

# Theory for long time polymer and protein dynamics: Basis functions and time correlation functions

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We develop methods for alleviating the major impediment in the extension to larger and more complex systems of our matrix method theory for describing the long time dynamics of flexible polymers and proteins in solution. This impediment is associated with the enormous growth in size of the required basis set with the addition of higher order mode coupling basis functions, which are needed to describe the influence on the dynamics of the “internal friction,” or equivalently of the memory function matrices. We use the first order eigenfunctions (the generalized Rouse modes) to construct an approximate mode coupling basis. Specific applications are made to united atom models of alkanes with a white noise structureless solvent, where the theory is compared with Brownian dynamics simulations to provide a no-parameter stringent test of the theory. Good convergence is found to the full second order treatment with the new basis set whose size scales more nearly with the size of the system rather than the cube of the system with the previous full basis. These technical improvements enable us to test the need for third order contributions to the dynamics of the longer alkanes and to compute the orientational time correlation functions probed by fluorescence depolarization and NMR experiments. Additional symmetry considerations provide further reductions in the required basis set sizes. © 1995 American Institute of Physics.

## I. INTRODUCTION

The dynamics of flexible polymers in solution are important for understanding the properties of many polymeric materials. For instance, the natural motions of many biological macromolecules appear to be essential to their proper functioning. Consequently, considerable experimental and theoretical work has been devoted towards understanding polymer dynamics.<sup>1-5</sup> In principle, if all the polymer-polymer, polymer-solvent, and solvent-solvent forces were known, the dynamics of the solvated polymers could be completely described by solving the classical equations of motion. The short-time dynamics of small polymers can indeed be studied with molecular dynamics simulations, but the required computer time grows explosively with polymer size. The long-time dynamics of large polymers, however, are inaccessible to these simulations due to the enormous computations required. For many biological macromolecules, though, it is precisely the long-time dynamics that are of interest. The long-time dynamics of synthetic polymers are likewise of importance in governing the glass transition temperature and, hence, the mechanical and rheological properties of bulk polymers.

The development of a theory for long-time polymer and protein dynamics requires the physical description and the testing of approximations for various qualitatively different features of this dynamics. First is the treatment of the internal chain dynamics of rather floppy molecules, a process requiring the theoretical description of phenomena loosely

referred to as involving “internal friction,” “internal viscosity,” “memory functions,” etc., phenomena that are currently not well understood. A second portion of the theory is associated with treating the polymer-solvent interactions on a molecular level. This portion requires testing and refining customary hydrodynamic models that are presumed to be applicable on longer time scales but that have not yet been tested microscopically for the types of multidimensional systems posed by the dynamics of flexible polymers in solution. The enormity of both of these problems has led us to consider their separate treatments, focusing initially on the least known problem of describing the long time internal dynamics of flexible long chain molecules.

This paper further develops a matrix expansion method first presented by Perico *et al.*<sup>6</sup> and Chang and Freed.<sup>7,8</sup> The matrix method is a generalization of the optimized Rouse-Zimm (ORZ) theory,<sup>9</sup> which, here, we call the generalized Rouse-Zimm (GRZ) theory.<sup>10</sup> The GRZ theory has been used to study the dynamics of a variety of polymer systems.<sup>11-19</sup> The matrix method provides a systematic procedure for including the contributions from internal friction and memory functions, contributions that are neglected by the simpler GRZ theory. In cases where comparison has been made between the GRZ theory and experiment or computer simulation,<sup>18,19</sup> the GRZ theory produces reasonable approximations. It is not yet clear, however, which aspect of the theory is responsible for the discrepancy between the theory and experiment. Improvements to the GRZ theory require

knowledge of the origins of these discrepancies, which may arise from using an inaccurate potential function, an inadequate treatment of the internal chain dynamics, an inadequate theory for the polymer–solvent interactions, or an inaccurate model for the hydrodynamic interactions. Consequently, here we focus exclusively on one possible source of error, namely that of describing the internal chain dynamics, a problem that has received little detailed theoretical analysis.

The matrix method yields approximations to the time autocorrelation functions which are represented in terms of the eigenfunctions and eigenvalues of the  $N$ -particle Liouville operator for the dynamics of a single chain in a white-noise model for the solvent. The long time dynamics theory only requires as input the friction coefficients and a series of equilibrium averages. These equilibrium averages may be obtained either from the computer simulations over short times or, in principle, from theory. Then, the matrix method theory provides estimates of the time correlation functions over an extended time. We test our theory by comparing the time correlation functions obtained from Brownian dynamics simulations against the time correlation functions provided by the theory. This comparison is free of the uncertainties in potentials commonly incurred when comparing theory with experiment. As the simulated trajectories are fairly long and the statistical error is negligible,<sup>20</sup> the simulated time correlation functions are considered to be exact for testing the theory.

When the matrix method theory is limited to using a linear basis in the “bead” positions, the theory reduces to the generalized Rouse (GR) theory (the GRZ theory without hydrodynamic interactions). This GR model represents an enormous improvement over the simple Rouse model since the GR theory describes the influence on the dynamics of the local chain stiffness, conformational transitions, etc., that are omitted from the simple Rouse model. However, the GR model completely ignores the internal friction, which, as demonstrated in Ref. 7, affects the long time chain dynamics. As we include more and more higher order basis functions in the matrix method, the theory produces a more accurate description of this internal chain friction and equivalently includes more contributions from the memory function matrix. These additional basis functions lead to considerable improvements in the agreement between theory and simulation for the long time dynamics ( $t \geq 100$  ps).

A computationally intense portion of the matrix method involves solving the eigenvalue problem for the Liouville operator, a process that rapidly becomes prohibitive as the size of the basis set grows. Symmetry considerations (described here and not used previously) provide some reduction in the basis set size, but the basis set problems are still enormous. For example, when using a united atom model for the dynamics of pentacosane ( $C_{25}H_{52}$ ), the first order (the GR model) basis set contains 24 basis functions, the second order has 7200, and the 3rd order has 1 083 600. The diagonalization of the latter is becoming prohibitive, but the situation is far worse upon passage to more realistic all-atom models for the pentacosane dynamics, where, the first order basis set yields 76 basis functions, while the second order basis set

already contains over 200 000 functions. Computations with the higher order basis sets rapidly become too time consuming. Since the second and higher order basis functions describe the influence of internal friction, this explosive increase in the size of basis sets represents the greatest present impediment to extending the matrix expansion method to include the necessary higher order contributions and to larger systems.

Previous tests of the theory have focused on the  $P_1(t)$  dipole correlation functions, but it is also of interest to consider the orientational correlation function  $P_2(t)$  for comparison with fluorescence depolarization and NMR relaxation experiments. The first order basis set for calculating the united atom model  $P_2(t)$  of pentacosane has 300 basis functions, while the second order basis contains 45 150. Thus, the size of the basis set (for a given order) grows considerably in the transition from  $P_1(t)$  to  $P_2(t)$ . In extending the theory to larger systems, such as those posed by more complicated polymers or proteins, this growth in computational intensity becomes a severe impediment.

The present paper develops and tests approximation schemes designed to alleviate the problem of the explosive growth in the number of basis functions with increasing order and with polymer size. The new techniques lead to eigenvalue problems with dimensions scaling more closely with the size of the systems. This enormous reduction in the required basis set size also enables us to compute and thereby test the predictions of the theory for the  $P_2(t)$  correlation functions. The tests and applications are performed using united atom models of alkanes, while a future paper will present the generalizations to the all-atom model, generalizations rendered possible by virtue of the computational advances developed here.

Section II briefly reviews the basic equations underlying the theories applied in this paper. Section III summarizes the matrix method theory used to estimate the polymer dynamics. Section IV presents the details of the Brownian dynamics simulations employed for calculating the time correlation functions. Section V describes the alkane chain potentials that are used both for the simulations and the theory to provide parameter-free unambiguous tests of the theory. Finally, Sec. VI discusses the effectiveness of various basis sets for estimating long-time polymer dynamics.

## II. BASIC EQUATIONS

We briefly review those aspects of the theories and methods that are necessary to explain the new advances and developments. For simplicity, the applications consider a polymer model with the following properties: (1) The linear polymer is composed of  $N$  identical united-atom beads. No explicit degrees of freedom are assigned to the white-noise random solvent. The solvent affects the motion of the polymer through frictional and stochastic forces acting on each of the beads in the polymer. (2) The bead friction coefficient is assumed to be frequency-independent. (3) The frictional force is taken to be large, so inertial effects can be neglected. (4) All hydrodynamic interactions between different beads are neglected. Previous applications of the GRZ theory to treat the dynamics of small aqueous hormones and protein

fragments have considered more complicated models with internal monomer structures and hydrodynamic interactions.<sup>18,19</sup> The limitation here to simple linear, homopolymer models is designed solely for furthering the development of that portion of the general theory associated with describing the “internal friction.”

The dynamics of this model polymer is described by either (1) a set of Langevin equations or (2) a Smoluchowski equation. The two formulations are completely equivalent.<sup>1,21,22</sup> The Langevin equations for the model are

$$\begin{aligned} \frac{dr_i(t)}{dt} &= -\frac{1}{\xi} \frac{\partial U[\mathbf{r}(t)]}{\partial r_i(t)} + X_i^*(t), \\ &= 1, 2, \dots, 3N, \end{aligned} \quad (2.1)$$

where

$$\begin{aligned} \mathbf{r}(t) &= \{r_1(t), r_2(t), \dots, r_{3N}(t)\} = \{\mathbf{q}_1(t), \mathbf{q}_2(t), \dots, \mathbf{q}_N(t)\} \\ &= [x_1(t), y_1(t), z_1(t), x_2(t), y_2(t), z_2(t), \dots, x_N(t), \\ &\quad \times y_N(t), z_N(t)] \end{aligned}$$

represents the  $3N$  Cartesian coordinates of the  $N$  polymer beads,  $U[\mathbf{r}(t)]$  is the potential energy,  $\xi$  is the friction coefficient acting on each bead, and  $X_i^*(t)$  is a Gaussian random variable with the properties,

$$\begin{aligned} \langle X_i^*(t) \rangle &= 0, \\ \langle X_i^*(t) r_j(t') \rangle &= 0, \quad \text{for } t > t', \\ \langle X_i^*(t) X_j^*(t') \rangle &= 2 \frac{k_B T}{\xi} \delta_{ij} \delta(t-t'), \end{aligned} \quad (2.2)$$

where  $k_B$  is Boltzmann's constant,  $T$  is the temperature,  $\beta = 1/(k_B T)$ ,  $\delta_{ij}$  is the Kronecker delta function,  $\delta(t-t')$  is the Dirac delta function, and  $\langle \dots \rangle$  denotes the equilibrium average,

$$\langle \dots \rangle = \frac{\int d\mathbf{r} \exp[-\beta U(\mathbf{r})] (\dots)}{\int d\mathbf{r} \exp[-\beta U(\mathbf{r})]}. \quad (2.3)$$

The corresponding Smoluchowski equation is

$$\frac{\partial P(\mathbf{r}, t | \mathbf{r}_0, 0)}{\partial t} = \mathcal{D}P(\mathbf{r}, t | \mathbf{r}_0, 0), \quad (2.4)$$

where  $P(\mathbf{r}, t | \mathbf{r}_0, 0)$  denotes the probability that the coordinates of the  $N$  particles at time  $t$  are  $\mathbf{r}$ , given that the coordinates of the  $N$  particles at time 0 are  $\mathbf{r}_0$ , and where  $\mathcal{D}$  is defined by

$$\mathcal{D} = \sum_{j=1}^{3N} \left[ \frac{k_B T}{\xi} \frac{\partial^2}{\partial r_j^2} + \frac{1}{\xi} \frac{\partial}{\partial r_j} \frac{\partial U(\mathbf{r})}{\partial r_j} \right]. \quad (2.5)$$

Our interest lies in computing time correlation functions  $\langle f(0)g(t) \rangle$  where  $f$  and  $g$  are functions of  $\mathbf{r}$ . “Exact” time correlation functions are obtained from conventional Brownian dynamics simulations based on the numerical solutions of the Langevin equations (2.1). The matrix method for approximating the same time correlation functions begins with the Smoluchowski equation (2.4). Comparison of the “exact” time correlation functions from Brownian dynamics simulations against the estimated time correlation functions from the matrix method tests the effectiveness of the matrix

method because both simulation and theory employ the identical potentials. Thorough comparisons of this nature are possible for smaller polymers, but even the Brownian dynamics simulations become too intensive computationally for large polymers. Consequently, the adequacy of the matrix method for the smaller system instills confidence in its use for providing reasonable estimates of the time correlation functions for larger and more complex polymers since the matrix method requires much less computer time for computing the time correlation functions than their direct computation from simulations.<sup>7,8</sup>

### III. MATRIX METHOD

This section reviews the necessary details of the matrix method theory from Refs. 6, 7, and 8. It is convenient to introduce the adjoint of  $\mathcal{D}$ ,

$$\mathcal{L} = \mathcal{D}^\dagger = \sum_{j=1}^{3N} \left[ \frac{k_B T}{\xi} \frac{\partial^2}{\partial r_j^2} - \frac{1}{\xi} \frac{\partial U(\mathbf{r})}{\partial r_j} \frac{\partial}{\partial r_j} \right]. \quad (3.1)$$

The time correlation function  $\langle f(0)g(t) \rangle$  is defined by

$$\langle f(0)g(t) \rangle = \langle f(0) \exp[\mathcal{L}t]g(0) \rangle, \quad (3.2)$$

where  $f$  and  $g$  are any two dynamic observables and  $\exp[\mathcal{L}t]g(0)$  is the formal solution to the equation of motion

$$\frac{\partial g(t)}{\partial t} = \mathcal{L}g(t). \quad (3.3)$$

A complete, orthonormal set  $\{\psi_n\}$  of eigenfunctions of  $\mathcal{L}$  is introduced,

$$\mathcal{L}\psi_n = -\lambda_n \psi_n, \quad n = 1, 2, \dots \quad (3.4)$$

The inner product is defined to be compatible with the definition of the equilibrium average,

$$(\chi_i, \chi_j) = \frac{\int d\mathbf{r} \exp[-\beta U(\mathbf{r})] \chi_i \chi_j}{\int d\mathbf{r} \exp[-\beta U(\mathbf{r})]} = \langle \chi_i \chi_j \rangle. \quad (3.5)$$

The time correlation function  $\langle f(0)g(t) \rangle$  is expressed in terms of the eigenfunctions  $\{\psi_n\}$  and the eigenvalues  $\{\lambda_n\}$  of  $\mathcal{L}$  as

$$\langle f(0)g(t) \rangle = \sum_n \langle f \psi_n \rangle \langle \psi_n g \rangle \exp[-\lambda_n t]. \quad (3.6)$$

An approximation to the exact time correlation function is obtained by introducing a basis set expansion. Thus, a subset of the complete set of eigenfunctions  $\{\psi_n\}$  of  $\mathcal{L}$  is approximated by expressing  $\psi_n$  in terms of a set of basis functions  $\{\phi_i\}$ ,  $i = 1, 2, \dots, M$ ,

$$\psi_n \approx \sum_{i=1}^M B_{in} \phi_i. \quad (3.7)$$

The  $B_{in}$  are determined by solving the matrix eigenvalue problem,

$$\mathbf{FB} = \mathbf{SB}\boldsymbol{\lambda}, \quad (3.8)$$

subject to the normalization constraint

$$\mathbf{B}^T \mathbf{SB} = \mathbf{I}, \quad (3.9)$$

where  $\mathbf{I}$  is the unit matrix,

$$S_{ij} = \langle \phi_i \phi_j \rangle, \quad (3.10)$$

$$F_{ij} = \langle \phi_i \mathcal{L} \phi_j \rangle = \sum_{k=1}^{3N} \left( -\frac{k_B T}{\xi} \right) \left\langle \frac{\partial \phi_i}{\partial r_k} \frac{\partial \phi_j}{\partial r_k} \right\rangle, \quad (3.11)$$

and  $\lambda$  is the diagonal matrix of (approximate) eigenvalues  $\lambda'_1, \lambda'_2, \dots$ . Finally, the approximate time correlation function becomes

$$\langle f(0)g(t) \rangle \approx \sum_n \left( \sum_i B_{in} \langle f \phi_i \rangle \right) \left( \sum_j B_{jn} \langle \phi_j g \rangle \right) \times \exp[-\lambda_n t]. \quad (3.12)$$

The matrix method provides the time correlation function in terms of equilibrium averages only, the  $\mathbf{S}$  and  $\mathbf{F}$  matrices of Eqs. (3.10) and (3.11). The accurate determination of equilibrium averages by simulation methods requires orders of magnitude less computation than necessary for simulating the long-time dynamics.<sup>7,8,18,19</sup> The difficulty in applying the matrix method, however, lies in choosing an appropriate set of basis functions  $\{\phi_i\}$ . Previous work has focused upon choices of  $\phi_i$  that produce accurate descriptions for the long-time dynamics because simulation methods are often suitable only for describing the short time behavior. However, the previously used basis sets grow enormously with the size of the system and therefore rapidly become untenable. We test the effectiveness of various considerably reduced sets of basis functions by comparing the “exact” time correlation functions from the Brownian dynamics simulations against the time correlation functions estimated using Eqs. (3.8)–(3.12). The equilibrium averages  $S_{ij}$  and  $F_{ij}$  in Eqs. (3.10) and (3.11) are calculated from the same Brownian dynamics simulations used to provide the “exact” time correlation functions. Thus, any differences between the “exact” and estimated time correlation functions are due solely to the approximations of the matrix method theory.

#### IV. BROWNIAN DYNAMICS SIMULATIONS

The Brownian dynamics simulations are performed using the standard algorithm of van Gunsteren and Berendsen.<sup>23,24</sup> The Langevin equations (2.1) are solved numerically by iterating the finite difference equations,

$$r_i(n+1) = r_i(n) + \frac{F_i(n)}{\xi} \Delta t + \frac{1}{2} \frac{F'_i(n)}{\xi} (\Delta t)^2 + \chi_{in}, \quad (4.1)$$

$$i = 1, \dots, 3N,$$

where  $\Delta t$  is the time step,  $F_i(n) = -\partial U(\mathbf{r})/\partial r_i$  is the force acting on the  $i$ th coordinate,  $F'_i(n) = [F_i(n) - F_i(n-1)]/\Delta t$  is the finite difference approximation to the time derivative of the force, and  $\chi_{in}$  is a random positional displacement taken from a Gaussian distribution with zero mean and variance  $2(k_B T/\xi)\Delta t$ .

The simulations used to calculate dipole time correlation functions (defined in Sec. VI below) are made with a time step of 5 fs. Each time correlation function is calculated from a single trajectory in which the system is allowed to equilibrate for 10 ns, after which data are gathered for 390 ns. The simulations for calculating  $P_2(t)$  use a time step of 7 fs.

Each time correlation function is calculated from 12 trajectories. In each trajectory, the system is allowed to equilibrate for 1 ns, after which data is gathered for 7 ns.

#### V. SYSTEMS STUDIED

All the systems considered in this paper consist of a united-atom alkane chain in a solvent at a temperature of  $T=300$  K. The alkane chain is modeled as a string of  $\text{CH}_2$  or  $\text{CH}_3$  units. The solvent is treated as a structureless continuum with a viscosity  $\eta$  of 0.84 centipoise. The solvent exerts a viscous damping force on the alkane chain. Each  $\text{CH}_2/\text{CH}_3$  united atom is treated as a sphere with hydrodynamic radius  $R=1.53$  Å. The friction coefficient is calculated using Stokes' law  $\xi=6\pi\eta R$ , and hydrodynamic interactions are ignored.

The calculations for the dipole time correlation functions take the internal potential  $U$  of the alkane chain, except for one modification, from the GROMOS package.<sup>25</sup> This potential has the general form

$$U = U_{\text{bond}} + U_{\text{angle}} + U_{\text{dihedral}} + U_{\text{nonbond}}. \quad (5.1)$$

The bond length potential is

$$U_{\text{bond}} = \sum_{i=1}^{N_b} \frac{1}{2} K_b (l_i - l_0)^2, \quad (5.2)$$

where  $N_b$  is the number of bonds,  $l_i$  is the length of bond  $i$ ,  $l_0=1.53$  Å is the GROMOS equilibrium bond length for alkanes, and  $K_b$  is the bond length force constant for alkanes. We use  $K_b=160$  kcal mol<sup>-1</sup> Å<sup>-2</sup>, which is smaller than  $K_b$  in GROMOS by a factor of 5. This change does not significantly affect the long-time dynamics and allows the Brownian dynamics time step  $\Delta t$  to be longer. The bond angle potential is

$$U_{\text{angle}} = \sum_{i=1}^{N_\theta} \frac{1}{2} K_\theta (\theta_i - \theta_0)^2, \quad (5.3)$$

where  $N_\theta$  is the number of bond angles,  $\theta_i$  is the  $i$ th bond angle,  $\theta_0=111^\circ$  is the GROMOS equilibrium bond angle for alkanes, and  $K_\theta=110$  kcal mol<sup>-1</sup> rad<sup>-2</sup> is the bond angle force constant. The dihedral angle potential is

$$U_{\text{dihedral}} = \sum_{i=1}^{N_\phi} K_\phi (1 + \cos 3\phi_i), \quad (5.4)$$

where  $N_\phi$  is the number of dihedral angles,  $\phi_i$  is the  $i$ th dihedral angle, and  $K_\phi=1.4$  kcal/mol. The nonbonded potential  $U_{\text{nonbond}}$  uses a 6-12 Lennard-Jones potential to describe the interaction between two nonbonded united atoms. More details are given in Ref. 25. The  $P_2(t)$  calculations use a slightly different internal potential  $U$  for the alkane chains. Details are given in Refs. 7 and 8.

#### VI. RESULTS AND DISCUSSION

We first study the effectiveness of various basis sets for estimating the normalized dipole time correlation function

$$C_{I,J}(t) = \frac{\langle [\mathbf{q}_J(0) - \mathbf{q}_I(0)] \cdot [\mathbf{q}_J(t) - \mathbf{q}_I(t)] \rangle}{\langle [\mathbf{q}_J(0) - \mathbf{q}_I(0)] \cdot [\mathbf{q}_J(0) - \mathbf{q}_I(0)] \rangle} \quad (6.1)$$

$$= \frac{\langle [x_J(0) - x_I(0)][x_J(t) - x_I(t)] \rangle}{\langle [x_J(0) - x_I(0)][x_J(0) - x_I(0)] \rangle}. \quad (6.2)$$

All of our calculations are based on Eq. (6.2), but, given spatial isotropy, the same results should emerge by interchanging  $x, y$ , and  $z$ .

### A. Symmetry considerations

Let us consider polynomial basis functions of the form  $l_{i\alpha}, l_{i\alpha}l_{j\beta}, l_{i\alpha}l_{j\beta}l_{k\gamma}, l_{i\alpha}l_{j\beta}l_{k\gamma}l_{m\delta}, \dots$ , where  $i, j, k, m, \dots$  are integers between 1 and  $N-1$ ,  $\alpha, \beta, \gamma, \delta, \dots$  can be the  $x, y$ , or  $z$  directions, and, for instance,  $l_{ix} = x_{i+1} - x_i$  is the  $x$ -component of the bond vectors. If all of these basis functions were included in the basis set, the basis set would be complete, and the matrix method would produce exact results. But such a basis set contains an infinite number of basis functions and thus is not useful for calculations. Therefore, we investigate the accuracy of calculations using various subsets of the complete, infinite basis set.

Many possible basis functions can be excluded by considerations of symmetry. To illustrate this, consider the matrix method estimate [see Eq. (3.12)] of  $C_{I,J}(t)$  of equation (6.2),

$$C_{I,J}(t) \approx \frac{1}{\langle (x_J - x_I)(x_J - x_I) \rangle} \sum_n \left[ \sum_i B_{in} \langle (x_J - x_I) \phi_i \rangle \right] \times \left[ \sum_j B_{jn} \langle \phi_j (x_J - x_I) \rangle \right] \exp[-\lambda_n t]. \quad (6.3)$$

Basis functions  $\phi_p$  of the form  $l_{iy}, l_{iz}, l_{ix}l_{jy}, l_{ix}l_{jz}, l_{iy}l_{jz}, l_{iy}l_{jy}, l_{iz}l_{jz}, \dots$  yield  $\langle (x_j - x_i) \phi_p \rangle = 0$  by symmetry. Thus, these classes of  $\phi_p$  have no effect on  $C_{I,J}(t)$ . All functions with an even number of  $l$ 's as well as many functions with an odd number of  $l$ 's can be excluded in this fashion. This leaves us with functions  $\phi_p$  of the form  $l_{ix}, l_{ix}l_{jx}l_{kx}, l_{ix}l_{jy}l_{ky}, l_{ix}l_{jz}l_{kz}, \dots$ . This result follows generally from the fact that the Liouville operator and its adjoint are invariant to rotations of the coordinate system. Thus, the eigenfunctions  $\psi_n$  of  $\mathcal{L}$  must transform as representations of the three-dimensional rotation group. The dipole correlation function in Eq. (6.1) applies for a vector quantity. Consequently, only the  $\psi_n$  transforming as vectors are required. These symmetry conditions are more straightforward to apply than those used previously,<sup>7</sup> and, furthermore, they produce a greater reduction in the required number of basis functions at a given order.

### B. Generalized Rouse and mode coupling basis

Applying the matrix method with the basis set

$$\{l_{ix}[i=1, \dots, N-1]\} \quad (\text{basis set I})$$

to calculate  $C_{I,J}(t)$  of Eq. (6.2) is equivalent to using the generalized Rouse theory. A more accurate approximation to  $C_{I,J}(t)$  is obtained by adding more functions to basis set I. Chang and Freed<sup>7</sup> use the mode coupling basis set<sup>26,27</sup>

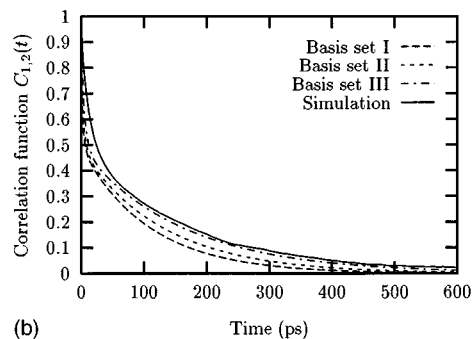
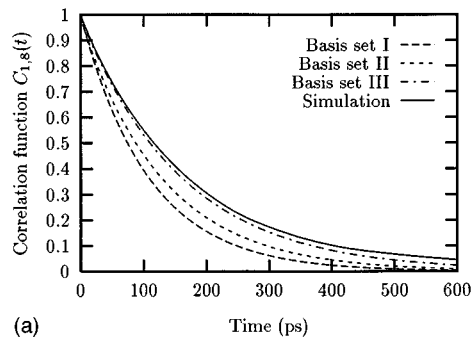


FIG. 1. Comparison between the theoretical dipole time correlation functions, estimated by the matrix method using basis sets I, II, and III, and the time correlation functions calculated directly from Brownian dynamics simulations for (a) octane,  $C_{1,8}(t)$ ; (b) octane,  $C_{1,2}(t)$ .

$$\{l_{ix}[i=1, \dots, N-1], l_{ix}l_{jx}l_{kx}[i, j, k=1, \dots, N-1; i \geq j \geq k]\} \quad (\text{basis set II})$$

along with Eq. (6.2) to estimate the normalized time correlation functions  $C_{1,2}(t), \dots, C_{1,N}(t)$  for alkane chains of varying lengths. Because the only contributing eigenfunctions must transform as vectors, an improved basis set also includes the effects of  $l_{ix}l_{jy}l_{ky}$  and  $l_{ix}l_{jz}l_{kz}$ . We use the “second order” basis set

$$\{l_{ix}[i=1, \dots, N-1], l_{ix}(\mathbf{l}_j \cdot \mathbf{l}_k)[i, j, k=1, \dots, N-1; j \geq k]\} \quad (\text{basis set III}),$$

where  $l_j$  is the vector  $\{l_{jx}, l_{jy}, l_{jz}\}$ , to estimate the representative  $C_{1,2}(t)$  and  $C_{1,N}(t)$ . The former illustrates the fastest, most local motions, while the latter describes the slowest, most global motions. We note that the new basis functions introduced in expanding basis set I to basis set III are not orthogonal to the (original) functions in basis set I. Reference 7 orthogonalizes the trilinear basis functions to the linear ones of basis set I, but this extra step is not used here. The orthogonalization is unnecessary since solving the matrix eigenvalue problem of Eqs. (3.8) and (3.9) does not require basis function orthogonality because of the metric matrix  $\mathbf{S}$ .

Figures 1 and 2 are for octane and pentadecane, respectively, and demonstrate that calculations using basis set III provide superior approximations to the simulations than calculations using basis sets I or II. Basis set III yields an excellent representation of the long-time dynamics, but the short-time dynamics with this basis set are not quite as accurate. The errors at shorter times are more pronounced for

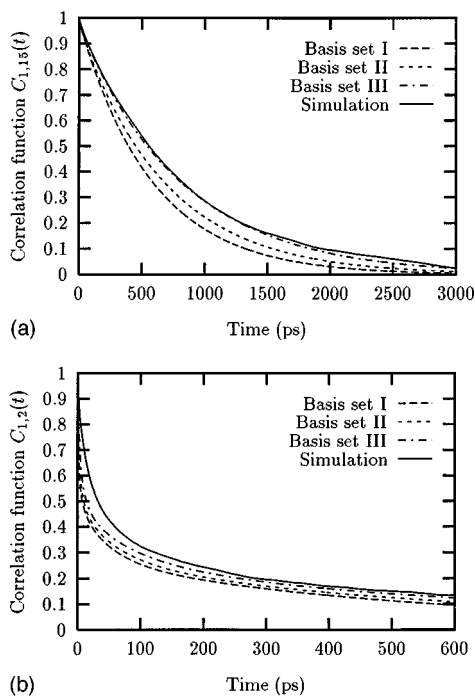


FIG. 2. Comparison between the theoretical dipole time correlation functions, estimated by the matrix method using basis sets I, II, and III, and the time correlation functions calculated directly from Brownian dynamics simulations for (a) pentadecane,  $C_{1,15}(t)$ ; (b) pentadecane,  $C_{1,2}(t)$ .

the more local  $C_{1,2}(t)$  than the more global  $C_{1,N}(t)$ . Basis set III produces some improvement over basis set II for the shorter time dynamics, and it also obviates the need for third order contributions that are not insignificant with basis set II for octane<sup>7</sup> (see below). Computations with a simple Rouse model are not displayed since Ref. 7 shows the Rouse model correlation functions provide a very poor representation of the simulated correlation functions because of the dynamical influences of local chain stiffness that are ignored in the simple Rouse model.

The number of functions in basis set III can, however, become unmanageably large for long polymers since the size of basis set III scales roughly as  $N^3$  for the united atom alkane model, where  $N$  is the number of monomers. Consequently, we now explore ways of significantly reducing the number of basis functions without loss of accuracy in describing the long-time dynamics. Let  $\lambda_1^{(1)}, \lambda_2^{(1)}, \dots, \lambda_{(N-1)}^{(1)}$  be the approximate eigenvalues, arranged in increasing order, of  $\mathcal{L}$  as obtained from the “first order” basis set I. Let  $\psi_{1x}^{(1)}, \psi_{2x}^{(1)}, \dots, \psi_{(N-1)x}^{(1)}$  be the corresponding approximate eigenfunctions from Eq. (3.7) (called the generalized Rouse modes). Thus,  $\psi_{1x}^{(1)}$  provides the first order estimate to the eigenfunction with the slowest decay, called the slowest mode,  $\psi_{2x}^{(1)}$  provides the first order estimate to the eigenfunction of the next slowest decaying mode, and so on. Let  $\psi_{1y}^{(1)}, \psi_{2y}^{(1)}, \dots, \psi_{(N-1)y}^{(1)}$  be the functions obtained by replacing all the  $x$ 's in  $\psi_{1x}^{(1)}, \psi_{2x}^{(1)}, \dots, \psi_{(N-1)x}^{(1)}$  with  $y$ 's, and let  $\psi_{1z}^{(1)}, \psi_{2z}^{(1)}, \dots, \psi_{(N-1)z}^{(1)}$  be the corresponding functions with  $z$ 's. Rotational invariance implies the interchangeability of  $x, y$ , and  $z$  in  $\mathcal{L}$ , and, hence,  $\psi_{1y}^{(1)}, \psi_{2y}^{(1)}, \dots, \psi_{(N-1)y}^{(1)}$  and  $\psi_{1z}^{(1)}, \psi_{2z}^{(1)}, \dots, \psi_{(N-1)z}^{(1)}$  are also approximate eigenfunctions of

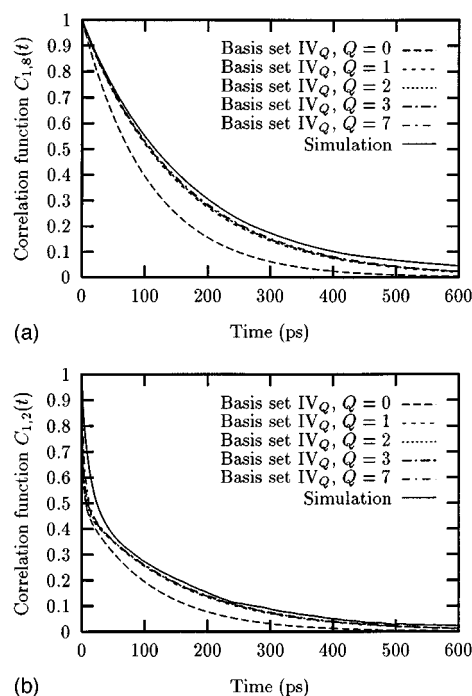


FIG. 3. Comparison of the dipole time correlation functions estimated by the matrix method using basis set  $IV_Q$  and the time correlation functions calculated directly from Brownian dynamics simulations for (a) octane,  $C_{1,8}(t)$ ; (b) octane,  $C_{1,2}(t)$ . Note that the matrix method with basis set  $IV_Q$  and  $Q=0$  is equivalent to the matrix method with basis set I, and the matrix method using basis set  $IV_Q$  with  $Q=7$  is equivalent to using basis set III.

$\mathcal{L}$  [with the same eigenvalues as  $\psi_{1x}^{(1)}, \psi_{2x}^{(1)}, \dots, \psi_{(N-1)x}^{(1)}$ , respectively]. It is also convenient to introduce the notation  $\boldsymbol{\psi}_i^{(1)} [i=1, 2, \dots, N-1]$  to represent the vector  $\{\psi_{ix}^{(1)}, \psi_{iy}^{(1)}, \psi_{iz}^{(1)}\}$ . We expect that the slowest-decaying first-order eigenfunctions contain the most information about the long-time dynamics. Thus, basis set I is augmented by adding new basis functions constructed from the slowest-decaying first-order eigenfunctions of basis set I. This produces the basis set

$$\{l_{ix} [i=1, \dots, N-1], \psi_{ix}^{(1)} [\boldsymbol{\psi}_j^{(1)} \cdot \boldsymbol{\psi}_k^{(1)}] \\ [i, j, k=1, \dots, Q; j \geq k]\}, \quad (\text{basis set } IV_Q),$$

where  $0 \leq Q \leq N-1$ . The  $Q=0$  case reduces basis set  $IV_{Q=0}$  to basis set I, while using  $Q=N-1$  is equivalent to retaining all of basis set III. Note that the size of basis set  $IV_Q$  scales roughly as  $N+Q^3$ . Hence, basis set  $IV_Q$  produces a substantial reduction in size if  $Q \ll N$ . Figures 3, 4, and 5 exhibit comparisons between theory with basis set  $IV_Q$  and simulations for various dipole correlation functions of octane, pentadecane, and pentacosane, respectively, and for several values of  $Q$ . These figures demonstrate that calculations using basis set  $IV_Q$  with small  $Q$  yield practically identical  $C_{i,j}(t)$  as calculations using basis set III or basis set  $IV_Q$  with large  $Q$ . In all of the illustrated cases, the basis set  $IV_Q$  with  $Q=3$  or 4 produces almost identical results as the full second order basis set III. Moreover, the size of basis set  $IV_Q$  with small  $Q$  is miniscule in comparison to basis set III or basis set  $IV_Q$

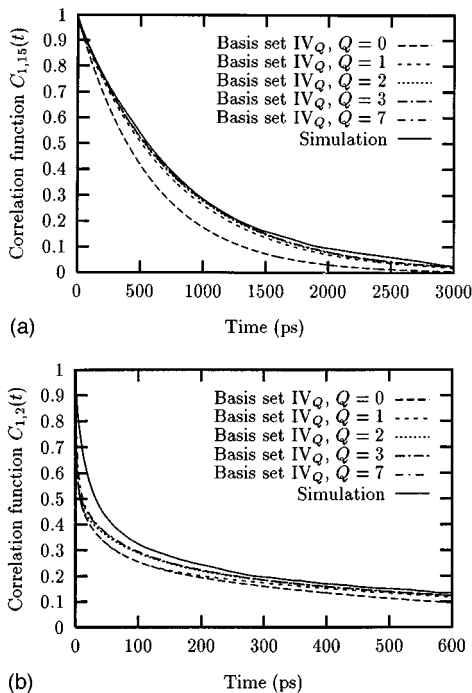


FIG. 4. Comparison between the dipole time correlation functions estimated by the matrix method using basis set  $IV_Q$  and the time correlation functions calculated directly from Brownian dynamics simulations for (a) pentadecane,  $C_{1,15}(t)$ ; (b) pentadecane,  $C_{1,2}(t)$ . Note that the matrix method with basis set  $IV_Q$  with  $Q=0$  is equivalent to the matrix method with basis set I.

with large  $Q$ . For example, the reasonably accurate basis set  $IV_Q$  with  $Q=3$  for pentadecane contains 32 functions, while basis set III for pentadecane contains 1484 functions. Thus, calculations using basis set  $IV_Q$  with small  $Q$  are as accurate as calculations using basis set III but are much faster to implement. Hence, treatments now become possible for systems with considerably larger  $N$ .

The technique used to construct basis set  $IV_Q$  is generally applicable. Initially a first order calculation is performed using a relatively small basis set to produce approximate eigenfunctions and eigenvalues. Then, the initial first order basis set is extended by adding basis functions constructed from the slowest modes<sup>28</sup> of the first order calculation. This procedure can be iterated (incrementing  $Q$ ) until convergence produces a suitable basis set. We have used this technique to test the effect of augmenting basis sets III or  $IV_Q$  with higher order basis functions. Pentalinear functions of the form  $l_{i\alpha}l_{j\beta}l_{k\gamma}l_{m\delta}l_{n\epsilon}$  (or, more precisely, the appropriate symmetry-constrained linear combinations) do not appear to alter the computed  $C_{I,J}(t)$  significantly, except in the case of  $C_{1,25}(t)$  for pentacosane, where using the basis set

$$\{l_{ix} \quad [i=1, \dots, N-1], \psi_{ix}^{(1)}[\psi_j^{(1)} \cdot \psi_k^{(1)}]$$

$$[i, j, k=1, \dots, Q; j \geq k],$$

$$\psi_{ix}^{(1)}[\psi_j^{(1)} \cdot \psi_k^{(1)}][\psi_m^{(1)} \cdot \psi_n^{(1)}]$$

$$[i=1, \dots, R; \text{all possible pairs of pairs}$$

$$\{\{j, k\}, \{m, n\}\} \text{ with } j, k, m, n=1, \dots, R\}$$

$$(\text{basis set } V_{Q,R})$$

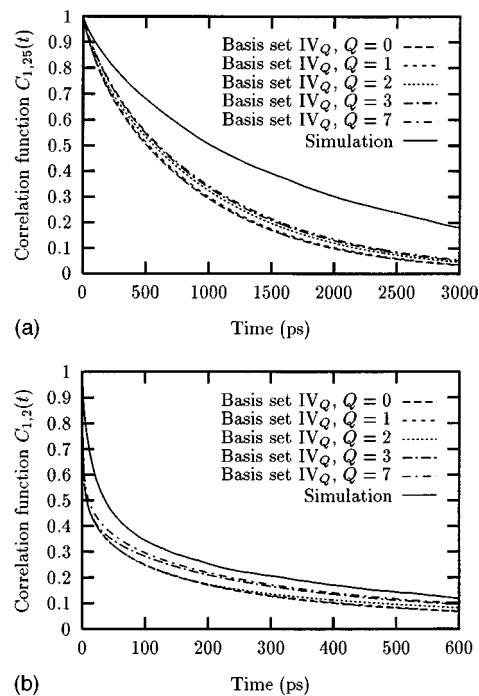


FIG. 5. Comparison between the dipole time correlation functions estimated by the matrix method using basis set  $IV_Q$  and the time correlation functions calculated directly from Brownian dynamics simulations for (a) pentacosane,  $C_{1,25}(t)$ ; (b) pentacosane,  $C_{1,2}(t)$ . Note that the matrix method with basis set  $IV_Q$  with  $Q=0$  is equivalent to the matrix method with basis set I.

produces some improvement in the estimated time correlation function, as illustrated in Fig. 6. Adding still higher order basis functions to basis set  $V_{Q,R}$  does not appear to yield any further change in the computed  $C_{1,25}(t)$  for pentacosane.

### C. Orientational correlation function

While infrared and dielectric relaxation experiments measure  $C_{I,J}(t)$ , NMR experiments provide the Fourier transform of  $P_2(t)$  at selected frequencies, and fluorescence depolarization experiments are capable of producing the entire orientational correlation functions  $P_2(t)$ . Thus, we now consider various basis sets for computing the long time por-

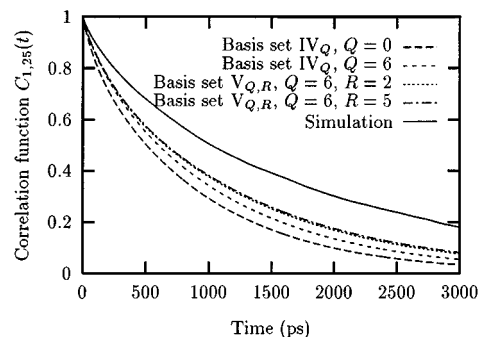


FIG. 6. Comparison between  $C_{1,25}(t)$  for pentacosane estimated by the matrix method using basis sets  $IV_Q$  and  $V_{Q,R}$  and  $C_{1,25}(t)$  calculated directly from Brownian dynamics simulations. Note that the matrix method using basis set  $IV_Q$  with  $Q=0$  is equivalent to the matrix method using basis set I.

tion of the normalized time correlation functions for the orientational correlation function  $P_2^{IJ}(t)$  associated with any bond vector  $\mathbf{r}_{IJ} = \mathbf{q}_J - \mathbf{q}_I$ ,

$$\begin{aligned} P_2^{IJ}(t) &= \frac{3}{2} \langle \cos^2 \theta_{IJ}(t) \rangle - \frac{1}{2} \\ &= \frac{3}{2} \left\langle \frac{[\mathbf{r}_{IJ}(t) \cdot \mathbf{r}_{IJ}(0)]^2}{r_{IJ}^2(t)r_{IJ}^2(0)} \right\rangle - \frac{1}{2}. \end{aligned} \quad (6.4)$$

As described below, the required basis sets are significantly larger than those necessary for computing  $C_{I,J}(t)$ . Hence, the present simplifications are essential for enabling the computations to be performed for larger systems.

First  $P_2(t)$  is transformed into the form of the correlation function  $\langle a(t)a(0) \rangle$ . Introduce the expansion in terms of components,

$$\begin{aligned} \langle \cos^2 \theta_{IJ}(t) \rangle &= \left\langle \left[ \frac{\mathbf{r}_{IJ}(t)}{r_{IJ}(t)} \cdot \frac{\mathbf{r}_{IJ}(0)}{r_{IJ}(0)} \right]^2 \right\rangle \\ &= \langle [\hat{\mathbf{r}}_{IJ}(t) \cdot \hat{\mathbf{r}}_{IJ}(0)]^2 \rangle, \end{aligned} \quad (6.5)$$

where  $\hat{\mathbf{r}}_{IJ}$  is the normalized vector,  $\hat{\mathbf{r}}_{IJ} = (\mathbf{r}_{IJ}/r_{IJ})$ , and  $r_{IJ} = \sqrt{x_{IJ}^2 + y_{IJ}^2 + z_{IJ}^2}$ . Equation (6.5) can be expanded into six separate correlation functions,

$$\begin{aligned} \langle \cos^2 \theta_{IJ}(t) \rangle &= \langle \hat{r}_{I,x}(t)^2 \hat{r}_{I,x}(0)^2 \rangle + \langle \hat{r}_{I,y}(t)^2 \hat{r}_{I,y}(0)^2 \rangle + \langle \hat{r}_{I,z}(t)^2 \hat{r}_{I,z}(0)^2 \rangle \\ &\quad + 2 \langle \hat{r}_{I,x}(t) \hat{r}_{I,y}(t) \hat{r}_{I,x}(0) \hat{r}_{I,y}(0) \rangle \\ &\quad + 2 \langle \hat{r}_{I,y}(t) \hat{r}_{I,z}(t) \hat{r}_{I,y}(0) \hat{r}_{I,z}(0) \rangle + 2 \langle \hat{r}_{I,z}(t) \hat{r}_{I,x}(t) \hat{r}_{I,z}(0) \hat{r}_{I,x}(0) \rangle. \end{aligned} \quad (6.6)$$

The first three terms in the above equation should be equal because of rotational invariance, and the last three terms are likewise equal by symmetry. The right-hand side of Eq. (6.6) is therefore reduced to two terms,

$$\begin{aligned} \langle \cos^2 \theta_{IJ}(t) \rangle &= 3 \langle \hat{r}_{I,x}(t)^2 \hat{r}_{I,x}(0)^2 \rangle \\ &\quad + 6 \langle \hat{r}_{I,x}(t) \hat{r}_{I,y}(t) \hat{r}_{I,x}(0) \hat{r}_{I,y}(0) \rangle. \end{aligned} \quad (6.7)$$

The symmetry arguments described in Sec. VI A indicate that basis functions linear in the  $l_{i\alpha}$  cannot contribute to Eq. (6.7). Because the correlation functions in Eq. (6.7) contain bilinear variables transforming either as scalars or as second rank tensors, the lowest order calculation uses a basis set of the form  $l_{i\alpha} l_{j\beta}$ , where  $\alpha$  and  $\beta$  indicate the  $x$ ,  $y$ , or  $z$  directions, and  $i$  and  $j$  are the indices of the bond vectors.<sup>29</sup> More explicitly, we use

$$\{l_{i\alpha} l_{j\alpha}, \alpha = x, y, z, \quad [i, j = 1, \dots, N-1, i \leq j]\},$$

(basis set VI<sub>1</sub>)

as the first order basis functions for the first correlation functions on the right-hand side of Eq. (6.7). The first order basis set for the second correlation function on the right-hand side of Eq. (6.7) is likewise naturally chosen as

$$\{l_{ix} l_{jy} \quad [i, j = 1, \dots, N-1]\} \quad (\text{basis set VI}_2).$$

The two correlation functions on the right-hand side of Eq. (6.7) are evaluated separately using the appropriate first order basis sets. The value of  $P_2^{IJ}(t)$  is then obtained as the linear combination of these correlation functions according to Eq. (6.7). Because the simulation trajectories are of finite duration, they do not necessarily display all the exact symmetries properties, such as the equality of terms converting Eq. (6.6) to Eq. (6.7). We have checked this behavior by separately computing each of the six terms of Eq. (6.6), finding very near equality of the symmetry equivalent terms.

Further computations may, therefore, employ the simpler form of Eq. (6.7).

Figure 7 exhibits the correlation functions  $P_2^{IJ}(t)$  for different vectors  $\mathbf{r}_{IJ}$  as obtained using the above sets of basis functions. The agreement is reasonably good for the  $P_2^{14}(t)$  and  $P_2^{18}(t)$  orientational correlation functions of octane, but degrades somewhat with the correlation function for the faster and more local case of  $\mathbf{r}_{12}$ . The orientational correlation function  $P_2^{12}(t)$  decays much faster than does  $P_2^{14}(t)$  and  $P_2^{18}(t)$ , with all the  $P_2^{IJ}(t)$  decaying at roughly twice the rate of the corresponding  $C_{I,J}(t)$ . Since the theory is designed to treat the long time dynamics, the dynamical behavior for shorter times is sacrificed by the theory due to the insufficient treatment of the memory function matrix. Thus, the more rapidly decaying  $P_2(t)$  for  $\mathbf{r}_{12}$  is more poorly represented in first order than the slower  $P_2(t)$  for  $\mathbf{r}_{14}$  and  $\mathbf{r}_{18}$ .

Experience with computing  $C_{I,J}(t)$  indicates the need for additional basis functions beyond first order. The basis functions which contribute most significantly to the first three terms of Eq. (6.7) are expected by symmetry and by “mode coupling” arguments<sup>7</sup> to be symmetry adapted quartic factors  $l_{i\alpha} l_{j\alpha} l_{k\beta} l_{m\beta}$ , where  $i, j, k$ , and  $m$  designate the indices of each bond, and  $\alpha$  and  $\beta$  denote the  $x, y$ , or  $z$  components. This full second order basis set scales in size as  $N^4$  and rapidly becomes unwieldy. Thus, it is natural to develop an approximate second order basis set using the simplification procedures applied to  $C_{I,J}(t)$  along with symmetry considerations.

The approximate second order basis set is constructed using higher powers of the generalized Rouse modes. Let  $\psi_1^{(1)}, \psi_2^{(1)}, \dots, \psi_{N-1}^{(1)}$  again denote the first order generalized Rouse modes corresponding to the eigenvalues  $\lambda_1^{(1)}, \lambda_2^{(1)}, \dots, \lambda_{N-1}^{(1)}$ , where  $\lambda_1^{(1)} < \lambda_2^{(1)} < \dots < \lambda_{N-1}^{(1)}$ . The approximate second order basis set for the first correlation function on the right-hand side of Eq. (6.7) is



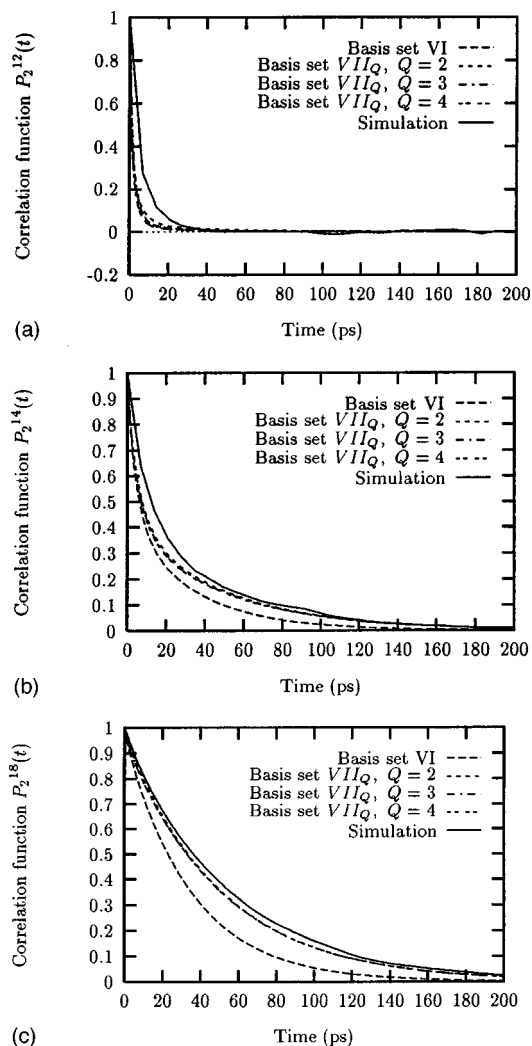


FIG. 7. Comparison between the correlation functions (a)  $P_2^{12}(t)$ ; (b)  $P_2^{14}(t)$ ; (c)  $P_2^{18}(t)$  for octane from the matrix method using basis set VI (lower curve) and basis set  $VII_Q$  for  $Q=2$ ,  $Q=3$ , and  $Q=4$  with that from the simulation (upper curve). The curves represent averages over 12 trajectories with durations of 7.0 ns.

$$\{l_{i\alpha}l_{j\alpha}, \alpha=x, y, \text{ and } z, [i, j=1, \dots, N-1, i \leq j],$$

$$\psi_{k\alpha}^{(1)}\psi_{l\alpha}^{(1)}[\psi_m^{(1)} \cdot \psi_n^{(1)}], \alpha=x, y, z,$$

$$[k, l, m, n=1, \dots, Q; k \leq l, m \leq n]\}$$

(basis set  $VII_{1Q}$ ).

By incrementing the value of  $Q$  from 1 to  $N-1$ , more and more second order basis functions are included, and the procedure is stopped when convergence is obtained. Since the eigenfunctions associated with the lowest eigenvalues contribute most to the long time portion of correlation functions, we expect to obtain rapid convergence for  $Q$  small. [The full second order basis for  $P_2(t)$  rapidly becomes too large for convenient computation.]

The full second order basis set for the second term  $\langle \hat{r}_{Ix}(t)\hat{r}_{Iy}(t)\hat{r}_{Ix}(0)\hat{r}_{Iy}(0) \rangle$  in Eq. (6.7) contains terms of the form  $l_x l_y (\mathbf{1} \cdot \mathbf{1})$ . Again, the approximate second order basis can be constructed from the Rouse modes  $\psi_i^{(1)}$ ,

$$\{l_{ix}l_{jy}, [i, j=1, \dots, N-1],$$

$$\psi_{kx}^{(1)}\psi_{ly}^{(1)}[\psi_m^{(1)} \cdot \psi_n^{(1)}], [k, l, m, n=1, \dots, Q; k \leq l, m \leq n]\}$$

(basis set  $VII_{2Q}$ ).

Figures 7 also displays  $P_2^{IJ}(t)$  for the vectors  $\mathbf{r}_{12}$ ,  $\mathbf{r}_{14}$ , and  $\mathbf{r}_{18}$  of octane from both the simulation and theory using the basis set  $VII_Q$ . The computations with  $Q=3$  and 4 are very close indicating that convergence is again quite rapid. The size of the approximate second order basis sets scale as  $N^2+Q^4$ . Thus, for  $Q \ll N$ , the approximate second order basis set is considerably smaller than that of the full second order basis set. We have also tried introducing third order terms, but no significant improvement is observed.

The agreement of the theory with the simulations for  $P_2^{IJ}(t)$  is somewhat poorer than that for the corresponding  $C_{I,J}(t)$ , especially at shorter times. This emerges from the fact that the  $P_2^{IJ}(t)$  decays roughly as the corresponding  $[C_{I,J}(t)]^2$ . Hence, the short time deficiency of the theory for  $C_{I,J}(t)$  becomes accentuated for  $P_2^{IJ}(t)$  where the errors are roughly twice as large on a logarithmic scale. Thus, the slower more global  $P_2^{18}(t)$  is computed more accurately than the faster more local  $P_2^{12}(t)$ .

## VII. SUMMARY

The original application of the mode coupling treatment for calculating time correlation functions<sup>7,8</sup> encounters severe computational difficulties due to the rapid growth in the basis set size with increasing system size. This paper demonstrates how the use of higher order basis functions constructed from the first order Rouse modes along with symmetry considerations can enormously reduce the required size of basis sets. For instance, the previous full second order computations for  $C_{I,J}(t)$  use a basis set whose size scales as  $N^3$  while the present treatment uses a basis set of size  $N+Q^3$ . The new reduced size basis produces converged second order results with  $Q \ll N$ . These improvements in basis set become even more crucial for treating the orientational correlation function  $P_2^{IJ}(t)$ , where a full second order basis set scales in size as  $N^4$ , while the present treatment obtains convergence with a basis set of size  $N^2+Q^4$  for  $Q \ll N$ . The techniques presented in this paper allow us to perform second order computations for  $P_2^{IJ}(t)$  as well as to demonstrate the irrelevance of third order contributions for the longer alkane chains.

## ACKNOWLEDGMENTS

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