Maximum-Correlation Mode-Coupling Approach to the Smoluchowski Dynamics of Polymers

Angelo Perico* and Roberto Pratolongo

Instituto di Studi Chimico-Fisici di Macromolecole Sintetiche e Naturali,
National Research Council, Via De Marini 6, 16149 Genova, Italy

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ABSTRACT: The Smoluchowski generalized diffusion equation with hydrodynamic interactions is used to derive the dynamics of polymers in solution. The time correlation functions (TCF) of bond vector variables are calculated using a mode-coupling expansion. While the first-order expansion represents the optimized Rouse−Zimm (ORZ) theory, higher orders result in an explosive number of elements in the basis set adopted to expand the eigenfunctions of the dynamic operator. An optimum approximation is generated by adding to the ORZ basis set, linear in the chosen slow variables, selected nonlinear terms formed by increasing powers of only those slow variables having maximum correlation with the observed relaxing variable. When this maximum-correlation mode-coupling approximation (MCA) is applied to the generalized diffusion equation with full hydrodynamic interaction, a great improvement to the ORZ theory is obtained which is easily amenable to more reliable computations of local dynamics in polymers and proteins in solution. Applications to freely jointed chains, broken rods, and rods are discussed to show the usefulness of the MCA concept in deriving the dynamics of simple model chains with small or strong correlation between bond variables. The MCA theory with a basis set twice larger than that of the ORZ theory gives exact rotational correlation times for the rod with and without hydrodynamic interactions.

I. Introduction

There are many fields in which dynamic processes are important in determining the biological function of proteins and biological macromolecules: the most interesting of these include the activity of enzymes and molecular and cell recognition. Local dynamics and long-range relaxation are likewise of importance in governing bulk polymer properties such as glass transition temperature and the viscoelastic properties of polymer materials. These polymer dynamics occur in many time and spatial scales which are related to the complex multidimensional conformational energy surface, a rough landscape characterized by a large number of valleys, barriers and saddle points.[1,2] In principle, given an accurate empirical atomistic potential, the dynamics may be obtained by molecular dynamics (MD) simulations. But the most interesting dynamics occur on long time scales far beyond the possibilities of present computers even for small proteins[3] or long polymers.[4] Thus some type of reduced statistical mechanical approach is required to alleviate computations, leading in turn to a deeper understanding of the main phenomena underlying the biological or technological function and introducing attractive simplifications of the overwhelming information retained in an MD simulation.

On a sufficiently large time scale, greater than 10 ps, the generalized diffusion equation (GDE) in a complex potential is in principle the appropriate reduced approach, which takes advantage of a hydrodynamic description of the solvent and of friction and diffusion prevailing over inertial effects. For large scale properties of simple polymers in solution the atomistic potential can be substituted by a Gaussian chain with a δ-excluded volume interaction, and approximations to the GDE can be successfully obtained to derive viscoelastic behavior, dynamic structure factors, etc.[5] On the contrary, short and medium scale properties (such as fluorescence anisotropy, NMR and dielectric relaxation, and short wavelength structure factors) are more sensitive to realistic atomistic potential, while still depending on the polymer connectivity. In addition to these “local dynamics”, the dynamics of the active site of proteins or the dynamic contribution to the biological function in a biomacromolecule is characterized by strong cooperativity of the fluctuating three dimensional structure. In both cases dynamics cannot be described by simple polymer−solvent models but require the full generalized diffusion equation with an accurate atomistic description of the potential and of the polymer−solvent friction and hydrodynamic interactions. Much progress has been made in recent years on this challenging subject.

The pioneering work has been done by Zwanzig[6] and Bixon and Zwanzig.[7] Applying a projection operator technique,[8,9] a generalized Langevin equation (GLE) for the chosen slow variables of the many-body system is first derived, which is exactly equivalent to the GDE. If the slow variables are simply the bead coordinates of a Gaussian bead-spring model and the approximation of preaveraging the hydrodynamic interactions is assumed, the memory function term becomes identically zero and the GLE becomes a relaxation equation coinciding with the Rouse−Zimm theory of polymer dynamics. For a real system the corrections to the Rouse−Zimm theory are in the GLE memory function, which is of second order in the correction to linear interaction forces or in the difference between the exact diffusion tensor and its preaveraged form. The optimized Rouse−Zimm (ORZ) polymer dynamics simply ignore the memory function but include the effects of the potential of mean force, entering via the second moment correlation between “bond vectors” and the equilibrium averages of the atom inverse distances.[10] Higher order moments as well as nonpreaveraging corrections to the hydrodynamic interactions are discarded with the memory function.

The ORZ reduced theory has been extended to treat different sets of bond variables and realistic atomistic potentials. It has been shown that in the framework of

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ORZ dynamics all the time correlation functions describing the “local dynamics” can be derived exactly.[10,11] This reduced approach to local dynamics (ORZLD) uses a hydrodynamic description of the solvent, selects only part of the total degrees of freedom of the polymer (bonds or effective bonds) as “slow variables”, requires knowledge of the equilibrium averages of the bond vector correlation matrices and of the inverse bead distances, and models the friction coefficients of the atoms or group of atoms, “beads”, by the van der Waals additive method or the accessible surface area (ASA) method.[12] The most advanced models in the ORZLD hierarchy[10] calculate the input averages by a time average along an MD trajectory, taking into account non-nearest-neighbor interactions described by empirical force fields, together with the solvent effect.[12,13] The effects on local dynamics of the length of the trajectory[13] and of the choice of bead friction coefficients were discussed.[12,14] These tests on the ORZ extended models were performed to observe the effect of progressively increasing the degrees of freedom included into the slow variables to reduce the effect of the discarded memory function, improving the description of the friction coefficients of “atoms” and of the “group of atoms”, and increasing the accuracy in the description of the interactions between the solute “atoms” and between solute and solvent.

In addition, several comparisons with experiments (^{13}C NMR relaxation on synthetic polymers[15] and polysaccharides[16] and fluorescence anisotropy of single tryptophane-containing polypeptides[12,17,18]) were performed. The interesting result is that general qualitative, and in many cases even quantitative, agreement was found. This shows that ORZLD picks up general features of the real local dynamics in polymers due to the fact that the diffusion process in the multidimensional potential is described to first order, taking well into account correlated fluctuations in the different wells. The coupling of “short” MD with ORZLD seems able to describe local dynamics at least in the cases where the role of the conformational transitions is not the determinant process because the polymer is stiff or is too flexible.

On this basis a first-order model ORZLD was proposed for the local dynamics of proteins by observing that proteins in physiological conditions are primarily organized in stable three-dimensional (3D) structures, as experimentally determined by X-ray or by NMR. The dynamics of proteins can be better described, therefore, as the rotational diffusion of a fluctuating 3D structure, with fluctuations described by short (hundreds of picoseconds) MD trajectories.[19]

Although the first-order theory includes details of the nonquadratic potential in the computations of the bond correlation matrix and matrix of the equilibrium inverse distances, the extent of conformational transition effects retained in the theory is unclear. For this reason simple one-dimensional Smoluchowski models including potential barriers, but ignoring hydrodynamic interactions, were studied in the case of a particle in a 2−4 potential[20] and of a dipole undergoing one-dimensional torsional motion.[21,22] The advantage is that in these simple cases the exact solution to the correlation time for the relative TCF can be worked out together with suitable approximate methods for the calculation of the memory function effects to be extended to the multidimensional case (polymer). The above-mentioned papers showed that the ORZ approximation (or, better, optimized Rouse (OR) approximation, taking into account that hydrodynamic interactions were ignored) loses accuracy as the barrier height increases, as is expected in this case where the correlation time for the TCF and barrier transition time are of the same order of magnitude. Three methods were employed to produce approximations to the exact TCF. The continued fraction formalism turned out to be inefficient from a computational viewpoint even in the one-dimensional case. The matrix expansion method amounts to representing the TCF in terms of the eigenfunctions of the dynamic operator and approximating the eigenfunctions by expansions in basis sets of increasing order, selected in the spirit of a mode−mode coupling theory. This second method, which in some cases coincides with the continued fraction method, turned out to be much more computationally efficient but somewhat arbitrary in the choice of element form in the basis set. Finally the third method couples a jump model, derived from the equivalent Master equation for describing barrier transitions, to a diffusional model for describing fluctuations in the wells. This last method gave fairly good approximations in the whole range of barrier heights in the case of a multibarrier torsional system but has not yet been extended to the multidimensional case.

On the contrary, the matrix expansion method has recently been extended to the multidimensional case and applied to the calculations of local TCFs for simple models of united-atom alkanes.[23−25] The theoretical results were compared to the equivalent “exact” results obtained by Brownian dynamics simulations on the same system. Here the first-order OR basis is simply given by the x components of the sequence of bonds, the slow variables in the model, while the second, third, and higher order basis sets are chosen as trilinear, pentalinear, and higher odd products of all the bond components. Symmetry rules were derived to reduce the exploding number of elements emerging with the increase in the expansion order. It was found that the OR first-order theory fares remarkably well, and the longer the chain, the better, despite the frequent conformational transitions in one correlation time. In addition, the first few higher orders in the mode-coupling theory improve the agreement with simulations especially with longer times.

Despite the notable progress made in recent years, several aspects of the polymer dynamics theory remain to be clarified to get reliable molecular modeling of local dynamics. These include the role of corrections to preaveraged hydrodynamic interactions and to polymer−solvent interactions, a treatment of memory function extendible to long polymers or proteins, and the relative roles of correlated fluctuations in wells and conformational transitions.

In this paper we study the matrix expansion method for a Smoluchowski equation with hydrodynamic interactions. To simplify the analysis we have chosen simple polymer models, such as the freely jointed chain, the linear rod, and the broken rod models. These models completely disregard the problem of realistic intramolecular potentials and concentrate on the effects of constraining bonds to a fixed length. The simplicity of the polymer models will help to develop methods for reducing the enormous number of elements in the basis sets in the higher orders of the mode-coupling expansion.

We suggest a method for reducing the number of elements in the basis sets of the mode-coupling approach based on adding to the first-order linear basis set only those nonlinear elements which are composed of products of variables displaying the maximum correlation to the actually relaxing variable (maximum correlation approximation, MCA). This sorting procedure is used to generate an MCA mode-coupling solution to the full generalized diffusion equation, including hydrodynamic interactions. While simple applications to FJ, broken rods, and rods are considered here to show the usefulness of the method both in chains with small or strong bond correlations, applications of the MCA theory to more realistic models describing proteins and polymers will in future be given and the results compared to experimental local dynamics.

Section II presents the mode-coupling expansion solution to the multidimensional Smoluchowski diffusion equation with hydrodynamic interactions. The dynamic equations are solved for the bond TCFs and their correlation times. Section III discusses the problem of the basis sets in the mode coupling expansion. In section IV, results are presented for the bond correlation times of the broken rod model. In section V, the sorting procedure for reducing the number of terms in high-order basis sets in the matrix expansion is given, and the maximum correlation approximation to the solution of the diffusion dynamics is defined. Section VI summarizes the first-order ORZ theory, while section VII gives the MCA theory up to the second order in the mode-coupling expansion, including hydrodynamic interactions. In section VIII the MCA results for a rod with exact, preaveraged, or zero hydrodynamic interaction are given and compared to the respective exact results. Finally, in section IX a brief discussion and conclusion is given.

II. Matrix Expansion Solution to Smoluchowski Dynamics with Hydrodynamic Interaction

The multidimensional Smoluchowski equation for a linear polymer of $N + 1$ beads and N bonds describes the time evolution of the probability distribution function of the polymer configuration $\Psi(\mathbf{r},t)$

$$\frac{\partial}{\partial t}\psi(\mathbf{r};t) = \mathcal{D}\psi(\mathbf{r};t) \tag{2.1}$$

with $\mathcal{D}$, the diffusion operator, defined as

$$\mathcal{D}\psi = \sum_{i,j=0}^{N}[\nabla_i\cdot\mathbf{D}_{ij}\cdot(\nabla_j\psi + \psi(\nabla_j U/k_{\mathrm{B}}T))] \tag{2.2}$$

and

$$\mathbf{D}_{ij} = D_i\mathbf{H}_{ij} \tag{2.3}$$

the diffusion tensor with

$$\mathbf{H}_{ij} = \mathbf{1}\delta_{ij} + \zeta_i\mathbf{T}_{ij}(1 - \delta_{ij}) \tag{2.4}$$

$$\mathbf{T}_{ij} = (8\pi\eta r_{ij})^{-1}[\mathbf{1} + \mathbf{r}_{ij}\mathbf{r}_{ij}/r_{ij}^2] \tag{2.5}$$

the hydrodynamic interaction matrix and Oseen tensor, respectively. Here

$$D_i = k_{\mathrm{B}}T/\zeta_i \tag{2.6}$$

is the diffusion coefficient and ζ_i is the friction coefficient of bead i, while U is the potential and $\mathbf{r}$ is the $3(N + 1)$-dimensional vector coordinate of the beads $\mathbf{r}_n$, $n = 0, ..., N$.

The dynamics of the bond coordinates

$$\mathbf{l}_n = \mathbf{r}_n - \mathbf{r}_{n-1}, \quad n = 1, ..., N \tag{2.7}$$

are governed (as well as the bead coordinates)[26] by $\mathcal{L}$, the adjoint operator to $\mathcal{D}$

$$\frac{\partial}{\partial t}\mathbf{l} = \mathcal{L}\,\mathbf{l} \tag{2.8}$$

where

$$\mathcal{L} = \sum_{n=0}^{N}[\nabla_i\cdot\mathbf{D}_{ij}\cdot\nabla_j - (\nabla_i U/k_{\mathrm{B}}T)\cdot\mathbf{D}_{ij}\cdot\nabla_j] \tag{2.9}$$

and $\mathbf{l}$ is the $3N$-dimensional vector of the coordinate bond vectors $\mathbf{l}_n$.

By expansion of the conditional probability (solution to the Smoluchowski equation) in a complete set of eigenfunctions of $\mathcal{L}$, an arbitrary time correlation function of any two dynamic variables with zero average $f(\mathbf{l})$, $g(\mathbf{l})$ may be expressed in the standard form[20,27]

$$\langle f(t)g(0)\rangle = \sum_i\langle f|\psi_i\rangle\langle\psi_i|g\rangle\exp(-\lambda_i t) \tag{2.10}$$

where λ_i and ψ_i are the eigenvalues and the normalized eigenfunctions of the operator $\mathcal{L}$:

$$\mathcal{L}\,\psi_i = -\lambda_i\psi_i \tag{2.11}$$

The matrix expansion method for the calculation of the TCF $\langle f(t)g(0)\rangle$ requires the solution of the eigenvalue equation (eq 2.11) by expanding ψ_i in a set of (not necessarily orthogonal) basis functions $\Phi = \{\phi_m,\ m = 1, ..., M\}$:

$$\psi_i = \sum_m c_{mi}\phi_m \tag{2.12}$$

Then eq 2.11 is converted to the generalized matrix eigenvalue equation

$$\mathbf{FC} = \mathbf{SC}\Lambda \tag{2.13}$$

with Λ the diagonal matrix of the eigenvalues λ_m, $\mathbf{C}$ the matrix of coefficients c_m, $\mathbf{S}$ the metric matrix

$$S_{ij} = \langle\phi_i|\phi_j\rangle \tag{2.14}$$

and $\mathbf{F}$ the equilibrium force matrix[6]

$$F_{ij} = -\langle\phi_i|\mathcal{L}\,\phi_j\rangle = \sum_{mn}\langle(\nabla_m\phi_i)\cdot\mathbf{D}_{mn}\cdot(\nabla\nabla_n\phi_j)\rangle \tag{2.15}$$

The averages are calculated as

$$\langle a|b\rangle = \int\psi_0(\mathbf{r})a(\mathbf{r})b(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{2.16}$$

with $\psi_0(\mathbf{r})$ being the equilibrium distribution function.

The first-order partial derivatives in eq 2.15 can be conveniently calculated in terms of the bond components:

$$\frac{\partial\phi_i}{\partial r_{k\alpha}} = \frac{\partial\phi_i}{\partial l_{k\alpha}} - \frac{\partial\phi_i}{\partial l_{k+1,\alpha}} \tag{2.17}$$

As the eigenfunctions ψ_i are orthonormalized, the coefficient matrix **C** should satisfy the normalization equation

$$\mathbf{C}^T\mathbf{S}\mathbf{C} = \mathbf{1} \tag{2.18}$$

Using the transformation in (2.12) the TCF (eq 2.10) becomes

$$\frac{\langle f(t)g(0)\rangle}{\langle fg\rangle_{\mathrm{eq}}} = \frac{1}{\langle fg\rangle_{\mathrm{eq}}}\sum_m\Big(\sum_i c_{im}\langle f|\phi_i\rangle\Big)\Big(\sum_j c_{jm}\langle\phi_j|g\rangle\Big)\exp(-\lambda_m t) \tag{2.19}$$

If $f = g$, we get the expression for the time autocorrelation function of f, whose correlation time (CT) τ is, after application of eqs 2.13 and 2.18 to the integration of eq 2.19

$$\tau = \frac{1}{\langle f^2\rangle}\int_0^\infty\langle f(t)f(0)\rangle\,\mathrm{d}t = \frac{1}{\langle f^2\rangle}\sum_{i,j}\langle f|\phi_i\rangle\langle f|\phi_j\rangle(\mathbf{F}^{-1})_{ij} \tag{2.20}$$

It is important to note that the TCF and its CT in the matrix expansion method do not explicitly depend on the intramolecular potential, which enters the theory only via statistical averaging with the equilibrium distribution function. This can be appreciated by inspection of eqs 2.19 and 2.20 for the TCF and CT, respectively, and of the definitions of matrices **S** and **F**. Therefore, by introducing the proper distribution function, the theory may be applied to any polymer solution, taking into account different types of long-range and short-range interactions (flexible chains in good and poor solvents, stiff polymers, polymers with atomistic interactions).

Note that for any element ϕ_n of the basis the TCF (eq 2.19) becomes

$$C_n(t) = \frac{1}{\langle{\phi_n}^2\rangle}\sum_{m,i=1}^{M}(S_{ni}c_{im})^2\exp(-\lambda_m t) \tag{2.21}$$

Using properties in (2.13) and (2.18) the integration of (2.21) gives the CT

$$\tau_n = \frac{1}{\langle{\phi_n}^2\rangle}(\mathbf{S}\mathbf{F}^{-1}\mathbf{S})_{nn} \tag{2.22}$$

Note that the main problem in the calculation of the TCF is the derivation of the matrix **F**, eq 2.15, due to the complicated structure of the hydrodynamic interaction: this problem will be faced in sections VI and VII for a first and a reduced second-order basis set, respectively.

In all the applications in the following sections, the bead friction coefficient and the bond mean square lengths are assumed to be constant and equal to ζ and l^2, respectively.

III. Mode-Coupling Basis Sets for the Matrix Expansion

One-dimensional Smoluchowski dynamics can be used as a guide to the most difficult application of the matrix expansion method to multidimensional problems. In the case of the positional TCF $\langle x(t)x(0)\rangle$ for diffusion in a 2−4 potential in one dimension, a nonorthogonal basis set built with increasing powers of the positional variable was the optimal choice, giving the OR approximation[20] to first-order power. It is appealing to extend this procedure to the case, which is similar in principle, to the calculation of the TCFs of the bond vector components of a chain by choosing a basis set that includes products of increasing order of the bond components $l_{m\alpha}$, $m = 1, ..., N$, $\alpha = x, y, z$. This option was first proposed by Chang and Freed[23] in their extension of the matrix expansion method to the case of the Smoluchowski dynamics of alkanes in an empiric potential. Once again, this natural basis set gives the OR approximation to the lowest order $\{l_{mx}\}$. Higher order basis sets are obtained as products of the bond components or of the OR normal modes following the mode-coupling approach for the treatment of long time critical dynamics[23−25,28] Here, we follow many of the procedures developed by Freed et al.[23,25] to search for the important basis elements.

Given a chain of N bonds in d dimensions, a basis set containing all the possible powers and products of bond vector components up to the value b has a dimension M which is easily obtained by combinatorial rules as

$$M = \sum_{p=1}^{b}\binom{Nd + p - 1}{p} \tag{3.1}$$

The basis set including all the powers of the bond vector components is complete and in principle gives exact results. However, it is infinite and therefore basis sets with a reduced number of elements should be generated to supply approximations to the exact solution.

The dimension of the basis sets increases with b in such a way that the solution of the eigenvalue equation soon becomes impractical even for small values of b. Fortunately, not all the M elements of the basis set are required, because many of them make no contribution to

$$C_n(t) = \langle l_{nx}(t)l_{nx}(0)\rangle/\langle{l_{nx}}^2\rangle$$

The first-order basis set is given by the x components of the N bond vectors

$$\Phi_{\mathrm{I}} = \{l_{1x}, l_{2x}, ..., l_{Nx}\} \tag{3.2}$$

This is part of a general exclusion criterion: if $\Phi \equiv \{\Phi_1, \Phi_2\}$ is a basis set with Φ_1 and Φ_2 being two sets of components giving diagonal block matrices **S** and **F**, then Φ_1 and Φ give through eqs 2.21 and 2.22 the same TCF and CT.[23] The calculation of the TCFs of the bond vector components of a chain is accomplished by choosing basis sets that include products of increasing numbers of bond components $l_{m\alpha}$, $m = 1, ..., N$, $\alpha = x, y, z$. The first order includes only linear bond components $\{l_{mx}\}$, while higher order basis sets are obtained by adding trilinear, pentalinear, etc. products of bond components. In line with the previously stated exclusion criterion, none of the even products of bond components contribute.

A more precise and efficient requirement for reducing the number of elements at any order is supplied by the symmetry properties of the diffusion operator and its adjoint.[24] The diffusion operator and its adjoint are invariant to rotations of the coordinate system; as a consequence, considering bond vector correlations, the eigenfunctions of the diffusion operator and therefore the elements of the basis set should transform as vectors. This means that the second-order basis set is drastically reduced to

$$\Phi_{\mathrm{II}} \equiv \Phi_{\mathrm{I}} \cup \{l_{mx}(\mathbf{l}_p\cdot\mathbf{l}_q),\quad m, p = 1, ..., N;\ q = p, ..., N\} \tag{3.3}$$

whose dimension is

$$M_{\mathrm{II}} = N + N\binom{N+1}{2} \tag{3.4}$$

Similarly the third-order basis set becomes

$$\Phi_{\mathrm{III}} \equiv \Phi_{\mathrm{II}} \cup \{l_{mx}(\mathbf{l}_p\cdot\mathbf{l}_q)(\mathbf{l}_r\cdot\mathbf{l}_s),\ m, p = 1, ..., N;\ q, r = p, ..., N;\ s = r, ..., N\} \tag{3.5}$$

with dimension

$$M_{\mathrm{III}} = M_{\mathrm{II}} + N\sum_{i=1}^{N} i\binom{i+1}{2} \tag{3.6}$$

In the case of the broken rod model discussed below, when the matrix **S** becomes singular the eigenvalue equation may still be solved, by inversion of eq 2.13:

$$\mathbf{F}^{-1}\,\mathbf{SC} = \mathbf{C}\Lambda^{-1} \tag{3.7}$$

By addition of more and more terms, matrix **F** also becomes singular but the singular part of **F** gives zero contribution to the TCFs. In principle, the elements of the basis set responsible for the singularities should be identified and discarded. Given that this search procedure requires considerable computer time, an algorithm has been devised to solve automatically the full eigenvalue equation and calculate the CT of eq 2.22.

Increasing further the dimension of the basis set, the matrix **F** eventually becomes ill-conditioned and the matrix expansion fails, as found in the one-dimensional case.[20]

Even using the minimal basis sets dictated by the symmetry properties of the dynamic operator L, we can observe from eqs 3.4 and 3.6 that the number of elements explodes with increasing order and N. For instance, as N increases from 5 to 10 and 20, the second-order basis grows from 80 to 560 and 4220, while the third order basis increases from 780 to 17 610 and 473 920.

For this reason it is interesting to try to select from the combinations of all the elements of the minimal basis set of each order those terms contributing most to the long time behavior of the TCF. Following Freed *et al.*,[24,25] we could choose trilinear, pentalinear, etc. products of the linear OR vector modes instead of the bond vectors

$$\mathbf{m}_a = \sum_i c_{ia}\mathbf{l}_i \tag{3.8}$$

with $\{\mathbf{m}_a\}$ the first order approximation to the eigenfunctions $\{\psi_a\}$ of eq 2.11.

If the OR modes are sorted with the increasing value of the associated eigenvalue, the smaller indices are associated with the slower decaying modes, and products of modes decay with the sum of the respective eigenvalues. Therefore, in the spirit of the mode-coupling approach, it could be expected that only products (to any order) involving slow decaying modes contribute significantly to the long time dynamics. Thus we can build a reduced second-order basis set as

$$\Phi^{Q}{}_{\mathrm{II}} \equiv \{m_{1x}, m_{2x}, ..., m_{Nx}\} \cup \{m_{nx}(\mathbf{m}_p\cdot\mathbf{m}_q),\ n, p = 1, ..., Q;\ q = p, ..., Q;\ Q \le N\} \tag{3.9}$$

If $Q = 0$, this basis set reduces to the full first order basis set Φ_{I}, while if $Q = N$, this basis set is equivalent to the second order basis set Φ_{II}. The extension to Q-reduced third-order basis set from (3.5) is straightforward.

However, for the freely jointed chain the Q values necessary for accurate approximations of long time dynamics and therefore of CT are at any order very close to N. This shows that in the case of the diffusion of freely jointed bonds of fixed length the procedure does not work, in contrast with the case of alkanes in an atomistic potential.[24] For this reason we do not report results for the Q-basis sets. For future reference we note that even though the first-order eigenvalues differ by a significant factor (here a factor of 14 at $N = 5$), this does not mean that this sorting procedure is efficient. Therefore, a case by case check is required, or alternatively, other more efficient selection rules should be invoked.

IV. Model Calculations in the Free Draining Limit

Results for a simple polymer model, the broken rod, are presented and discussed here to show that a great improvement to the first-order ORZ theory of polymer solutions may be obtained with only a modest increase in computational effort by selecting those few nonlinear terms that are strongly correlated to the relaxing variable. All of the computations have been done by taking advantage of the high numerical precision and formal derivation tools provided by MATHEMATICA 2.2.[29]

The broken rod model is a chain characterized by N rigid bonds attached by rigid colinear joints, as in the rod, or connected by universal joints as in the freely jointed chain: different sequences of joints are considered between the two opposite limits of a freely jointed chain (all the joints are universal) and of a shish kebab rod (all the joints are rigid and colinear). The statistical properties of products of bond components in the broken rod are completely defined by taking into account that different bonds are statistically independent if they are separated at least by a universal joint or that the bonds in a rod sequence of length P, attached by universal joints to the remaining chain, display the statistical properties of a free rod of length P.

As the aim of this section is to justify a sorting procedure to reduce the basis set in the mode coupling approach, calculations are restricted to the easier free-draining limit.

Freely Jointed Chain. In the case of the first order basis $\{l_{1x}, l_{2x}, ..., l_{Nx}\}$ the overlap matrix is $S_{ij} = (l^2/d)\,\delta_{ij}$, in which d is the space dimension and the TCF in (2.21) becomes

$$C_n(t) = \frac{l^2}{d}\sum_{m=1}^{N} c_{nm}{}^2 \exp(-\lambda_m t) \tag{4.1}$$

with eigenvalues given as[30]

$$\sigma^{-1}\lambda_m = 4\sin^2(\pi m/(N+1)); \quad \sigma = \frac{dk_BT}{l^2\zeta} \tag{4.2}$$

The correlation time from eq 2.22 becomes

$$\tau_n = \frac{l^2}{d}(\mathbf{F}^{-1})_{nn} \tag{4.3}$$

In the case of the first-order basis set the matrix **F** is derived from eq 2.15 as the Rouse matrix for the bonds

$$\mathbf{F} = D\begin{pmatrix} 2 & -1 & 0 & \dots \\ -1 & 2 & -1 & \dots \\ 0 & -1 & 2 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{4.4}$$

which is easily inverted to get

$$\mathbf{F}^{-1} = \frac{D^{-1}}{N+1} \times \begin{pmatrix} N & N-1 & N-2 & \dots & 2 & 1 \\ N-1 & 2(N-1) & 2(N-2) & \dots & 4 & 2 \\ N-2 & 2(N-2) & 3(N-2) & \dots & 6 & 3 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 2 & 4 & 6 & \dots & 2(N-1) & N-1 \\ 1 & 2 & 3 & \dots & N-1 & N \end{pmatrix} \tag{4.5}$$

Using this equation, the first-order correlation time (eq 4.3) takes the final form

$$\sigma\tau_n = \frac{n(N-n+1)}{N+1} \tag{4.6}$$

This is a generalization of the correlation time for the bond vector time correlation function in the Rouse model[31] to any position n, any chain length N, and space dimensionality d.

The slope in $t = 0$, $-C_n'(0)$, turns out to be 2σ, independent of n and N.

The greatest additional contribution to the first order correlation time τ_n is made by the simple second-order reduced basis set of dimension $N + 1$, obtained by adding to the first-order basis set the element $l_{nx}(\mathbf{l}_n \cdot \mathbf{l}_n)$, which requires very little computational effort. In this approximation $\sigma\tau_n$ is given again by a rational expression

$$\sigma\tau_n \cong \frac{n(N-n+1)}{N+1} + k \tag{4.7}$$

where k is a rational number equal to $^1/_2$ for $d = 2$ and $^1/_4$ for $d = 3$.

The slope in $t = 0$ decreases to σ, independent of n and N, for the reduced second-order basis set. The full second-order and higher order basis sets further reduce the slope smoothly by small amounts that depend on n and N.

Tables 1 and 2 report the contribution of increasing expansion orders to the bond correlation times of chains of increasing length in three dimensions, for the end and central bond respectively. The correlation times defined in eq 2.18 are reported in adimensional form as $\sigma\tau_n$.

Table 1. Adimensional Correlation Times for the End Bonds $\sigma\tau_1$ as a Function of the Number of Bonds N in Three Dimensions and Contributions of the First Few Orders in the Matrix Expansion

N	first order	reduced II	full II	third order
1	0.5000	0.7500	0.7500	0.7500
2	0.6667	0.9167	0.9342	0.9540
3	0.7500	1.0000	1.01832	1.0414
4	0.8000	1.0500	1.06840	1.0918
5	0.8333	1.0833	1.1017	
6	0.8571	1.1071	1.1256	
7	0.8750	1.1250	1.1434	
8	0.8888	1.1388	1.1573	
9	0.9000	1.1500	1.1684	
10	0.9090	1.1590	1.1775	
$\gg 1$	$\sim$1.0000[a]	$\sim$1.2500[b]		

[a] From eq 4.6. [b] From eq 4.7.

Table 2. Adimensional Correlation Times for the Central Bond $\sigma\tau_c$ as a Function of the Number of Bonds N in Three Dimensions and Contributions of the First Few Orders in the Matrix Expansion

N	first order	reduced II	full II	third order
3	1.0000	1.2500	1.2939	1.3413
4	1.2000	1.4500	1.4967	1.5510
5	1.5000	1.7500	1.8008	
6	1.7143	1.9643	2.0162	
7	2.0000	2.2500	2.3036	
8	2.2222	2.4722	2.5265	
9	2.5000	2.7500	2.8051	
10	2.7272	2.9772	3.0329	
$\gg 1$	$\sim 0(N/4)$[a]	$\sim 0(N/4)$[b]		

[a] From eq 4.6. [b] From eq 4.7.

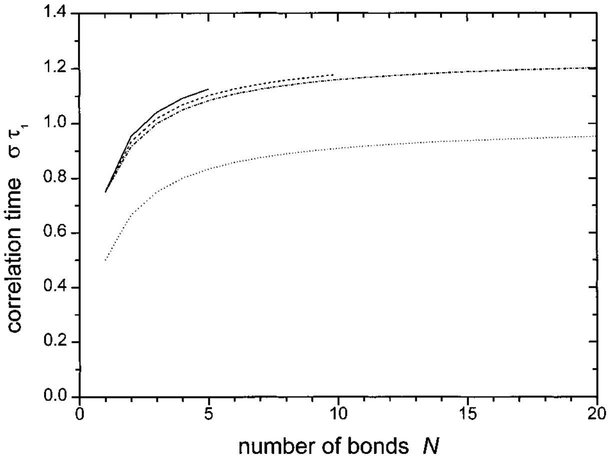

Figure 1. Correlation time $\sigma\tau_1$ for the end bonds as a function of the number of bonds N for several orders in the matrix expansion method. Key (from bottom to top): dotted line, first-order approximation; dashed−dotted line, reduced second order; dashed line, full second order; solid line, third order.

The main difference between the CT of the end and central bonds is related to the asymptotic behavior with N: while the former gives a constant asymptotically, the latter increases linearly with N. For this reason we report in Figures 1 and 2 $\sigma\tau_1$ and $\sigma\tau_c/N$, respectively, against the number of bonds. Not only does the first-order OR result make the largest contribution, but also, for the central bond, it represents, in the limit of large N, the exact result. Indeed, for the central limit theorem the distribution function for the FJ chain becomes the Gaussian distribution function for large N.

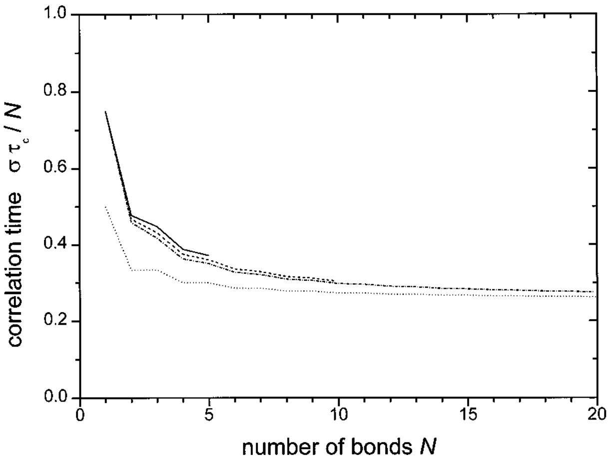

Figure 2. Normalized correlation time $\sigma\tau_c/N$ for a central bond as a function of the number of bonds N for several orders in the matrix expansion method. The labeling scheme is the same as in Figure 1.

As can be seen in Tables 1 and 2 and in Figures 1 and 2, the additional contribution of higher orders decreases rapidly. In the case of the end bond, the second order contributes an increase of 50% at $N = 1$ but less than 30% at large N, while the third order yields an additional contribution of around 2%. In the case of the central bond, the additional contribution at $N = 4$ is 25% and 3% for the second and third orders, respectively.

Tables 1 and 2 and Figures 1 and 2 show the role of the reduced second-order basis set more clearly. For the freely jointed chain there is a single element in the higher order basis sets that is responsible for the largest part of the memory contributions to the CT. The addition of the single term $l_{nx}(\mathbf{l}_n\cdot\mathbf{l}_n)$ to the first-order basis set of N elements generates a reduced second-order basis set of order $N + 1$ that greatly improves the first-order result and represents the main part of the memory contribution to τ_n, even though it requires no more computational effort than the OR first-order theory. The full second-order result, which includes many more terms in the basis set, adds very little to the reduced second-order result, while higher orders contribute only a few percent. Moreover, looking at short time behavior, we find that there is a sharp decrease from a slope of 2σ in the first order to σ in the reduced second order, while a further poor decrease continues with increasing orders.

If the freely jointed moments are approximated by the Gaussian moments, the Rouse results for the bond vector TCFs and CTs are obtained identically at any order in the matrix expansion. For the Gaussian chain, adding higher bond powers to the OR first-order basis set simply generates new eigenvalues without changing the Rouse ones in the eigenvalue equation, (2.10). These new eigenvalues contribute exponential terms in (2.13), whose coefficients are identically zero due to the values of the Gaussian moments. Thus it is clearly revealed that the Rouse solution to the Smoluchowski equation without hydrodynamic interactions is exact for a Gaussian chain. This represents a thorough check of the matrix expansion method in the calculation of memory function effects in Smoluchowski dynamics.

The Broken Rod Model. In Table 3, results for the adimensional bond correlation times $\sigma\tau_n$ in $d = 3$ dimensions for the broken rod model are presented.

Table 3. Adimensional Correlation Times $\sigma\tau_n$ for a Broken Rod of $N = 5$ Bonds[a]

		$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
uuuu	I	0.833	1.333	1.500	1.333	0.833
	II/1	1.083	1.333	1.500	1.333	0.833
	MCA	1.083	1.583	1.750	1.583	1.083
	MCA/n	1.099	1.621	1.790	1.621	1.099
	II	1.102	1.631	1.801	1.631	1.102
ruru	I	3.500	3.500	4.833	4.833	0.833
	II/1	3.750	3.750	4.833	4.833	0.833
	II/1,2	4.500	4.500	4.833	4.833	0.833
	II/3	3.500	3.500	5.083	5.083	0.833
	MCA	4.500	4.500	5.083	5.083	1.083
	MCA/n	4.683	4.683	6.269	6.269	1.112
	II	4.700	4.700	6.335	6.335	1.113
urru	I	0.833	9.500	9.500	9.500	0.833
	II/2	0.833	9.750	9.750	9.750	0.833
	II/2,3	0.833	10.50	10.50	10.50	0.833
	MCA	1.083	12.00	12.00	12.00	1.083
	MCA/n	1.130	13.45	13.45	13.45	1.130
	II	1.131	13.54	13.54	13.54	1.131
rrrr	I	17.50	17.50	17.50	17.50	17.50
	II/1	17.75	17.75	17.75	17.75	17.75
	II/1,2	18.50	18.50	18.50	18.50	18.50
	II/1,2,3	20.00	20.00	20.00	20.00	20.00
	II/1,2,3,4	22.50	22.50	22.50	22.50	22.50
	MCA/exact	26.25	26.25	26.25	26.25	26.25

[a] Key I, first order; II/*n*,*m*, ..., first order plus the trilinear diagonal terms $l_{nx}(\mathbf{l}_n\cdot\mathbf{l}_n)$, $l_{nx}(\mathbf{l}_m\cdot\mathbf{l}_m)$, ..., MCA, MCA basis set, eq 5.2; MCA/*n*, MCA basis set plus all the trilinear nondiagonal terms including bond $\mathbf{l}_n$; II, second order.

If we define a universal joint by *u* and a rodlike joint by *r*, the chain configuration is represented by a sequence of $N - 1$ letters chosen between *u* and *r*. The results for a chain of 5 bonds are presented for 4 configurations: *uuuu*, the freely jointed chain limit; *ruru*; *urru*; and *rrrr*, the rod limit. The correlation times are first calculated in the OR approximation using the first-order basis set, and then the effect of adding one or more second-order trilinear terms of the diagonal form $l_{nx}(\mathbf{l}_n\cdot\mathbf{l}_n)$ is reported until all the N diagonal terms are added. As justified in detail in the following section, this reduced basis set of $2N$ elements is defined as the MCA basis set. For the sake of comparison, the correlation times correct to the full second order are also reported.

Looking at the freely jointed chain of the N trilinear diagonal terms, only the $l_{nx}(\mathbf{l}_n\cdot\mathbf{l}_n)$ term contributes to the relaxation of the corresponding bond n, due to the fact that bonds with different n are uncorrelated. Adding all the cross trilinear terms in the second-order basis only improves the MCA result by a few percent. But of these cross terms the contribution of those terms including at least one $\mathbf{l}_n$ component (these results with extended MCA basis are reported in Table 3 as MCA/*n*) is by far the most significant. This shows the importance of elements that include bond components correlated to the relaxing bond.

In the opposite case of high correlation, the rod, we can observe that adding a single diagonal term has the same effect on all the bond correlation times of the rod, and adding more diagonal terms greatly improves the rod correlation time until with all the N trilinear diagonal terms the exact rod result is obtained:[5]

$$\sigma\tau_{\mathrm{ROD}} = \frac{N(N+1)(N+2)}{8} \tag{4.8}$$

Adding further terms of any order does not contribute any more.

As is well-known,[7] the exact result is $^3/_2$ the first-order result. It is important to observe that in the case of a rod, where the correlation between all the bonds in the chain is maximum, adding the N second-order diagonal terms to the OR basis set gives the exact result while OR turns out to be a poor approximation. This is an encouraging check for the matrix expansion method and for the definition of a sorting procedure to select the important terms in the basis set.

The intermediate broken rod cases are of particular interest. The correlation times of a rod segment get their maximum second-order value with the inclusion of all the trilinear diagonal terms containing bond components belonging to that particular rod segment; adding additional uncorrelated trilinear diagonal terms does not make any contribution. Further contributions, amounting to less than 20%, are obtained by adding the cross trilinear terms (compare MCA to II lines). But again the main contribution made by these cross terms comes from the few terms having at least one bond strongly correlated to the relaxing bond (MCA/n lines). Thus a concept emerges from this discussion: sorting in the basis set at any order only those terms which have the maximum correlation to the relaxing bond.

V. MCA Approximation

Analysis of the broken-rod model in the previous section suggested that fairly good approximations to higher orders may be generated by simply retaining those terms in the basis set which involve only products of bonds strictly correlated to the relaxing bond. In the case of the freely jointed chain, the second order was optimally reduced to the single term $l_{nx}(\mathbf{l}_n\mathbf{l}_n)$, because there is no correlation between two different bonds. In the case of a shish kebab rod of N beads, all the N terms $\{l_{ix}(\mathbf{l}_i\mathbf{l}_i),\ i = 1, ..., N\}$ are required to derive the exact dynamics of l_{nx} because all the bonds in the rod are correlated. Finally, P ($<N$) terms $l_{ix}(\mathbf{l}_i\mathbf{l}_i)$ are required in the case where the relaxing bond is part of a rod of length P in a broken rod chain. In general, we infer that we must retain in the second-order basis set only those trilinear terms having at least a factor strictly correlated to the relaxing bond

$$\Phi_{\mathrm{II}}^{\mathrm{MCA}} \equiv \Phi_{\mathrm{I}} \cup \{l_{mx}(\mathbf{l}_p\cdot\mathbf{l}_q);\ m, p, q \subset \Gamma_n\} \qquad (5.1)$$

with Γ_n the set of bond indices of the bonds most strongly correlated to the bond l_{nx}.

The choice of this basis set defines a second-order maximum correlation approximation (MCA). In the following we reduce this MCA basis to the case where $m = p = q = 1, ..., N$ including all the diagonal trilinear elements for a total of $2N$ terms, which we have shown are of importance to give a good approximation to the broken rod model:

$$\Phi_{\mathrm{II\ diag}}^{\mathrm{MCA}} \equiv \Phi_{\mathrm{I}} \cup \{l_{mx}(\mathbf{l}_m\cdot\mathbf{l}_m);\ m = 1, ..., N\} \qquad (5.2)$$

The inclusion in the basis set of all the N trilinear diagonal terms of (5.2) is a compromise that considers a good portion of the neighbor correlations and, at the same time, allows the equivalent description of the relaxation of all the N bonds. The rod and the freely jointed chain were chosen as examples of chains of strong and small correlations. The MCA theory is also expected to apply to chains with a different degree of neighbor correlation as described by atomistic intramolecular potentials; this will be tested in future work. The important point is that this MCA theory includes a minimum of terms ($2N$ in the theory developed in this paper), and therefore it is amenable to computations even for atomistic models including hydrodynamic interaction.

There are two further points we would like to stress. First, it is possible to produce optimum higher order approximations by applying the same concept of maximum correlation approximation to pentalinear products etc. Second, treatment of the MCA theory in this paper is confined to the case of the bond dynamic variables, but it is straightforward to extend it to different dynamic variables such as those required in the calculations of the orientational time correlation functions[11,24] of first-order $\langle\cos\theta(t)\rangle$ and second-order ${}^3/_2\langle\cos^2\theta(t)\rangle - {}^1/_2$.

VI. First-Order Mode-Coupling Theory

In the case of the first-order basis $\{l_{1x}, l_{2x}, ..., l_{Nx}\}$, the gradients in eq 2.15 are calculated as

$$\frac{\partial l_{ix}}{\partial r_{m\alpha}} = \delta_{x\alpha}\,(\delta_{im} + \delta_{i-1,m}) \qquad (6.1)$$

thus giving for $\mathbf{F}$, using the definition in (2.3)

$$F_{ij} = D\sum_{mn}\sum_{\alpha,\beta}\langle\delta_{x\alpha}(\delta_{im} - \delta_{i-1,m})H_{mn}^{\alpha\beta}\delta_{x\beta}(\delta_{jn} - \delta_{j-1,n})\rangle \qquad (6.2)$$

with α, β describing the Cartesian components, m,n the bead coordinates and $H_{ij}^{\alpha\beta}$ the α, β components of the hydrodynamic interaction tensor $\mathbf{H}_{ij}$.

Equation 6.2 is easily summed to get

$$F_{ij} = D\langle H_{ij}^{xx} - H_{i,j-1}^{xx} - H_{i-1,j}^{xx} + H_{i-1,j-1}^{xx}\rangle \qquad (6.3)$$

Now due to the rotational invariance we have

$$\langle H_{ij}^{xx}\rangle = H_{ij} = \delta_{ij} + (1 - \delta_{ij})\zeta_r\langle l/r_{ij}\rangle \qquad (6.4)$$

with H_{ij} the equilibrium averaged hydrodynamic interaction matrix and

$$\zeta_r = \zeta/6\pi\eta l \qquad (6.5)$$

the hydrodynamic interaction strength.

Introducing the definition

$$L_{ij} = H_{ij}^{+} = H_{ij} - H_{i,j-1} - H_{i-1,j} + H_{i-1,j-1} = (\mathbf{aHa}^T)_{ij} \qquad (6.6)$$

with $\mathbf{a}$ the bead to bond transformation rectangular $N \times (N + 1)$ matrix

$$\mathbf{a} = \begin{pmatrix} -1 & 1 & 0 & 0 & \ldots \\ 0 & -1 & 1 & 0 & \ldots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \qquad (6.7)$$

we finally get the well-known optimized Rouse–Zimm matrix:

$$F_{ij} = DL_{ij} \qquad (6.8)$$

When eq 6.8 is used together with eqs 2.13 and 2.14, the ORZ theory is obtained. Thus the first-order mode coupling theory coincides with the well-known ORZ theory.

Note also that in the case $\zeta_r = 0$, we have $H_{ij} = \delta_{ij}$ and

$$F_{ij} = D(\delta_{ij} - \delta_{i,j-1} - \delta_{i-1,j} + \delta_{i-1,j-1}) = D(\mathbf{a}\mathbf{a}^T)_{ij} = DL^R_{ij} \quad (6.9)$$

with

$$\mathbf{L}^R = \begin{pmatrix} 2 & -1 & 0 & \dots \\ -1 & 2 & -1 & \dots \\ 0 & -1 & 2 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

the well-known bond Rouse matrix, and eqs 2.13 and 2.14 represent the optimized Rouse theory.

VII. Matrix F in the Maximum Correlation Approximation

Given the MCA basis set, the matrix **F** of order $2N$ is written in blocks of order N

$$\mathbf{F} = \begin{pmatrix} \mathbf{F}^1 & \mathbf{F}^{12} \\ (\mathbf{F}^{12})^T & \mathbf{F}^2 \end{pmatrix} \quad (7.1)$$

Block $\mathbf{F}^1$ is the first-order matrix discussed in the previous section, while the two blocks $\mathbf{F}^{12}$ and $\mathbf{F}^2$ are calculated below.

Calculation of $\mathbf{F}^{12}$. In the MCA approximation, the calculation of the block $\mathbf{F}^{12}$ in (2.15) amounts to choosing l_{ix} for ϕ_i and $l_{jx}(\mathbf{l}_j\cdot\mathbf{l}_j)$ for ϕ_j. The gradient of the former term is given by (6.1), while that of the latter is derived using (2.17) and the bond derivative:

$$\frac{\partial}{\partial l_{n\beta}}[l_{jx}(\mathbf{l}_j\cdot\mathbf{l}_j)] = \delta_{jn}(l_j^2\delta_{\beta x} + 2l_{jx}l_{j\beta}) \quad (7.2)$$

By inserting (6.1), (2.17), and (7.2) in (2.15), the off-diagonal block is obtained as

$$\frac{F^{12}_{ij}}{D} = \langle (H^{xx}_{ij})^+ \, l_j^2\rangle + 2\sum_\beta \langle (H^{x\beta}_{ij})^+ l_{jx}l_{j\beta}\rangle \quad (7.3)$$

where the operator $(...)^+$ is defined in (6.6).

In the approximation of preaveraging the hydrodynamic interaction

$$H^{\alpha\beta}_{ij} \cong \langle H^{\alpha\beta}_{ij}\rangle = \delta_{\alpha\beta}H_{ij} \quad (7.4)$$

Equation 7.3, after the use of rotational invariance, becomes

$$\frac{F^{12}_{ij}}{D} \cong \frac{5}{3}L_{ij}\langle l_j^2\rangle \quad (7.5)$$

where we have also taken into account the rotational invariance property $\langle l_{jx}^2\rangle = {}^1/_3\langle l_j^2\rangle$.

If, in addition, we ignore the hydrodynamic interaction ($H_{ij} = \delta_{ij}$), eq 5.5 simplifies to

$$\frac{F^{12}_{ij}}{D} \cong \frac{5}{3}L^R_{ij}\langle l_j^2\rangle \quad (7.6)$$

Returning to the general case, by introducing the following partitioning into the hydrodynamic interaction

$$\mathrm{H}^{\alpha\beta}_{\mathrm{ij}} = \delta_{\mathrm{ij}} + \mathrm{f}_{\mathrm{ij}} + \frac{\mathrm{f}_{\mathrm{ij}}}{\mathrm{r}^2_{\mathrm{ij}}}\mathrm{r}^\alpha_{\mathrm{ij}}\,\mathrm{r}^\beta_{\mathrm{ij}} \quad (7.7)$$

with

$$f_{ij} = (1 - \delta_{ij})\frac{\zeta_i}{8\pi\eta r_{ij}} \quad (7.8)$$

we can further simplify the exact equation (eq 7.3) to

$$\frac{F^{12}_{ij}}{D} = L^R_{ij}\langle l_j^2\rangle + \langle f^+_{ij}\, l_j^2\rangle + 2L^R_{ij}\langle l_{jx}^2\rangle + 2\langle f^+_{ij}\, l_{jx}^2\rangle + 2\langle (f_{ij}\, r^x_{ij}\, r^x_{ij}/r^2_{ij})^+ l_j^2\rangle + 2\sum_\beta\langle (f_{ij}\, r^x_{ij}\, r^\beta_{ij}/r^2_{ij})^+ l_{jx}l_{j\beta}\rangle \quad (7.9)$$

Taking the rotational invariance into account once again we finally get:

$$\frac{F^{12}_{ij}}{D} = \frac{5}{3}L^R_{ij}\langle l_j^2\rangle + 2\langle f^+_{ij}\, l_j^2\rangle + \frac{2}{3}\langle [f_{ij}\,(\mathbf{r}_{ij}\cdot\mathbf{l}_j)^2/r^2_{ij}]^+\rangle \quad (7.10)$$

where the operator $(...)^+$ is applied only to $\mathbf{r}_{ij}$.

Calculation of $\mathbf{F}^2$. The elements of the block matrix $\mathbf{F}^2$ are derived from (2.15) by substituting $l_{ix}(\mathbf{l}_i\cdot\mathbf{l}_i)$ and $l_{jx}(\mathbf{l}_j\cdot\mathbf{l}_j)$ for ϕ_i and ϕ_j respectively. By using (2.17) with (7.2) in (2.15), the second diagonal block is obtained as

$$\frac{F^2_{ij}}{D} = \langle (H^{xx}_{ij})^+ \, l_j^2\, l_j^2\rangle + 2\sum_\beta\langle (H^{x\beta}_{ij})^+ \,(l_i^2 l_{jx}l_{j\beta} + l_j^2 l_{ix}l_{i\beta})\rangle + 4\sum_{\alpha,\beta}\langle (H^{\alpha\beta}_{ij})^+ l_{ix}l_{jx}l_{i\alpha}l_{j\beta}\rangle \quad (7.11)$$

In the approximation of preaveraging the hydrodynamic interaction, eq 7.11 after the use of rotational invariance becomes

$$F^2_{ij}/D \cong L_{ij}\left[\frac{7}{3}\langle l_i^2\, l_j^2\rangle + \frac{4}{3}\langle (\mathbf{l}_i\cdot\mathbf{l}_j)^2\rangle\right] \quad (7.12)$$

and the matrix **L** is substituted by the bond Rouse matrix $\mathbf{L}^R$ to get the free draining limit. We can further simplify the exact equation (eq 7.11) by the same procedure used in the derivation of $\mathbf{F}^{12}$ to obtain

$$\frac{F^2_{ij}}{D} = L^R_{ij}\left[\frac{7}{3}\langle l_i^2\, l_j^2\rangle + \frac{4}{3}\langle (\mathbf{l}_i\cdot\mathbf{l}_j)^2\rangle\right] + \frac{4}{3}\langle f^+_{ij}[(\mathbf{l}_i\cdot\mathbf{l}_j)^2 + 2l_i^2\, l_j^2]\rangle + \frac{2}{3}\langle [f_{ij}(\mathbf{r}_{ij}\cdot\mathbf{l}_j)^2/r^2_{ij}]^+\, l_i^2 + [f_{ij}(\mathbf{r}_{ij}\cdot\mathbf{l}_i)^2/r^2_{ij}]^+\, l_j^2\rangle + \frac{4}{3}\langle [f_{ij}(\mathbf{r}_{ij}\cdot\mathbf{l}_i)(\mathbf{r}_{ij}\cdot\mathbf{l}_j)/r^2_{ij}]^+(\mathbf{l}_i\cdot\mathbf{l}_j)\rangle \quad (7.13)$$

where once again the operator $(...)^+$ is applied only to functions of $\mathbf{r}_{ij}$. Thus eqs 6.8, 7.10, and 7.13 completely give the exact MCA matrix **F** in terms of a few equilibrium averages to be calculated using the proper distribution function or time averaging along a molecular dynamics trajectory. In addition, eqs 6.8, 7.5, and 7.12 describe the MCA matrix **F** in the preaveraging approximation, while substituting the bond matrix **L** in these latter equations by the Rouse matrix $\mathbf{L}^R$ gives the free draining case.

VIII. Rod Model with Hydrodynamic Interaction

It is important to compare the MCA results for the bond correlation time of a rod with hydrodynamic interaction to the exact result. The exact result for a shish kebab rod is obtained below for the partial draining case following the Kirkwood procedure, as applied by Doi–Edwards[5] to an approximate nondraining calculation of the rotational friction coefficient, but avoiding any approximation. Consider a shish kebab rod oriented according to the unit director $\mathbf{u}$ in a fluid characterized by a velocity gradient tensor ϵ and subject to a potential U. First we equate the total torque acting on the rod to the torque due to the thermodynamic potential

$$\sum_{n=-N/2}^{N/2} nl\mathbf{u} \times \mathbf{F}_n = -\mathcal{R}(k_B T \ln \psi + U) \tag{8.1}$$

where $\mathcal{R}$ is the rotational vector operator. The forces as a function of the mobility tensor and of the actual velocity fields are

$$\mathbf{F}_n = \zeta \sum_m (\mathbf{H}^{-1})_{nm}(\mathbf{V} + ml\,\boldsymbol{\omega} \times \mathbf{u} - \epsilon\cdot\mathbf{R} - ml\epsilon\cdot\mathbf{u}) \tag{8.2}$$

with $\mathbf{R}$ and $\mathbf{V}$ being the position and velocity vectors of the center of mass and ω the angular velocity of the rod. The mobility tensor of eq 2.4 may be written in the case of a rod as

$$\mathbf{H}_{ij} = P_{ij}\mathbf{1} + Q_{ij}\mathbf{uu} \tag{8.3}$$

where the coefficient of the anisotropic part, coinciding with the rod limit of f_{ij} of (7.8), is

$$Q_{ij} = \frac{3}{4}\zeta_r(1 - \delta_{ij})|i - j|^{-1} \tag{8.4}$$

The coefficient of the isotropic part is

$$P_{ij} = \delta_{ij} + \frac{3}{4}\zeta_r(1 - \delta_{ij})|i - j|^{-1} \tag{8.5}$$

which coincides with the rod limit of the matrix H_{ij} of (6.4).

Then the inverse of the mobility matrix takes the form

$$(\mathbf{H}^{-1})_{ij} = P^{-1}{}_{ij}\mathbf{1} + B^{-1}{}_{ij}\mathbf{uu} \tag{8.6}$$

with

$$\mathbf{B} = \mathbf{P} + \mathbf{P}\mathbf{Q}^{-1}\mathbf{P} \tag{8.7}$$

Inserting the forces of eq 8.2 into eq 8.1 and taking into account the structure of eq 8.6 and the property

$$\sum_{n=-N/2}^{N/2} n(\mathbf{H}^{-1})_{nm} = 0 \tag{8.8}$$

we get the following equation for the angular velocity:

$$\boldsymbol{\omega} = -(l^2\zeta\, c)^{-1}\mathcal{R}(k_B T \ln \psi + U) + \mathbf{u} \times (\epsilon\cdot\mathbf{u}) \tag{8.9}$$

Here is c given as

$$c = \frac{3}{2}\sum_{i,j=-N/2}^{N/2} ijP^{-1}{}_{ij} \tag{8.10}$$

From the hydrodynamics of the rotational motion of the rod we can identify immediately in eq 8.9 the second term on the right-hand side as the unperturbed angular velocity generated by the velocity gradient tensor ϵ and the coefficient of the rotational operator as the inverse of the rotational friction coefficient f_r:

$$f_r = l^2\zeta \sum_{i,j=-N/2}^{N/2} ijP^{-1}{}_{ij} \tag{8.11}$$

As the rotational friction coefficient f_r is related to the bond correlation time of the rod by the relationship

$$\sigma\tau_{\mathrm{ROD}} = \frac{3}{2}\frac{f_r}{l^2\zeta} \tag{8.12}$$

we finally get

$$\sigma\tau_{\mathrm{ROD}} = c = \frac{3}{2}\sum_{i,j=-N/2}^{N/2} ijP^{-1}{}_{ij} \tag{8.13}$$

This is the exact expression for the bond correlation time of a rod in the general partial draining case. In the free draining limit, $P_{ij} = \delta_{ij}$, and the exact expression of eq 4.8 is immediately recovered. In addition, eq 8.13 states that only the isotropic part of eq 8.6 contributes to the rod correlation time.

Let us now apply the MCA formalism of section VII to the case of the rod model. Equations 6.4, 7.10, and 7.13 simplify to

$$\langle l/r_{ij}\rangle = |i - j|^{-1} \tag{8.14}$$

$$\frac{F^{12}_{ij}}{D} = \frac{5}{3}L^R_{ij}l^2 + \frac{8}{3}Q^+_{ij}l^2 \tag{8.15}$$

$$\frac{F^2_{ij}}{D} = \frac{11}{3}L^R_{ij}l^4 + \frac{20}{3}Q^+_{ij}l^4 \tag{8.16}$$

where the rod limit of f^+_{ij} has been written using the definition in (8.4) in terms of Q_{ij}.

For the sake of comparison, the modified equations in the preaveraging approximations are also reported below. In the preaveraged approximation F^1 is still given by eq 6.4 with eq 8.14, while eqs 8.15 and 8.16 become, respectively:

$$\left(\frac{F^{12}_{ij}}{D}\right)_{pa} = \frac{5}{3}L_{ij}l^2 \tag{8.17}$$

$$\left(\frac{F^2_{ij}}{D}\right)_{pa} = \frac{11}{3}L_{ij}l^4 \tag{8.18}$$

Then eq 2.22 gives the desired MCA rod correlation time with exact or preaveraged hydrodynamic interactions. In the case of a rod, the matrix $\mathbf{S}$ is highly degenerate with all its elements equal to $^1/_3$ (henceforth we assume for simplicity $l = 1$). This simplifies eq 2.22 to

$$\sigma\tau_{\rm ROD} = \sum_{i,j=1}^{2N} (D\mathbf{F}^{-1})_{ij} \tag{8.19}$$

To proceed further in the analytical evaluation of this equation, we rewrite the exact equations, (6.8), (8.15), and (8.16), for the blocks of $\mathbf{F}$ by using definitions introduced in (8.3):

$$\frac{(\mathbf{F}^1)_{ij}}{D} = P^+{}_{ij} \tag{8.20}$$

$$\frac{(\mathbf{F}^{12})_{ij}}{D} = \frac{5}{3}P^+_{ij} + Q^+_{ij} \tag{8.21}$$

$$\frac{(\mathbf{F}^2)_{ij}}{D} = \frac{11}{3}P^+_{ij} + 3Q^+_{ij} \tag{8.22}$$

Gathering all these results the matrix $\mathbf{F}$ takes the form of a sum of direct products:

$$\frac{\mathbf{F}}{D} = \frac{1}{3}\begin{pmatrix} 3 & 5 \\ 5 & 11 \end{pmatrix} \otimes \mathbf{P}^+ + \begin{pmatrix} 0 & 1 \\ 1 & 3 \end{pmatrix} \otimes \mathbf{Q}^+ \tag{8.23}$$

The first and second terms on the right-hand side of (8.23) derive respectively from the isotropic and anisotropic parts of the mobility tensor $\mathbf{H}$ taking into account the partitioning of $\mathbf{H}$ of eq 8.3. But we have shown above that the anisotropic part of the mobility tensor does not contribute to the correlation time of the rod and therefore we can carry on ignoring in (8.23) the second term:

$$\frac{\mathbf{F}}{D} \approx \frac{1}{3}\begin{pmatrix} 3 & 5 \\ 5 & 11 \end{pmatrix} \otimes \mathbf{P}^+ \tag{8.24}$$

Now the inverse of the direct product in (8.24) is the direct product of the inverse of the two factors

$$D\mathbf{F}^{-1} \approx \frac{3}{8}\begin{pmatrix} 11 & -5 \\ -5 & 3 \end{pmatrix} \otimes (\mathbf{P}^+)^{-1} \tag{8.25}$$

and we can finally calculate the rod correlation time from (8.19) as the product of the sum of all the elements of each matrix in the direct product in (8.25) to get

$$\sigma\tau_{\rm ROD} = \frac{3}{2}\sum_{i,j=1}^{2N} (\mathbf{P}^+)^{-1}{}_{ij} \tag{8.26}$$

A simple manipulation of (8.13) quickly shows that (8.26) is identical to the exact expression. First the matrices $\mathbf{P}^+$ and therefore $\mathbf{P}^{-1}$ are written in terms of the bead to bond transformation matrices

$$\mathbf{P}^+ = \mathbf{a}\mathbf{P}\mathbf{a}^T; \quad \mathbf{P}^{-1} = \mathbf{a}^T(\mathbf{P}^+)^{-1}\mathbf{a} \tag{8.27}$$

Then eq 8.13 using the second part of eq 8.27 becomes

$$\sum_{i,j=-N/2}^{N/2} ijP^{-1}_{ij} = \sum_{p,q=1}^{N} (\sum_i ia^T_{ip})(\mathbf{P}^+)^{-1}_{pq}(\sum_i a_{qj}\, j) \tag{8.28}$$

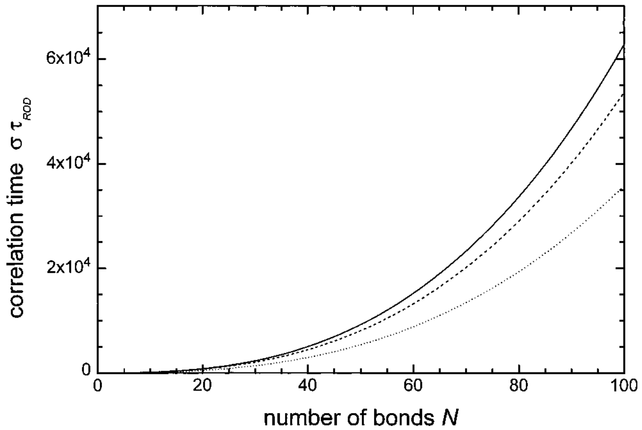

Figure 3. Correlation time $\sigma\tau_{\rm ROD}$ for the relaxation of a rod as a function of the rod length N: MCA approximation with exact (full curve) and preaveraged (dashed curve) hydrodynamic interaction; ORZ first-order mode coupling result (dotted curve). The exact partial draining result coincides with the MCA result (full curve).

Now from eq 6.7, it is immediately obtained that the two terms in parentheses in eq 8.28 are both equal to 1 and therefore

$$\sigma\tau_{\rm ROD} = \frac{3}{2}\sum_{i,j=-N/2}^{N/2} ijP^{-1}{}_{ij} = \frac{3}{2}\sum_{i,j=1}^{2N} (\mathbf{P}^+)^{-1}{}_{ij} \tag{8.29}$$

So it is finally shown that the MCA approximation gives the exact result for the bond correlation time of a rod not only in the free-draining case but also in the general partial-draining case.

In Figure 3 we report the adimensional correlation times calculated in the first order (ORZ) and in the MCA approximation with exact and preaveraged hydrodynamic interactions as a function of the number of bonds N. The MCA result with exact hydrodynamic interaction coincides, as stated above, with the exact result. The MCA approach represents a significant correction even in the preaveraging approximation, as can be appreciated by comparing the dashed curve (MCA) to the dotted curve (ORZ). Note that in the preaveraging approximation the MCA theory improves the first order theory by a factor of $^3/_2$ as in the free-draining case. On the contrary, the full MCA theory corrects the first order by a factor smoothly increasing with N and in average slightly larger than $^3/_2$.

We expect that the great improvement obtained by adding the N second-order diagonal terms to the ORZ basis set in the case of a rod may be extended to any rigid structure. In the case of proteins, a first approximation to the modeling of local dynamics was proposed[19] in terms of the ORZ rotational diffusion of the fluctuating, or rigid, three-dimensional structure. The upper second-order MCA approximation is expected to be a great improvement to this first-order description of protein dynamics.

IX. Conclusions

Smoluchowski dynamics, with hydrodynamic interactions, for a polymer solution is solved by the matrix-expansion method or mode-coupling approach. This method expands the eigenfunctions of the dynamic operator in basis sets of increasing number of elements chosen, as increasing powers of the bond vector components or in general of the slow variables. The exploding number of elements occurring with increasing power are reduced by the method of maximum correlation approximation (MCA), which amounts to including in the basis set powers of only those variables which present the maximum correlation to the relaxing physical variable. The dynamics is solved for the bond correlation times and the bond time correlation functions without any approximation in the hydrodynamic interactions and is formally calculated in the MCA approximation. The MCA approximation, involving in its actual second-order version only basis sets of $2N$ elements, describes the broken rod models well, thus proving reliable for both low and high correlated chains. While the first order in the mode coupling expansion represents the optimized Rouse–Zimm theory, by adding only N terms to the first-order basis, the actual second order MCA is sufficient to give exact results for the limit case of a rod. The MCA concept is strongly supported by these results: local dynamic properties of real polymers are expected to be well described by adding to the first-order basis set those higher order terms (trilinear and even pentalinear terms in the case of the relaxation of bond vector variables) composed of products of the proper symmetry of the slow variables most correlated to the relaxing physical variable.

It should be noted that the MCA picture is consistent with the concept of localized cooperative motions as found in MD simulations[4] or in the wide experimental experience on the local dynamics of polymer solutions. Thus at the first-order level the dynamics of a chain should take into account the linear bond variables to describe the connectivity of the polymer chain. But for a flexible chain the relaxation of a bond is asymptotic with the length of the chain. This means that to derive the first-order dynamics of a bond in a flexible chain only the bonds in a definite correlation length are required. To higher orders, odd powers of the variables which are again more strictly correlated to the relaxing variable should be taken into account. In a real chain there is therefore a balance between localization and chain cooperativity. This balance is mediated by correlations between the variables involved: the MCA approximation to the mode-coupling expansion of diffusion dynamics gives a quantitative description of this localization–cooperation balance in a polymer solution.

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