A Reduced Description of the Local Dynamics of Star Polymers

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ABSTRACT: A reduced description of the ORZLD local dynamics of homogeneous star polymers in Θ solutions is presented. The reduced description directly uses bond variables whose dynamics are solved in terms of normal bond modes. The bond modes enable us to take advantage of the symmetry of the star, thus drastically reducing the computer time required to diagonalize the involved matrices. The behavior of the reduced relaxation modes as a function of mode range, flexibility, and hydrodynamic interaction is obtained and discussed. An improved description is given of the bond relaxations for a partially stretched star model including the core segment concentration effect.

Introduction

In a recent paper[1] (hereafter referred as paper 1) we presented a model for static and dynamic properties of homogeneous star polymers in Θ conditions. The model, of the type ORZLD (optimized Rouse–Zimm local dynamics),[2] is devised to describe accurately the local dynamics of a star polymer with a discrete number of beads by a linear Langevin equation in a mean-field potential. The star polymer is described as a semiflexible chain with partially stretched arms to take roughly into account the segment concentration effect in the star core.[3,4]

ORZLD is given in terms of matrices **H** and **A** describing respectively the hydrodynamic interaction between beads and the structural matrix including static correlation with all the beads in the polymer chain. Although the important variables in the ORZLD model are the polymer bonds (effective, or real), the theory uses also the bead coordinates. This turns out to be a little redundant for linear chains. For star polymers a direct description in terms of bonds not only removes this redundance but also cuts down drastically the order of the matrices **H** and **A** to diagonalize.[5]

Paper 1 used the full bead description, and the order of the matrices to diagonalize was equal to the total number of beads in the star. Treating long-arm stars therefore resulted in long time-consuming computations, which limits the molecular weight amenable to calculation.

In this paper we give a reduced description of the dynamics of star polymers based on bond representation and full exploitation of the symmetry of a homogeneous star. This reduced description implies the diagonalization of only two matrices of order equal to the number of bonds in a single arm and results in an enormous saving of computing time. Here it is also shown how static and dynamic quantities can be expressed in this reduced description. All the eigenvalues, eigenvectors, and diagonal elements necessary to evaluate these properties are explicitly calculated and related to the full description. Illustration and discussion are concentrated on the important case of semiflexible polymer stars. Finally the bond relaxation calculations of paper 1 are revisited to confirm and better describe, for large molecular weight, the behavior already found there.

Before describing the reduced version of our ORZLD dynamic model for star polymers, we note that not all the main physical consequences of the high segment density in the interior of the star have been considered in the model. In fact our approach uses a preaveraged hydrodynamic interaction, thus ignoring the nonpreaveraging correction. It is well-known[6-8] that this correction is of increasing importance with an increase in the number of star arms f, as the hydrodynamic interaction computations are very sensitive to the high segment concentration in the star core. The nonpreaveraging correction strongly affects the intrinsic viscosity, as can be seen by Monte Carlo simulations.[6,9,10] The first cumulant of the structure factor, Ω, can be calculated directly with and without preaveraging of the hydrodynamic interaction. The relative error, $\Delta\Omega/\Omega$, is found to be on the same order as that obtained for linear chains only for $f < 4$ but on the order of up to 40% for $f > 100$ at intermedium wavevector.[7] Thus our model can be applied directly to dynamic calculations only for small f values. For a higher number of arms a comparison between exact and preaveraged theory can be given for the first cumulant. The first cumulant, in fact, is derived exactly from static averages, without knowing the exact space-time distribution function.[11,12] These static averages are then computed by generalized Gaussian procedures, using the statistical properties of the partially stretched, freely rotating arm star. Finally this comparison should be used as a guide in the discussion on local dynamic properties and on the dynamic structure factor derived using the reduced version of our ORZLD star model. Computations in this sense are in progress.

ORZLD Dynamics for the Bond Variables

In a homogeneous star, the n beads, of equal friction coefficient ζ, are conventionally ordered as $i = 1$ for the star center and $i = 2, ..., N + 1; N + 2, ..., 2N + 1; ..., Nf + 1$ for the bead sequence of the f arms, each one of N bonds. The bead coordinate $\mathbf{R}_i$ evolves in time according to a linearized Langevin equation[2]

$$\frac{\partial}{\partial t}\mathbf{R}_i(t) + \sigma\sum_{j=1}^{n}(\mathbf{HA})_{ij}\mathbf{R}_j(t) = \mathbf{v}^*_i(t) \qquad (1)$$

with $\mathbf{v}^*_i(t)$ the random velocity and

$$\sigma = 3k_BT/l^2\zeta \qquad (2)$$

the bond rate constant, with l^2 the mean-square length of each vector bond $\mathbf{l}_i$. The matrices **H** and **A** are given on the basis of the static bond correlation matrix

$$\mathbf{U}_{ij}^{-1} = \langle \mathbf{l}_i\cdot\mathbf{l}_j\rangle/l^2 \qquad (3)$$

and the adimensional mean inverse distances $\langle l/R_{ij}\rangle$. In

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the Gaussian approximation, this average is in turn given in terms of $\mathbf{U}^{-1}$:

$$\langle 1/R_{ij}\rangle = l(6/\pi)^{1/2}(\langle R_{ij}^2\rangle)^{-1/2} \tag{4}$$

and

$$\langle R_{ij}^2\rangle = l^2 \sum_{r,s=i+1}^{j} \mathbf{U}_{rs}^{-1} \qquad j > i \tag{5}$$

These static averages are defined in terms of the equilibrium distribution function

$$\langle \mathbf{l}_i\cdot\mathbf{l}_j\rangle = c^{-1}\int \mathrm{d}\{\mathbf{R}_i\}\exp(-V(\{\mathbf{R}_i\})/k_BT)(\mathbf{l}_i\cdot\mathbf{l}_j) \tag{6}$$

with

$$c = \int \mathrm{d}\{\mathbf{R}_i\}\exp(-V(\{\mathbf{R}_i\})/k_BT) \tag{7}$$

and $V(\{\mathbf{R}_i\})$ the intramolecular potential.

Remarkable simplifications are obtained for flexible, semiflexible, and RIS models.[13,14]

Given $\mathbf{U}^{-1}$ and $\langle 1/R_{ij}\rangle$, the structural matrix **A** and the hydrodynamioc interaction matrix **H** are calculated as

$$\mathbf{A} = \mathbf{M}^{\mathrm{T}}\begin{pmatrix} 0 & 0 \\ 0 & \mathbf{U} \end{pmatrix}\mathbf{M} \tag{8}$$

$$H_{ij} = \delta_{ij} + \zeta_r\langle 1/R_{ij}\rangle(1-\delta_{ij}) \tag{9}$$

where **U** is the inverse of $\mathbf{U}^{-1}$ and

$$\zeta_r = \zeta/6\pi\eta_0 l \tag{10}$$

is the hydrodynamic interaction strength. In a Θ solution, ζ_r has been estimated theoretically and experimentally to have the value 0.25.[15,16] The bead-to-bond vector transformation **M**, which is a function of the architecture of the polymer, is defined for a homogeneous star polymer as[1]

$$\mathbf{M}_{1i} = n^{-1} \qquad i = 1, ..., n$$

$$\mathbf{M}_{ii} = 1 \qquad i = 2, ..., n$$

$$\mathbf{M}_{i+1\,i} = -1$$
$$i = 2, ..., N; N+2, ..., 2N; ... (f-1)N+2, ..., fN$$

$$\mathbf{M}_{i1} = -1 \qquad i = 2, N+2, 2N+2, ..., (f-1)N+2$$

$$\mathbf{M}_{ij} = 0 \qquad \text{otherwise} \tag{11}$$

Static and dynamic quantities are then obtained in terms of the $(n-1)$ nonzero eigenvalues λ_a and eigenvectors $\{\mathbf{Q}_{ia}\}$ obtained by diagonalization of the product matrix **HA**.

In the case of homogeneous star polymers it is possible to reduce drastically the order $Nf+1$ of the matrix to diagonalize, transforming the Langevin equation for beads into the corresponding equation for the bonds and taking advantage of the symmetry of the star. In addition, improved descriptions of the local dynamics in the ORZLD hierarchy are obtained by simply choosing more accurate bond variables (virtual bonds, backbone bonds, backbone and lateral chain bonds).[14] These are further reasons in favor of the evaluation of dynamics in terms of bond variables instead of bead ones.

The bond vectors are obtained from the bead coordinates as

$$\mathbf{l}_{i-1} = \sum_j \mathbf{M}_{ij}\mathbf{R}_j \qquad i = 1, ..., n \tag{12}$$

Equation 12 together with eq 11 defines, in addition to the real bond vectors $\mathbf{l}_1, \mathbf{l}_2, ..., \mathbf{l}_{n-1}$, a fictitious bond vector $\mathbf{l}_0$ related to the position of the center of mass. Multiplying eq 1 by **M** to the left, we obtain, using also eq 8

$$\frac{\partial}{\partial t}\mathbf{l}'(t) + \sigma\mathbf{M}\mathbf{H}\mathbf{M}^{\mathrm{T}}\begin{pmatrix} 0 & 0 \\ 0 & \mathbf{U} \end{pmatrix}\mathbf{l}'(t) = \mathbf{M}\mathbf{v}^*(t) \tag{13}$$

with $\mathbf{l}'$ the column of the n bond vectors defined by eq 12 and $\mathbf{v}^*(t)$ the column of the random velocities of the n beads. Introducing the rectangular matrix **a** obtained from **M** after suppressing the first row, we get for the reduced column **l**, obtained suppressing $\mathbf{l}_0$ in $\mathbf{l}'$, the Langevin equation for the bond variables:

$$\frac{\partial}{\partial t}\mathbf{l}(t) + \sigma\mathbf{L}\mathbf{U}\mathbf{l}(t) = \mathbf{a}\mathbf{v}^*(t) = \mathbf{v}'(t) \tag{14}$$

with

$$\mathbf{L} = \mathbf{a}\mathbf{H}\mathbf{a}^{\mathrm{T}} \tag{15}$$

l and **v**′ columns of order $n-1$, and **L** and **U** matrices of order $n-1$. The solution of eq 14 is obtained via the standard procedure[17] by transforming to normal coordinates ξ_a

$$\mathbf{l}_i = \sum_{a=1}^{n-1}\mathbf{Q}_{ia}\xi_a \tag{16}$$

with

$$\mathbf{Q}^{-1}\mathbf{L}\mathbf{U}\mathbf{Q} = \mathbf{\Lambda} \tag{17}$$

and **Λ** the matrix of the eigenvalues of **LU** coincident with the nonzero eigenvalues of **HA**. It is worth noting that the matrix **LU** is in general nonsymmetric and **Q** nonorthogonal, with the exception of the Gaussian case where **U** = 1. In normal coordinates the equation becomes

$$\left(\frac{\partial}{\partial t} + \sigma\lambda_a\right)\xi_a(t) = \mathbf{v}'_a(t) \tag{18}$$

with the time correlation for the random velocities

$$\langle \mathbf{v}'_a(t)\cdot\mathbf{v}'_b(t')\rangle = \frac{6k_BT}{\zeta}\nu_a\delta_{ab}\delta(t-t') \tag{19}$$

and mean normal-mode square length

$$\langle \xi_a^2\rangle = l^2\mu_a^{-1} \tag{20}$$

The elements μ_a and ν_a are the diagonal elements of the diagonal matrices $\mathbf{Q}^{\mathrm{T}}\mathbf{U}\mathbf{Q}$ and $\mathbf{Q}^{-1}\mathbf{L}\mathbf{Q}^{-1\mathrm{T}}$, respectively, and are related to λ_a by

$$\lambda_a = \mu_a\nu_a \tag{21}$$

It is important to note that the actual μ_a and ν_a defined for the bond equation are quite different from the corresponding quantities defined for the bead equation.[2,17]

The time correlation function for the normal modes results in

$$\langle \xi_a(t)\cdot\xi_b(0)\rangle = \delta_{ab}\langle \xi_a^2\rangle\exp(-\sigma\lambda_a t) \tag{22}$$

From the transformation (16) and the properties (20) and

(22) the bond orientational correlation function (TCF)[18] is simply obtained as

$$\mathbf{M}_1^{i}(t) = \langle \mathbf{l}_i(t)\cdot\mathbf{l}_i(0)\rangle/l^2 = \sum_{a=1}^{n-1} \mathbf{Q}_{ia}{}^2\mu_a{}^{-1} \exp(-\sigma\lambda_a t) \quad (23)$$

A full reduced description can now be obtained by generalization of the approach of Sammler and Schrag[5] to take into account the symmetry of the homogeneous star.

Reduced Description

Note that the matrices **L** and **U** can be written in blocks, each of order N, the number of beads in an arm, f identical blocks on the diagonal representing the contribution internal to each individual arm and $f(f-1)$ identical off-diagonal blocks representing the two-arm contribution.

$$\mathbf{F} = \mathbf{LU} = \begin{pmatrix} \mathbf{L}_1 & \mathbf{L}_2 & \mathbf{L}_2 & \mathbf{L}_2 \\ \mathbf{L}_2 & \mathbf{L}_1 & \mathbf{L}_2 & \mathbf{L}_2 \\ \mathbf{L}_2 & & & \mathbf{L}_1 \end{pmatrix} \begin{pmatrix} \mathbf{U}_1 & \mathbf{U}_2 & \mathbf{U}_2 & \mathbf{U}_2 \\ \mathbf{U}_2 & \mathbf{U}_1 & \mathbf{U}_2 & \\ \mathbf{U}_2 & & & \mathbf{U}_1 \end{pmatrix} \quad (24)$$

The matrices $\mathbf{L}_1$ and $\mathbf{L}_2$ are simply derived using the block properties of matrices **a** and **H** as

$$(\mathbf{L}_1)_{ij} = \sum_{a=1}^{2N+1}\sum_{b=1}^{N+1} \mathbf{a}_{ia}\mathbf{H}_a b\mathbf{a}_{jb} \quad (25)$$

$$(\mathbf{L}_2)_{ij} = \sum_{a=1}^{2N+1}\sum_{b=1}^{N+1} \mathbf{a}_{N+i,a}\mathbf{H}_{ab}\mathbf{a}_{jb} \quad (26)$$

Similarly, $\mathbf{U}_1$ and $\mathbf{U}_2$ are obtained from the diagonal, **D**, and off-diagonal, **S**, blocks of order N in $\mathbf{U}^{-1}$:

$$\mathbf{U}_1 = \mathbf{U}_2 + (\mathbf{D}-\mathbf{S})^{-1} \quad (27)$$

$$\mathbf{U}_2 = -[\mathbf{D} + (f-1)\mathbf{S}]\mathbf{S}(\mathbf{D}-\mathbf{S})^{-1} \quad (28)$$

The product matrix of block matrices, type **L** or **U**, is again a matrix of the same form; therefore, from eq 24

$$\mathbf{F} = \begin{pmatrix} \mathbf{A} & \mathbf{B} & \mathbf{B} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} & \mathbf{B} & \mathbf{B} \\ \mathbf{B} & & & \mathbf{A} \end{pmatrix} \quad (29)$$

with

$$\mathbf{A} = \mathbf{L}_1\mathbf{U}_1 + (f-1)\mathbf{L}_2\mathbf{U}_2 \quad (30)$$

$$\mathbf{B} = \mathbf{L}_1\mathbf{U}_2 + \mathbf{L}_2\mathbf{U}_1 + (f-2)\mathbf{L}_2\mathbf{U}_2 \quad (31)$$

Taking advantage of the fact that matrices related by similar transformations have the same eigenvalues, the eigenvalues of the matrix **F** are obtained in two steps. First the block matrix **F** is reduced to a block diagonal matrix by an orthogonal transformation **T** of order f

$$\mathbf{F}' = \mathbf{T}^{\mathrm{T}}\mathbf{LUT} = \begin{pmatrix} \mathbf{F}_D' & 0 & & \\ 0 & \mathbf{F}_D' & & \\ & & 0 & \\ & & 0 & \mathbf{F}_N' \end{pmatrix} \quad (32)$$

with

$$\mathbf{T} = \begin{pmatrix} 1 & 1 & 1 & 1 & & & 1 \\ -1 & 1 & 1 & 1 & & & 1 \\ 0 & -2 & 1 & 1 & & & 1 \\ 0 & 0 & -3 & 1 & & & 1 \\ & & & & & & \\ 0 & & & & -(f-2) & 1 & 1 \\ 0 & & & & 0 & -(f-1) & 1 \end{pmatrix} \quad (33)$$

and

$$\mathbf{F}_D' = \mathbf{A} - \mathbf{B} \quad (34)$$

$$\mathbf{F}_N' = \mathbf{A} + (f-1)\mathbf{B} \quad (35)$$

Then the two different blocks $\mathbf{F}_D'$ and $\mathbf{F}_N'$ are diagonalized as

$$\mathbf{Q}_D{}^{-1}\mathbf{F}_D'\mathbf{Q}_D = \Lambda^D \quad (36)$$

$$\mathbf{Q}_N{}^{-1}\mathbf{F}_N'\mathbf{Q}_N = \Lambda^N \quad (37)$$

Therefore, the **F** matrix of any ORZ homogeneous star of f arms of length N has N eigenvalues of degeneracy $f-1$ and N nondegenerate eigenvalues for a total of Nf eigenvalues.[19] Finally the matrix of the eigenvectors is easily obtained by the product of **T** and **a** block diagonal matrix as

$$\mathbf{Q} = \mathbf{T}\begin{pmatrix} \mathbf{Q}_D & 0 & & \\ 0 & \mathbf{Q}_D & 0 & \\ & & \mathbf{Q}_D & 0 \\ & & 0 & \mathbf{Q}_N \end{pmatrix} = \begin{pmatrix} \mathbf{Q}_D & \mathbf{Q}_D & \mathbf{Q}_D & \mathbf{Q}_D & \mathbf{Q}_N \\ -\mathbf{Q}_D & \mathbf{Q}_D & \mathbf{Q}_D & \mathbf{Q}_D & \mathbf{Q}_N \\ 0 & -2\mathbf{Q}_D & \mathbf{Q}_D & \mathbf{Q}_D & \mathbf{Q}_N \\ & 0 & -3\mathbf{Q}_D & \mathbf{Q}_D & \mathbf{Q}_N \\ & & & & \\ 0 & & 0 & -(f-1)\mathbf{Q}_D & \mathbf{Q}_N \end{pmatrix} \quad (38)$$

Note that if $\mathbf{Q}_D$ and $\mathbf{Q}_N$ contain normalized eigenvectors a normalized **Q** is obtained simply by multiplying each column i of the first $f-1$ columns by β_i with

$$\beta_i = 1/[i(i+1)]^{1/2} \quad (39)$$

and the last column by $1/\sqrt{f}$ to obtain finally

$$\mathbf{Q} = \begin{pmatrix} \beta_1\mathbf{Q}_D & \beta_2\mathbf{Q}_D & \beta_{f-1}\mathbf{Q}_D & \mathbf{Q}_N/\sqrt{f} \\ -\beta_1\mathbf{Q}_D & \beta_2\mathbf{Q}_D & \beta_{f-1}\mathbf{Q}_D & \mathbf{Q}_N/\sqrt{f} \\ 0 & -2\beta_2\mathbf{Q}_D & \beta_{f-1}\mathbf{Q}_D & \mathbf{Q}_N/\sqrt{f} \\ & & & \\ 0 & & (f-1)\beta_{f-1}\mathbf{Q}_D & \mathbf{Q}_N/\sqrt{f} \end{pmatrix} \quad (40)$$

Using eq 40, it is straightforward to show that both μ_a and ν_a are resolved in N $\mu_a{}^D$ and $\nu_a{}^D$ of $(f-1)$ degeneracy and N nondegenerate $\mu_a{}^N$ and $\nu_a{}^N$ whose expressions result in

$$(\mathbf{Q}_D{}^T(\mathbf{U}_1 - \mathbf{U}_2)\mathbf{Q}_D)_{aa} = \mu_a{}^D \quad (41)$$

$$[\mathbf{Q}_D{}^{-1}(\mathbf{L}_1 - \mathbf{L}_2)\,(\mathbf{Q}_D{}^{-1})^T]_{aa} = \nu_a{}^D \quad (42)$$

$$[\mathbf{Q}_N{}^T[\mathbf{U}_1 + (f-1)\mathbf{U}_2]\mathbf{Q}_N]_{aa} = \mu_a{}^N \quad (43)$$

$$\{\mathbf{Q}_N{}^{-1}[\mathbf{L}_1 + (f-1)\mathbf{L}_2](\mathbf{Q}_N{}^{-1})^T\}_{aa} = \nu_a{}^N \quad (44)$$

The reduced description of the ORZ dynamics of any homogeneous star of f branches of length N is given in conclusion in terms of the eigenvalues $\lambda_a{}^D$ and $\lambda_a{}^N$ and eigenvectors $\{\mathbf{Q}_{ia}{}^D\}\{\mathbf{Q}_{ia}{}^N\}$ together with the related quantities $\mu_a{}^D$, $\mu_a{}^N$ and $\nu_a{}^D$, $\nu_a{}^N$ with $a = 1, 2, ..., N$.

Summarizing the reduced procedure amounts to the following: read the input matrices **D** and **S** of order N; read (or calculate in the case of the Gaussian approximation) the inverse distances between beads on the same and in different arms (and calculate the relative **H** counterpart); calculate the inverse of (**D** − **S**); construct matrices $\mathbf{L}_1$, $\mathbf{L}_2$, $\mathbf{U}_1$, and $\mathbf{U}_2$; derive matrices $\mathbf{F}_D'$ and $\mathbf{F}_N'$; diagonalize matrices $\mathbf{F}_D'$ and $\mathbf{F}_N'$ to get degenerate and nondegenerate eigenvalues $\lambda_a{}^D$ and $\lambda_a{}^N$ and eigenvector matrices $\mathbf{Q}_D$ and $\mathbf{Q}_N$; calculate, using $\mathbf{Q}_D$ and $\mathbf{Q}_N$ and $\mathbf{U}_i$ and $\mathbf{L}_i$, the diagonal elements $\mu_a{}^D$, $\mu_a{}^N$ and $\nu_a{}^D$, $\nu_a{}^N$. Note that also in the case $f = 2$, i.e., the linear chain of length $2N + 1$, the dynamics calculations are reduced to the diagonalization of two matrices of order N with relative saving of computing time.

Static and Dynamic Properties

As an example, the fundamental TCF of eq 23, by use of eq 40 and taking into account that

$$\sum_{i=1}^{f-1}\beta_i{}^2 = (f-1)/f \quad (45)$$

is reduced to the form

$$M_i{}^1(t) = (f-1)f^{-1}\sum_{a=1}^{N}(\mathbf{Q}_{ia}{}^D)^2(\mu_a{}^D)^{-1}\exp(-\sigma\lambda_a{}^D t) + f^{-1}\sum_{a=1}^{N}(\mathbf{Q}_{ia}{}^N)^2(\mu_a{}^N)^{-1}\exp(-\sigma\lambda_a{}^N t) \quad (46)$$

including only $2N$ terms.

Note that since the bond length is normalized,[18] it turns out that

$$(f-1)f^{-1}\sum_{a=1}^{N}(\mathbf{Q}_{ia}{}^D)^2(\mu_a{}^D)^{-1} + f^{-1}\sum_{a=1}^{N}(\mathbf{Q}_{ia}{}^N)^2(\mu_a{}^N)^{-1} = 1 \quad (47)$$

The reduced description can be applied, as well, to all the static and dynamic quantities of interest. For instance, for the intrinsic viscosity, which requires only the eigenvalues, we get

$$[\eta] = \frac{N_A l^2 \zeta}{6\eta_0 M}[(f-1)\sum_{a=1}^{N}(\lambda_a{}^D)^{-1} + \sum_{a=1}^{N}(\lambda_a{}^N)^{-1}] \quad (48)$$

and a similar formula for the properties related only to the eigenvalues.

For properties like the dynamic structure factors it is enough to express in terms of bonds $\mathbf{l}_i$ the dynamic distances $\langle|\mathbf{r}_i(t) - \mathbf{r}_j(0)|^2\rangle$ with $\mathbf{r}_i$ the distance of bead i from the center of mass. For the static structure factor we need only the static distances

$$\langle|\mathbf{r}_i - \mathbf{r}_j|^2\rangle/l^2 = \sum_{p=j}^{i-1}\langle l_p{}^2\rangle/l^2 + 2\sum_{p=j}^{i-2}\sum_{q=j+i}^{i-1}\langle \mathbf{l}_p\cdot\mathbf{l}_q\rangle/l^2 \; (i > j) \quad (49)$$

for i and j on the same arm and

$$\langle|\mathbf{r}_i - \mathbf{r}_j|^2\rangle l^2 = \langle|\mathbf{r}_i - \mathbf{r}_1|^2\rangle/l^2 + \langle|\mathbf{r}_j - \mathbf{r}_1|^2\rangle/l^2 - 2\langle(\mathbf{r}_i - \mathbf{r}_1)\cdot(\mathbf{r}_j - \mathbf{r}_1)\rangle/l^2 = \langle|\mathbf{r}_i - \mathbf{r}_1|^2\rangle/l^2 + \langle|\mathbf{r}_j - \mathbf{r}_1|^2\rangle/l^2 - 2\sum_{p=1}^{i-1}\sum_{q=1}^{j-1}\langle \mathbf{l}_p\cdot\mathbf{l}_q\rangle/l^2 \quad (50)$$

for i and j on different arms, with $\mathbf{r}_1$ the position of the center of the star and p and q running on different arms. Equations 16 and 40 give for $\langle \mathbf{l}_p\cdot\mathbf{l}_q\rangle$ on the same arm

$$\langle \mathbf{l}_p\cdot\mathbf{l}_q\rangle/l^2 = (f-1)f^{-1}\sum_{a=1}^{N}\mathbf{Q}_{pa}{}^D\mathbf{Q}_{qa}{}^D(\mu_a{}^D)^{-1} + f^{-1}\sum_{a=1}^{N}\mathbf{Q}_{pa}{}^N\mathbf{Q}_{qa}{}^N(\mu_a{}^N)^{-1} \quad (51)$$

and

$$\langle \mathbf{l}_p\cdot\mathbf{l}_q\rangle/l^2 = -f^{-1}\sum_{a=1}^{N}\mathbf{Q}_{pa}{}^D\mathbf{Q}_{qa}{}^D(\mu_a{}^D)^{-1} + f^{-1}\sum_{a=1}^{N}\mathbf{Q}_{pa}{}^N\mathbf{Q}_{qa}{}^N(\mu_a{}^N)^{-1} \quad (52)$$

on different arms. Equations 51 and 52 are generalizations of eq 47 to different bonds in the same or in different arms, respectively.

Full Bead Description

The full bead description is obtained from the reduced one according to the following procedure.

The hydrodynamic eigenvalue problem, expressed in bead coordinates relative to eq 1, is

$$\mathbf{HAS} = \mathbf{S}\begin{pmatrix}0 & 0\\ 0 & \Lambda'\end{pmatrix} \quad (53)$$

with Λ' the matrix of the nonzero eigenvalues of **HA**. Multiplying on the left by **a** and using eqs 15 and 8, one obtains

$$\mathbf{LUaS} = \mathbf{aS}\begin{pmatrix}0 & 0\\ 0 & \Lambda'\end{pmatrix} \quad (54)$$

Taking into account the structure of **a** and that the first column in **S** is the constant eigenvector corresponding to the center of mass motion, it is recognized that **aS** takes the form

$$\mathbf{aS} = (0 \quad \mathbf{Q}') \quad (55)$$

As a consequence, eq 54 is reduced to eq 17 by suppressing the center of mass motion and $\mathbf{Q}'$ and Λ' are identified with **Q** and Λ, respectively. It remains to construct **S** from the knowledge of **Q** and of the constant eigenvector. Equation 55 can be written using matrices of order n as

$$\begin{pmatrix} n^{-1/2} & n^{-1}\sum_i \mathbf{S}_{i2} & n^{-1}\sum_i \mathbf{S}_{i3} & n^{-1}\sum_i \mathbf{S}_{in} \\ 0 & & \mathbf{Q} & \end{pmatrix} = \mathbf{MS} \quad (55')$$

Equation 55′ cannot be inverted to obtain **S** directly, as we do not know the first row on the right-hand side.

In the free-draining case, due to the properties of **A** and the orthogonality of **S**, we have

$$\sum_i \mathbf{S}_{ia}{}^{FD} = n^{1/2}\delta_{1a} \tag{56}$$

and therefore eq 55′ can be immediately inverted to give

$$\mathbf{S}^{FD} = \mathbf{M}^{-1}\begin{pmatrix} n^{-1/2} & 0 \\ 0 & \mathbf{Q} \end{pmatrix} \tag{57}$$

written in unnormalized form.

The matrix $\mathbf{M}^{-1}$ can be written in blocks as

$$\mathbf{M}^{-1} = \begin{pmatrix} 1 & \mathbf{v} & \mathbf{v} & & \mathbf{v} \\ 1 & \mathbf{A} & \mathbf{B} & & \mathbf{B} \\ 1 & \mathbf{B} & \mathbf{A} & & \mathbf{B} \\ & & & & \\ 1 & \mathbf{B} & & \mathbf{B} & \mathbf{A} \end{pmatrix} \tag{58}$$

with **v** a row of order N of elements

$$\mathbf{v}_i = -(N - i + 1)/n \tag{59}$$

and **A** and **B**, matrices of order N, of elements

$$A_{ij} = -(N - j + 1)/n \qquad j > i$$

$$A_{ij} = (n - N + j - 1)/n \qquad j \le i \tag{60}$$

$$B_{ij} = -(N - j + 1)/n \tag{61}$$

Using eq 40 for **Q** and eq 58 for $\mathbf{M}^{-1}$, we get for $\mathbf{S}^{FD}$ after final normalization

$$\mathbf{S}^{FD} = \begin{pmatrix} n^{-1/2} & 0 & 0 & 0 & \mathbf{R}_N \\ n^{-1/2} & \beta_1\mathbf{S}_D & \beta_2\mathbf{S}_D & \beta_{f-1}\mathbf{S}_D & \mathbf{S}_N \\ n^{-1/2} & -\beta_1\mathbf{S}_D & \beta_2\mathbf{S}_D & \beta_{f-1}\mathbf{S}_D & \mathbf{S}_N \\ n^{-1/2} & 0 & -2\beta_2\mathbf{S}_D & \beta_{f-1}\mathbf{S}_D & \mathbf{S}_N \\ & & & & \\ n^{-1/2} & & & -(f-1)\beta_{f-1}\mathbf{S}_D & \mathbf{S}_N \end{pmatrix} \tag{62}$$

where

$$(\mathbf{R}_N)_j = -\frac{f^{1/2}\alpha_j}{n}\sum_{i=1}^{N}(N - i + 1)(\mathbf{Q}_N)_{ij} \tag{63}$$

$$(\mathbf{S}_D)_{ij} = \gamma_j\sum_{a=1}^{i}(\mathbf{Q}_D)_{aj} \tag{64}$$

$$(\mathbf{S}_N)_{ij} = f^{1/2}\alpha_j\sum_{a=1}^{i}(\mathbf{Q}_N)_{aj} + (\mathbf{R}_N)_j \tag{65}$$

and the normalization constants α_j and γ_j are obtained from

$$(\mathbf{R}_N)_j{}^2 + f\sum_{i=1}^{N}(\mathbf{S}_N)_{ij}{}^2 = 1 \tag{66}$$

$$\sum_{i=1}^{N}(\mathbf{S}_D)_{ij}{}^2 = 1 \tag{67}$$

Thus in the free-draining case the bead description is completely obtained in reduced terms.

In the partial-draining case eq 56 is substituted by

$$\sum_a \mathbf{S}_{ai}{}^{-1} = n^{1/2}\delta_{i1} \tag{56′}$$

The full solution of eq 55′ for **S** is then obtained taking into account eq 56′ and the normalization conditions. For star polymers of large f and large N this procedure is highly computer time consuming and therefore it is advisable to use the reduced description in bond coordinates of the previous section after transforming configurational observables in functions of bond coordinates. This can be easily done in the case of local dynamics and of structure factor (see previous section). Anyway, if a full bead description is required, it is still possible to avoid the above-described cumbersome computations by using the standard approximation:[20]

$$\mathbf{S}_{ia} \approx \mathbf{S}_{ia}{}^{FD} \tag{68}$$

This approximation is correct within a few percent for these polymer models and therefore can be used confidently.

Relaxation Spectra for Semiflexible Stars

Although the reduced approach is valid for any ORZ model, in this section we focus on semiflexible stars modelized as a freely rotating chain (FRC)[1] with valence angle ϑ and stiffness parameter

$$p = -\cos\vartheta \tag{69}$$

The correlation of the bond vectors attached to the star center is taken as

$$\langle \mathbf{l}_1{}^i \cdot \mathbf{l}_1{}^j \rangle = \alpha \tag{70}$$

for any two different arms with $\mathbf{l}_1{}^i$ the first bond of arm i.

Note that this condition assigns to the star center a degree of flexibility increasing with f. This is probably unphysical for real stars obtained by chemical synthesis.[21]

The results obtained for these FRC stars are easily generalized to more refined star models, as the partially stretched star, following paper 1.

For any ORZ star model, as well as for Gaussian stars,[5] the degenerate eigenvalues are f independent, while the nondegenerate eigenvalues are f dependent. This follows from the eigenvalue equations (36) and (37) taking into account that the A–B matrix, due to the structure of A and B (eqs 30 and 31), is f independent.

All the eigenvalues turn out to be almost independent of the correlation at the star center α, with the exception of the largest nondegenerate eigenvalue $\lambda_N{}^N$. This eigenvalue, which is also almost N independent, cumulates almost all the dependence on α of the model. As α decreases to the minimum possible value $\alpha_m = -(f-1)^{-1}$, the star becomes symmetric at the star center satisfying the equation:[1]

$$\langle P^2 \rangle = 0 \qquad \mathbf{P} = \sum_{i=1}^{f}\mathbf{l}_1{}^i \tag{71}$$

As a consequence, a degree of freedom is frozen and the correspondent eigenvalue $\lambda_N{}^N$ takes an infinite value:

$$\lim_{\alpha\to\alpha_m} \lambda_N{}^N \approx (|\alpha - \alpha_m|)^{-1} \tag{72}$$

As α increases, $\lambda_N{}^N$ decreases, taking in the free-draining flexible case the value $f^2/(f-1)$ for $\alpha = 0$ and reaching a

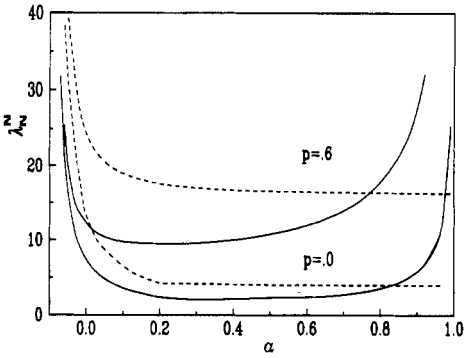

Figure 1. Highest nondegenerate eigenvalue λ_N^N as a function of the correlation at the star center α, for $p = 0.0$ and 0.6: partial draining (full curves), free draining (dashed curves).

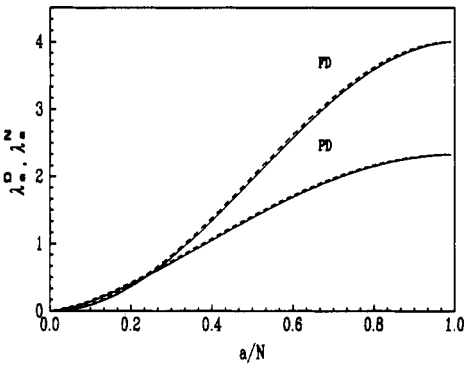

Figure 2. Degenerate eigenvalues λ_a^D (full curves) and nondegenerate eigenvalues λ_a^N (dashed curves) in the free- and partial-draining conditions.

constant, f-dependent, asymptotic value at $\alpha = 1$ (see Figure 1). The hydrodynamic interactions for small α simply lower the curve of λ_N^N versus α. For higher α values λ_N^N increases and finally diverges with the **H** matrix for $\alpha = 1$. This is due to the divergence of the inverse distances between the second beads of different arms (the first bonds of each arm are coincident in the limit $\alpha = 1$). This result is an artifact of the actual model which could be easily overcome. Nevertheless it is irrelevant in the region of highest interest in α: $\alpha \leq 0$. Increasing the stiffness does not change the qualitative behavior but simply gives higher curves.

After separation of the particular λ_N^N eigenvalue, the general behavior with the mode number of the remaining nondegenerate eigenvalues λ_a^N and of the degenerate eigenvalues λ_a^D is sketched by the known analytic form of the degenerate eigenvalues in the Gaussian free-draining case (Rouse star)

$$(\lambda_a^D)_R = 4 \sin^2 \{\pi(2a + 1)/[2(2N + 1)]\} \qquad a = 0, 1, ..., N - 1 \quad (73)$$

coincident with the odd Rouse eigenvalues for a linear chain of length $2N + 1$.

It turns out that, if the eigenvalues are reported against the normalized index a/N, the plot becomes, in fairly good approximation, N independent for $N \geq 50$. This result is confirmed for any hydrodynamic interaction or stiffness.

In Figure 2 the eigenvalues for a flexible star ($p = 0$) are reported in the free- and partial-draining cases ($\zeta_r = 0.25$). The arm length is fixed at $N = 100$ to guarantee an N-independent plot. It is noteworthy that the curves for degenerate and nondegenerate (with exclusion of λ_N^N) eigenvalues have only slight differences. As an example, in the Rouse case the nondegenerate eigenvalues are fairly well approximated by the even eigenvalues of the Rouse linear chain of length $2N + 1$ (see eq 73).

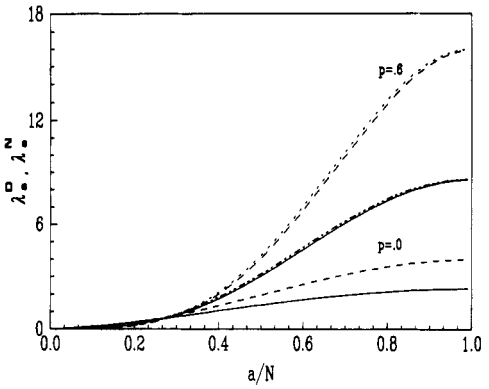

Figure 3. Degenerate eigenvalues λ_a^D in the free- (- - -) and partial-draining (—) cases and nondegenerate eigenvalues λ_a^N in the free- (· · ·) and partial-draining (– · · –) cases. Upper curves p = 0.6; lower curves $p = 0.0$ (in this case nondegenerate curves are graphically undistinguishable from the degenerate ones).

In Figure 3 the effect of stiffness p is described. Again degenerate and nondegenerate eigenvalues lie almost on the same curve. The raising of the eigenvalues due to stiffness and the effect of the hydrodynamic interaction are quite similar to those reported in the linear case.[14]

For the diagonal elements μ_a^D, μ_a^N, ν_a^D, and ν_a^N defined in eqs 41–44, the following properties should be underlined. In the Gaussian case ($\alpha = 0$, $p = 0$) the bond correlation matrix is simply the unit matrix ($\mathbf{U} = 1$, $\mathbf{U}_1 = 1$, $\mathbf{U}_2 = 0$), and therefore $\mu_a^D = \mu_a^N = 1$; ν_a^D and ν_a^N become simply the Gaussian eigenvalues $(\lambda_a^D)_0$ and $(\lambda_a^N)_0$, and the **Q** matrix is symmetric. On the contrary, for a semiflexible star μ_a^D and μ_a^N are approximately given by the inverse of the star degenerate and nondegenerate characteristic ratios, C_a^D and C_a^N, which are the eigenvalues of the matrix $\mathbf{U}^{-1}$. The small differences are due to the nonorthogonality of the **Q** transformation. ν_a^D and ν_a^N are almost independent of the stiffness, the slight dependence being due again to the nonorthogonality of **Q**. These diagonal elements are instead strongly dependent on the Rouse connectivity of the chain and on the hydrodynamic interaction strength, both informations being absorbed in eq 15 defining **L**. If the small effect of the nonorthogonality of **Q** is ignored, ν_a^D and ν_a^N are well approximated by the eigenvalues of the symmetric matrix **L**. Summarizing

$$\nu_a^D \approx (\lambda_a^D)_0; \quad \nu_a^N \approx (\lambda_a^N)_0 \quad (74)$$

$$\mu_a^D \approx (C_a^D)^{-1}; \quad \mu_a^N \approx (C_a^N)^{-1} \quad (75)$$

This suggests a useful approximation, valid in a few percent, of eq 21 for the eigenvalues λ_a:

$$\lambda_a \approx (\lambda_a)_0 C_a^{-1} \quad (76)$$

which is an extension to star models of a similar property of linear models.[14] Here $(\lambda_a)_0$ is the eigenvalue for a Gaussian star with hydrodynamic interaction and eq 76 separates the stiffness effect C_a^{-1} from connectivity and hydrodynamic interaction effects.

Bond Relaxation of Partially Stretched Stars

Here we take advantage of the reduced bond description to improve the calculation of the bond relaxation times including larger molecular weights than those reported in paper 1. As a matter of fact, with the actual reduced description, an arm length N up to 300 bonds (independently from f) can be treated as opposed to the previous 30 bonds (for $f = 12$). Therefore, some features of the local relaxation behavior can be better described.

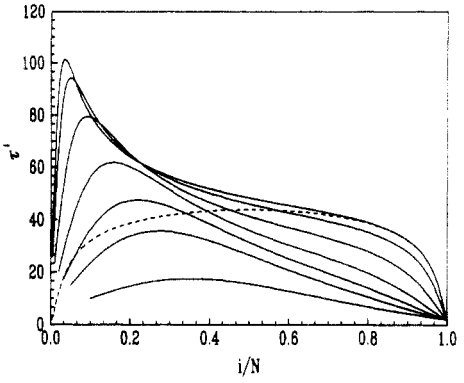

Figure 4. Bond correlation times τ^i as a function of the relative distances to the star center i/N; $f = 12$, $\alpha = -(f-1)^{-1}$, and freely rotating stars with $p = 0.77$. Solid curves from top to bottom: $N = 300, 200, 100, 50, 30, 20$, and 10. Dashed curve: linear chain of length $N = 300$.

We take as a measure of the local dynamics the correlation time for the second-order time correlation function (as measured in fluorescence anisotropy or NMR relaxation) $P_2^i(t)$ for bond i:[18]

$$\tau^i = \int_0^\infty P_2^i(\sigma t)\, d\sigma t \qquad (77)$$

As well-known,[18] in ORZLD, $P_2^i(t)$ is a simple analytic function of $M_1^i(t)$, reported in eq 46.

In a homogeneous star, bonds on the same position on different arms have identical TCF $P_2^i(\sigma t)$. Therefore, for a complete description, it is sufficient that i changes from 1, at the star center, to N.

In Figure 4 we improve Figure 2 of paper 1, reporting τ^i as a function of i/N for freely rotating stars (FRC) with $p = 0.77$ (this stiffness is characteristic of linear polymers PS in Θ conditions[1]) and several values of N with $10 \le N \le 300$. Also reported is the curve for the linear chain at $N = 300$. While in the outer regions of the star the bond relaxation times stick to those of the linear chain, in the inner region a strong slowing down appears given a maximum in τ^i, located at a small constant distance near the star center and asymptotically increasing with N.

The slowing down of the correlation time τ^i was discussed in a detailed way in paper 1 (see as an example Figure 4 of paper 1 and the related comments). Here, taking advantage of the computations at larger molecular weights, the asymmetry introduced by the star architecture is better elucidated. For very large arms, disregarding a small number of internal bonds attached to the star center, the physical dynamic behavior of the star displays a large increase in τ^i approaching the star center. The small portion of internal bonds showing a decrease in τ^i near the star center is strictly model dependent and reminiscent of approximation (70). A more physical dynamic description of this small region requires knowledge of the real chemical structure of the branching point. Clearly rigid connections and different valence angles between different arms will reduce strongly the mobility of the first few bonds, canceling the small internal well of Figure 4. Nevertheless, for a very long arm star, the model catches the main architecture effects with exclusion of this small region effect. In addition, in Figure 6 the segment concentration effect in the interior of the star is taken into account. The behavior of τ^i with N is better elucidated in Figure 5 (Figure 5 of paper 1) where the correlation time of the bond at the star center τ^1 and of the bond at the maximum slowing down τ^m are reported against $1/N$ to obtain an improved extrapolation to $N \to \infty$, using values of $N \le 300$. Comparing with Figure 5 of paper 1, which

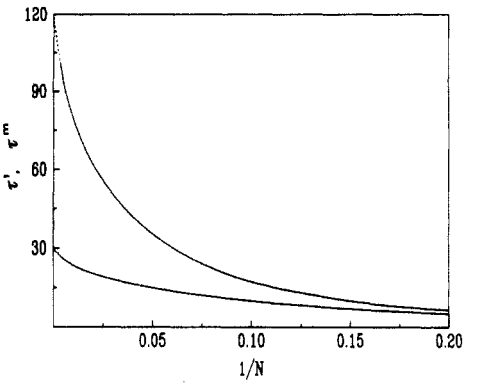

Figure 5. Correlation times τ^1 (lower curve) and τ^m, as a function of N^{-1} for FRC stars with $p = 0.77$, $f = 12$, and $\alpha = -(f-1)^{-1}$. Dotted curves: extrapolation to $N \to \infty$.

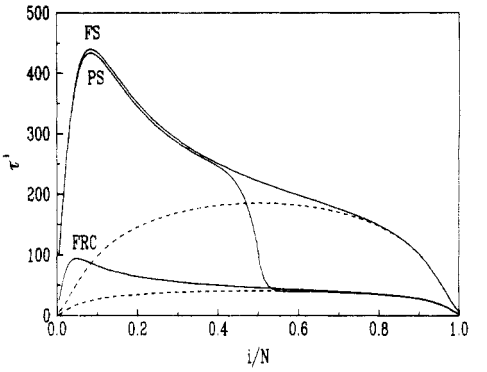

Figure 6. Bond correlation time τ^i as a function of i/N for an arm length $N = 200$, $f = 12$, and $\alpha = -(f-2)^{-1}$. FS: fully stretched arm model with $p = 0.87$. PS: partially stretched arm model with $p = 0.77$, $p' = 0.87$, and $N' = N/2$. FRC: freely rotating chain star model at $p = 0.77$. Linear freely rotating chain of a length $N = 200$ (dashed curves): upper curve, $p = 0.87$; lower curve, $p = 0.77$.

used $N \le 30$, the extrapolated values of τ^m result in a factor 1.4 higher. Nevertheless, the asymptotic behavior is confirmed.

Figure 6, Figure 3 of paper 1, represents fully, partially, and FRC star models for τ^i. The partially stretched star model, assumed to describe roughly the effect of the segment concentration in the interior of the star, is defined in paper 1 as having the first N' bonds in the arm of stiffness p' and the remaining bonds of stiffness p. This model with $p = 0.77$, $p' = 0.87$, and $N' = N/2$ sticks, at $i/N < 0.5$, to the fully stretched model ($p = 0.87$), and, at $i/N > 0.5$, to the FRC model ($p = 0.77$) which in turn sticks to the linear chain for $i/N \to 1$. Despite the rough model used here, what we can expect for a more detailed model of the internal concentration effect is just a smoother transition between the two limits as i/N increases.

Conclusions

A reduced description has been presented of the statics and dynamics of star polymers in Θ condition. The ORZLD type theory is given in terms of bond variables and solved in terms of reduced bond normal modes. This enables us to save an enormous quantity of computing time as equations are given to derive eigenvectors and eigenvalues of matrices of order $Nf + 1$ in terms of eigenvector and eigenvalues of two matrices of order N. The general behavior of the reduced relaxation modes is described and discussed as a function of mode range, flexibility, hydrodynamic interaction, and correlation at the star center. The theory can be applied to the calculation of any static and dynamic quantity given in terms of bond vectors or

static and dynamic internal distances. In a following paper this star model and reduced description will be applied to the derivation of the behavior of static and dynamic structure factors.

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