of submatrices, each have dimensions $[f(n_0 + 1) + n_0 - 1] \times n_b$. Within these submatrices are the hydrodynamic interactions occurring between submolecules on the backbone and the Ith arm. Their elements are defined as

$$V_I(i,j) = +a(-i + j + I(n_0 + 1))$$

for

$$i = 1, 2, 3, \ldots, I(n_0 + 1) - 1$$

and

$$V_I(i,j) = -a(+i + j - I(n_0 + 1) + 1)$$

for

$$i = I(n_0 + 1), I(n_0 + 1) + 1, \ldots, f(n_0 + 1) + n_0 - 1 \quad (29)$$

with column index j varying from 1 to n_b for each submatrix. Finally, the elements of the $f - 1$ submatrices denoted $\mathbf{W}_I$ are defined by

$$W_I(i,j) = -a(i + j + I(n_0 + 1)) \qquad i, j = 1, 2, 3, \ldots, n_b \quad (30)$$

This submatrix represents the hydrodynamic interaction occurring between submolecules on arms separated by $I(n_0 + 1)$ backbone springs. In general, the N_s eigenvalues of the **L** matrix for these regular combs vary between 0 and 5 for values of h^* between 0.00 and 0.25. All these eigenvalues are nondegenerate when $n_0 \neq n_b$. However, when $n_0 = n_b$, n_b of the eigenvalues are doubly degenerate; these eigenvalues are again the same as the odd-indexed eigenvalues for a linear chain composed of $2n_b$ springs when computed for the same degree of hydrodynamic interaction. Closed-form expressions for the eigenvalues of a small regular comb can be found in Table V.

G. Rings. A ring is a purely cyclic structure composed of the same number of beads and springs. Its structure, just as for linear chains, can be summarized in terms of a single parameter indicating the chain length. In this section, we employ the number of springs N_s. Since rings are actually a special class of cyclic combs (NBB = N_s, NBR = 0; NBEAD(I) and NBPB(I) are undefined), the prescriptions of section III.B can be used to show that the $N_s \times N_s$ **L** matrix for rings is

$$L_{ij} = a_r(|i - j| + 1) \qquad i, j = 1, 2, 3, \ldots, N_s \quad (31)$$

with

$$a_r(i) = 2[h_r(0) - h_r(1)] \qquad i = 1$$
$$= 2h_r(i - 1) - h_r(i) - h_r(i - 2) \qquad i = 2, 3, 4, \ldots, N_s \quad (32)$$

and

$$h_r(n) = 1 \qquad n = 0, N_s$$
$$= h^*[2/[n(1 - n/N_s)]]^{1/2} \qquad n = 1, 2, 3, \ldots, N_s - 1 \quad (33)$$

The elements of **L**, and its N_s eigenvalues, are identical with those of the **HA** matrix originally reported by Bloomfield and Zimm[4] even though a different bead numbering scheme is used here. Most of these eigenvalues are doubly degenerate and vary between 0 and 4 as long as h^* varies between 0.00 and 0.25; one eigenvalue is always zero. Closed-form expressions for the degenerate eigen-

values of selected rings are listed in Table VI; the expressions are ordered in terms of the magnitude of the eigenvalue and are simply indexed from 1 to $(N_s - 1)/2$ or 1 to $(N_s - 2)/2$ depending on whether N_s is odd or even.

H. Regular Cyclic Combs. A regular cyclic comb is a cyclic comb with equal length arms attached at regular intervals to its (closed-loop) backbone. Its structure can be summarized in terms of the same three parameters used for regular combs: f, the number of arms; n_b, the number of beads per arm; and n_0, the number of backbone beads between the arms. The total numbers of beads, springs, and normal modes of motion are $f(n_0 + n_b + 1)$, $f(n_0 + n_b + 1)$, and $f(n_0 + n_b + 1) - 1$, respectively. Alternatively, a regular comb could be characterized by NBB = $f(n_0 + 1)$; NBR = f; NBPB(I) = $I(n_0 + 1)$, and NBEAD(I) = n_b with $I = 1, 2, 3, ..., f$. From the prescription for cyclic combs of section III.B, the **L** matrix for a regular cyclic comb is

$$\mathbf{L} = \begin{bmatrix} \mathbf{A} & \mathbf{V}_1 & \mathbf{V}_2 & \mathbf{V}_3 & \cdots & \mathbf{V}_{f-1} & \mathbf{V}_f \\ \mathbf{V}_1^T & \mathbf{U} & \mathbf{W}_1 & \mathbf{W}_2 & \cdots & \mathbf{W}_{f-2} & \mathbf{W}_{f-1} \\ \mathbf{V}_2^T & \mathbf{W}_1 & \mathbf{U} & \mathbf{W}_1 & \cdots & \mathbf{W}_{f-3} & \mathbf{W}_{f-2} \\ \mathbf{V}_3^T & \mathbf{W}_2 & \mathbf{W}_1 & \mathbf{U} & \cdots & & \\ \cdot & \cdot & \cdot & & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot & \cdot \\ \mathbf{V}_{f-1}^T & \mathbf{W}_{f-2} & & & \cdots & \mathbf{U} & \mathbf{W}_1 \\ \mathbf{V}_f^T & \mathbf{W}_{f-1} & & & \cdots & \mathbf{W}_1 & \mathbf{U} \end{bmatrix} \quad (34)$$

As found for regular combs, most of the submatrices in the above expression are square and symmetric; only the f submatrices $\mathbf{V}_I$ and their transposes are not. The **A** submatrix, of order $f(n_0 + 1)$, represents all the hydrodynamic interaction occurring between submolecules on the cyclic backbone; its elements are

$$A_{ij} = a_r(|i - j| + 1) \qquad i, j = 1, 2, 3, ..., f(n_0 + 1) \quad (35)$$

The **U** submatrix, found f times on the diagonal, represents the hydrodynamic interaction occurring between submolecules on the same straight-chain branch. It is of order n_b and its elements are again given by eq 20. The f submatrices $\mathbf{V}_I$, located in the top row, have dimensions $f(n_0 + 1) \times n_b$. These submatrices contain the hydrodynamic interaction occurring between submolecules on the cyclic backbone and the Ith straight-chain arm. Their elements are defined as

$$V_I(i,j) = +a_v(-i + I(n_0 + 1) - 1, j)$$

for

$$i = 1, 2, 3, ..., I(n_0 + 1) - 1$$

and

$$V_I(i,j) = -a_v(+i - I(n_0 + 1), j)$$

for

$$i = I(n_0 + 1), I(n_0 + 1) + 1, ..., f(n_0 + 1) \quad (36)$$

with

$$a_v(i,j) = h_v(i,j) + h_v(i+1, j-1) - h_v(i, j-1) - h_v(i+1, j) \quad (37)$$

$$h_v(i,j) = 1 \quad \text{if } j = 0, \text{ and } i = 0 \text{ or } f(n_0 + 1)$$
$$= h^* \left[\frac{2}{i[1 - i/[f(n_0 + 1)]] + j} \right]^{1/2} \quad \text{otherwise.} \quad (38)$$

Column index j varies from 1 to n_b. The last set of $f - 1$ submatrices, denoted $\mathbf{W}_I$, are each of order n_b; their elements are defined by

$$W_I(i,j) = -a[i + j + I(n_0 + 1)(1 - I/f)]; \quad i, j = 1, 2, 3, ..., n_b \quad (39)$$

This submatrix represents all of the hydrodynamic interaction occurring between two submolecules on different arms separated by $I(n_0 + 1)$ backbone springs. In contrast to regular combs, not all the $\mathbf{W}_I$ submatrices defined here are unique; it can be shown with eq 39 that $\mathbf{W}_I = \mathbf{W}_{f-I}$.

In general, the N_s eigenvalues of the **L** matrix for these regular combs vary between 0 and 5 for values of h^* within 0.00 and 0.25. The eigenvalues are either nondegenerate or doubly degenerate. The number of nondegenerate eigenvalues depends on whether f is an odd or even number. For f odd there are $n_0 + n_b + 1$ nondegenerate eigenvalues; for f even there are $2(n_0 + n_b + 1)$ nondegenerate eigenvalues. One of these nondegenerate eigenvalues is always zero; none of the degenerate or nondegenerate eigenvalues are the same as those found for purely linear or cyclic chains. Closed-form eigenvalue expressions for a small cyclic comb are reported in Table V.

IV. Block Diagonal Representations of L for Simple Chain Geometries

The dynamic properties predicted for very large bead–spring chains are of considerable interest since these chains correspond to high molecular weight homopolymers. These properties, however, are the most difficult to compute because the number of steps required in the eigenvalue portion of the computation roughly increases with the cube of the chain size. Only for some highly symmetric chain geometries can the efficiency of the eigenvalue computation be substantially improved. Here the improvements are obtained by transforming the **L** matrix to an equivalent block-diagonal form; the eigenvalue problem then reduces to computing the eigenvalues of several smaller (and symmetric) submatrices instead of computing those of one large matrix. The only block-diagonal forms of **L** presented here are for chains with linear, regular star, regular H, and ring geometries. Most of these forms are new.

A. Linear Chains. Both block-diagonal forms of **L** for linear chains are denoted as **L′** and are obtained with the following similarity transformation.

$$\mathbf{L}' = \mathbf{\Omega}^{-1}\mathbf{L}\mathbf{\Omega} \quad (40)$$

In general, this type of transformation will not affect the eigenvalues. For linear chains **L′** is always a diblock matrix but the form of each block depends on whether the number of springs in the chain is odd or even. When N_s is even, the transformation matrix **Ω** is constructed with two square and symmetric submatrices each of order $N_s/2$ and its inverse is simply its transpose.

$$\mathbf{\Omega} = \frac{1}{2^{1/2}} \begin{bmatrix} \bar{\mathbf{I}} & -\bar{\mathbf{I}} \\ \mathbf{I} & \mathbf{I} \end{bmatrix} \quad (41)$$

Submatrix **I** is the identity matrix and

$$\bar{\mathbf{I}} = \begin{bmatrix} 0 & \cdots & 0 & 0 & 1 \\ 0 & \cdots & 0 & 1 & 0 \\ & & 1 & 0 & 0 \\ & \cdot & & & \\ & \cdot & & & \\ 0 & 1 & & & 0 \\ 1 & 0 & \cdots & & 0 \end{bmatrix} \quad (42)$$

The two blocks along the diagonal of **L′**, denoted **L°** and **L^e**, are square, symmetric and of order $N_s/2$ with elements

$$L_{ij}^{\circ} = a(|i - j| + 1) + a(i + j) \qquad i, j = 1, 2, 3, ..., N_s/2 \quad (43)$$

and

$$L_{ij}^{e} = a(|i - j| + 1) - a(i + j) \qquad i, j = 1, 2, 3, ..., N_s/2 \quad (44)$$

Table VI
Closed-Form Expressions for the Doubly Degenerate Eigenvalues of Selected Rings[a]

eigenvalue expression	restriction
$\lambda_p = 4 \sin^2 [\pi p/N_s]$	$h^* = 0$ and $p = 1, 2, ..., (N_s - 1)/2$ or $p = 1, 2, ..., (N_s - 2)/2$
$\lambda_1 = 3(1 - 3^{1/2}h^*)$	$N_s = 3$
$\lambda_1 = 2(1 - 2^{1/2}h^*)$	$N_s = 4$
$\lambda_1 = (1/2)[5 - 5^{1/2} + 5(-(5/2)^{1/2} + 3/2^{1/2} - 2/3^{1/2})h^*]$ $\lambda_2 = (1/2)[5 + 5^{1/2} + 5(-(5/2)^{1/2} - 3/2^{1/2} + 2/3^{1/2})h^*]$	$N_s = 5$
$\lambda_1 = a_r(1) + a_r(2) - a_r(3) - a_r(4)$ $\lambda_2 = a_r(1) - a_r(2) - a_r(3) + a_r(4)$	$N_s = 6$
$\lambda_1 = a_r(1) + 2^{1/2}[a_r(2) - a_r(4)] - a_r(5)$ $\lambda_2 = a_r(1) - 2a_r(3) + a_r(5)$	$N_s = 8$

[a] Note: use eq 32 to evaluate a_r.

$\mathbf{L}^o$ and $\mathbf{L}^e$ are submatrices that happen to contain the odd- and even-indexed eigenvalues of $\mathbf{L}$, respectively; more generally, the superscripts on these submatrices indicate the odd or even symmetry of their eigenvectors with respect to the center of the chain.

Similarly for chains with N_s odd, the transformation matrix Ω is

$$\Omega = \frac{1}{2^{1/2}} \begin{bmatrix} & \bar{\mathbf{I}} & & 0 & & \bar{\mathbf{I}} & \\ & & & 0 & & & \\ 0 & \cdots & 0 & 2^{1/2} & 0 & \cdots & 0 \\ & & & 0 & & & \\ & -\mathbf{I} & & 0 & & \mathbf{I} & \end{bmatrix} \quad (45)$$

with $\mathbf{I}$ and $\bar{\mathbf{I}}$ both of order $(N_s - 1)/2$. This time though $\mathbf{L}^e$ is of order $(N_s - 1)/2$, $\mathbf{L}^o$ is of order $(N_s + 1)/2$, and their elements are

$$L_{11}^o = a(1) \quad (46)$$

$$L_{i1}^o = L_{1i}^o = 2^{1/2}a(i) \qquad i = 2, 3, 4, ..., (N_s + 1)/2 \quad (47)$$

$$L_{ij}^o = a(|i - j| + 1) + a(i + j - 1) \qquad i, j = 2, 3, 4, ..., (N_s + 1)/2 \quad (48)$$

and

$$L_{ij}^e = a(|i - j| + 1) - a(i + j + 1) \qquad i, j = 1, 2, 3, ..., (N_s - 1)/2 \quad (49)$$

B. Regular Stars. The block-diagonal form of $\mathbf{L}$ for regular stars is found by performing several matrix operations on its secular equation.

$$0 = |\mathbf{L} - \lambda\mathbf{I}| \quad (50)$$

Only matrix operations which do not affect the determinant (and eigenvalues) are chosen. First, by use of eq 19 to represent $\mathbf{L}$ in the secular equation, the submatrices in row $i + 1$ are subtracted from those in row i, and the result is placed in row i for each row except row f. Then the submatrices in row f are replaced with the sum of all original rows. Next submatrix column i is replaced by the sum of the submatrices in columns 1 through i. Finally column f is multiplied by the scalar $-i/f$ and the result is summed to column i for columns 1 through $f - 1$. The resulting block-diagonal form of $\mathbf{L}$ contains f symmetric blocks each of order n_b; $f - 1$ of these blocks are identical and have elements

$$L_{ij}^o = a(|i - j| + 1) + a(i + j) \qquad i, j = 1, 2, 3, ..., n_b \quad (51)$$

The elements of the remaining block are

$$L_{ij}^e = a(|i - j| + 1) - (f - 1)a(i + j) \qquad i, j = 1, 2, 3, ..., n_b \quad (52)$$

For both submatrices, the superscripts only indicate the symmetry of their eigenvectors with respect to the center bead. Note that the expression for $\mathbf{L}^o$, and hence its eigenvalues, only depends on n_b and h^*. These degenerate eigenvalues are the same as the odd eigenvalues of a linear chain composed of $2n_b$ springs. The eigenvalues of $\mathbf{L}^e$, however, only reduce to the even eigenvalues of a linear chain when $f = 2$.

This more concise representation for regular stars was first reported by Mitsuda[28] and Osaki et al.;[6,29] the $\mathbf{L}^o$ and $\mathbf{L}^e$ submatrices of this section are identical with their $\mathbf{H}_1$ and $\mathbf{H}_2$ matrices, respectively. Their derivation, however, differed from the one presented here in that their formalism did not use coordinates that translated with the chain.

C. Regular H Chains. This derivation parallels that for regular stars. Start with the secular equation of $\mathbf{L}$ but use the form of $\mathbf{L}$ for regular H chains (eq 52). Replace the entries in submatrix columns 2 and 3 with their sum and difference, respectively; repeat these operations on columns 4 and 5. Next, perform the analogous operations on the rows to recover the matrix symmetry. Subsequently, interchange submatrix columns 3 and 4 and rows 3 and 4. Finally, divide each element in the submatrices by 2 and multiply submatrix column 1 and row 1 by $2^{1/2}$; the former operation reduces the determinant by $2^{n_0+1+4n_b}$ and the latter increases it by 2^{n_0+1}. All of these operations reduce the secular equation to three blocks. One block, $\mathbf{L}_H$, is a matrix of order $n_0 + 1 + 2n_b$ defined by

$$\mathbf{L}_H = \begin{bmatrix} \mathbf{A} & 2^{1/2}\mathbf{V}_1 & 2^{1/2}\mathbf{V}_2 \\ 2^{1/2}\mathbf{V}_1^T & \mathbf{U} + \mathbf{W} & 2\mathbf{W}_1 \\ 2^{1/2}\mathbf{V}_2^T & 2\mathbf{W}_1 & \mathbf{U} + \mathbf{W} \end{bmatrix} \quad (53)$$

The other two, $\mathbf{L}^o$, are each of order n_b and defined as before by eq 51. The eigenvalues of $\mathbf{L}_H$ depend on n_0, n_b, and h^*; those of $\mathbf{L}^o$ only depend on n_b and h^*. Moreover, the eigenvalues of $\mathbf{L}^o$ for these regular H chains also appear in linear chains composed of $2n_b$ springs when computed for the same degree of hydrodynamic interaction; the superscript on this matrix indicates the odd symmetry of its eigenvectors with respect to bead 1 or bead $n_0 + 2$ when it is applied to regular H chains.

D. Rings. The derivation of the two block-diagonal forms that decouple the eigenvalues from the $\mathbf{L}$ matrix parallels that for linear chains and is not duplicated here. As found for linear chains, the diblock form of rings depends on whether the number of springs in the chain is odd or even. For N_s odd, all the eigenvalues of $\mathbf{L}$ except the eigenvalue which is zero are doubly degenerate. These eigenvalues are summarized in terms of a single symmetric submatrix of order $(N_s - 1)/2$ with elements

$$L_{ij}^e = a_r(|i - j| + 1) - a_r(i + j) \quad (54)$$

For even N_s, the eigenvalue that is zero and the largest eigenvalue are nondegenerate; the remaining $N_s - 2$ eigenvalues are doubly degenerate. This largest nondegenerate eigenvalue is always given by

$$\lambda_{N_s} = \sum_i (-1)^{i+1} a_r(i) = 4[1 + \sum_{n=1}^{N_s-1} (-1)^n h_r(n)] \quad (55)$$

and the degenerate eigenvalues are summarized by a submatrix of order $(N_s - 2)/2$ containing elements

$$L_{ij}^e = a_r(|i - j| + 1) - a_r(i + j + 1) \quad (56)$$

Note that in the free-draining limit, the submatrix $\mathbf{L}^e$ of a linear chain composed of N_s springs is the same as $\mathbf{L}^e$ for a ring composed of $N_s + 1$ springs. Hence, these chains share some of the same eigenvalues as previously reported by Tanaka and Yamakawa.[30]

V. Conclusions and Discussion

The BSM has been generalized to predict the solution dynamics of any assortment of identical beads connected by Hookean springs. The new ability to predict the properties of any chain has several immediate applications: (1) it can be used to predict the ability of VE and OFB properties to characterize the long-chain structure in homopolymers, (2) it can be used to fit dynamic data of new more complicated chain structures, and (3) it enables investigations of the dynamic properties of irregular chain structures which invariably are present to some degree as polydispersity components in real samples of regular star, H, and comb geometries.

A second important result of this work is that the exact properties of these idealized chains can be computed more efficiently; this result is of considerable interest because the properties of large chains, which correspond to high molecular weight homopolymers, are more easily obtained. The efficiency improved because (1) the normal coordinate system was constructed from coordinates that translate with the chain, which ensures that the relaxation spectrum can be computed from a symmetric matrix, and (2) several new and more concise block-diagonal forms of these matrices have been found for selected chain geometries.

The BSM has already allowed us to obtain quantitative predictions of OFB and VE properties for several simple chain geometries. The generalized formulation presented here will enable us to continue and substantially expand our explorations of the polymer characterization potential of these and other chain dynamics experiments. It is already clear that the character of the modification of the relaxation time spectrum changes substantially from one type of branching to another; some of these changes should be readily observed experimentally while others are predicted to be marginally detectable. Interpretation of measured properties requires careful quantitative comparisons of such predictions and the measured properties. Such comparisons are now under way for stars and regular combs; examinations of enough different chain geometries should provide a realistic assessment of the branching characterization potential of chain dynamics experiments. An illustrative summary of quantitative predictions for OFB and VE properties for selected chain geometries based on this generalized model is currently in preparation.[31] In addition, in a subsequent paper, the questions of why these Gaussian predictions appear to fit data measured under non-Θ conditions and how long-chain structure of homopolymers may be interpreted from these measurements are addressed. The BSM treatment presented here has been condensed for publication; an expanded version is available on request.[32]

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