Reciprocal distance averages for the necklace model

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(Received 18 February 1980)

A method to evaluate reciprocal interbead distance averages is proposed. These averages are computed in the frame of the elastic necklace model with the distribution function of a linear polymer chain distorted by the flow. The resulting set of coupled equations are solved numerically for chains of increasing size, up to $Z = 9$ beads.

INTRODUCTION

The exact diagonalization procedure[1,2] of the HA and H matrices in the Zimm[3] theory for the ideally flexible necklace model of randomly coiled linear macromolecules in laminar flow made possible the calculation of the intrinsic stress and birefringence tensors in the limit of vanishing gradient[4]. In such a case, the coil is not yet noticeably deformed by the flow, and the matrix elements of the hydrodynamic tensor H[5] remain independent of the gradient. In fact, premature averaging of the Oseen tensor in order to linearize the hydrodynamic diffusion equation replaces the original tensor interaction by a scalar interaction proportional to an average value of the inverse interbead distance. The averages are taken with the unperturbed distribution function[5]:

$$\langle R_{jk}^{-1}\rangle_0 = \left(\frac{6}{\pi}\right)^{1/2} \langle R_m^2\rangle_0^{-1/2} = \left(\frac{6}{\pi}\right)^{1/2} \frac{m^{-1/2}}{b_0} \qquad (1)$$

for any pair of beads located at $\vec{r}_j$, $\vec{r}_k$ and $j,k = 0, 1, \ldots, N$. (N is the number of statistically independent links and $m = |j-k|$).

In laminar flow, the molecule gets expanded and oriented, and the solution shows streaming birefringence[5]. Deformation changes, the intramolecular distances and the change of shape of the molecule are accurately described by the exact distribution function of the coil in non-zero gradient[6].

This paper proposes a method to evaluate the inverse interbead distance averages of a flexible linear macromolecule in a transverse gradient flow in order to get a more appropriate description of the gradient-dependent properties of dilute polymer solutions with the necklace model.

NOTATION

In the necklace model, the molecule is represented by $Z = N + 1$ beads (numbered from 0 to N) connected by N elastic links. The root mean square length of each link in solution at rest is b_0. We define a configuration of the molecule in the space of normal coordinates by the $3Z$-dimensional vector $\vec{u}$:

$$\vec{U} \equiv \{u_k^\alpha\},\ k = 0,\ 1, \ldots, N;\ \alpha = 1,\ 2,\ 3 \qquad (2)$$

The index k runs over the normal modes and the index α labels the Cartesian components of each one. These components of the k^{th}-mode are usually called (ξ_k, ζ_k, η_k) in the literature[1-6] but the choice (u_k^1, u_k^2, u_k^3) is better suited for our purposes.

The steady state solution of the linearized diffusion equation with a constant transverse gradient is[6]

$$\psi(\vec{U}) = \prod_{k=1}^{N} \varphi_k(\vec{U}_k) \qquad (3)$$

where

$$\varphi_k(\vec{u}_k) = C_k \exp\left(-\frac{1}{2b_0^2} \sum_{\alpha,\alpha'=1}^{3} \tilde{S}_k^{\alpha\alpha'}(\beta) u_k^\alpha u_k^{\alpha'}\right) \qquad (4)$$

are the distribution functions of the independent modes. Here $\tilde{S}_k^{\alpha,\alpha'}$ are the matrix elements of the 3×3 symmetrical matrix $\tilde{S}_k$:

$$\tilde{S}_k = \begin{pmatrix} \frac{3\mu_k}{1+\beta_k^2}(1+2\beta_k^2) & -\frac{3\mu_k}{1+\beta_k^2}\beta_k & 0 \\ -\frac{3\mu_k}{1+\beta_k^2}\beta_k & \frac{3\mu_k}{1+\beta_k^2} & 0 \\ 0 & 0 & 3\mu_k \end{pmatrix} \qquad (5)$$

and $\beta_k = \beta/\lambda_k$. The quantity β is the reduced rate of shear[5] and λ_k, u_k are the non-zero eigenvalues of the HA and A matrices, respectively. The value of the constant $C_k = (3\mu_k/\pi(1+\beta_k^2))3/2$ follows from the normalization condition:

$$\int d\vec{u}_k \varphi_k(\vec{u}_k) = 1 \qquad (6)$$

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0032-3861/80/101171-04$02.00

If we define the $3N \times 3N$ symmetrical matrix S by its matrix elements:

$$S_{kk'}^{\alpha\alpha'} = \tilde{S}_k^{\alpha,\alpha'}\ \delta_{kk'} \tag{7}$$

the normalized distribution function (3) can be written ($b_0 = 1$):

$$\psi(\vec{u}) = C.\ \exp\left\{ -\frac{1}{2} \sum_{k,k'=1}^{N} \sum_{\alpha,\alpha'=1}^{3} S_{kk'}^{\alpha\alpha'}\ u_k^{\alpha}\ u_{k'}^{\alpha'} \right\} \tag{8a}$$

or, in a more compact form:

$$\psi(\vec{u}) = C\ \exp\left(-\frac{1}{2} \vec{u} T S \vec{u} \right) \tag{8b}$$

where $C = \prod_k C_k$ and $\vec{U}^T$ is the transposed vector $\vec{U}$. From now on, the symbol $\langle \ldots \rangle_\beta$ stands for the mean values computed with the weight given by equation (8).

The solution of the eigenvalue problem[3,5]

$$Q^{-1}\ H A\ Q = \Lambda \tag{9}$$

brings the transformation matrix Q from normal coordinates to the position vectors $\vec{r}_j \equiv (x_j^1, x_j^2, x_j^3)\ (j = 0, 1, \ldots N)$ of the beads:

$$x_j^{\alpha} = \sum_{e=0}^{N} Q_{je} u_e^{\alpha} \alpha = 1, 2, 3 \tag{10}$$

Finally, the matrix elements of the hydrodynamic interaction tensor H are:

$$H_{jk} = \delta_{jk} + \sqrt{2} h^* \langle R_{jk}^{-1} \rangle (1 - \delta_{jk}) \tag{11}$$

where h^* is the hydrodynamic interaction parameter[1].

MEAN VALUES

In the usual treatment, it is assumed gradient independent inverse distances R_m^{-1} between any two beads separated by m links since they are computed as the average value $\langle R_m^{-1} \rangle_0$ with solution at rest. Due to the constancy of H and consequently of Λ, it turns out that the theory fails to describe the gradient dependence of some components of the stress tensor, such as the intrinsic viscosity.

This limitation of the model can be removed in the frame of a 'preaveraging procedure' by replacing the cartesian components of the Oseen tensor $T_m^{\alpha\alpha'}$ with the average $\langle T_m^{\alpha\alpha'} \rangle_\beta$. This approximation preserves the tensor character of the hydrodynamic interaction since there will be, in general, non-vanishing contributions for $\alpha \neq \alpha'$ coming from the off-diagonal matrix elements of $\tilde{S}_k$ (Equation 5). We shall assume in the following that we can replace the tensor $\langle T_m \rangle_\beta$ by the scalar $(6\pi\eta_0)^{-1} \langle R_m^{-1} \rangle_\beta$ times the 3×3 identity tensor. Here η_0 is the viscosity of the solvent.

Our main objective is the computation of the averages $I^{(N)}{}_m$ defined as:

$$I_m^{(N)} = \langle R_m^{-1} \rangle = \int d\vec{u} R_m^{-1}(\vec{u}) \psi(\vec{u}) \tag{12}$$

for a chain of $Z = N + 1$ beads. It is a $3N$-dimensional integral of the inverse interbead distance expressed as a function of the normal modes, weighted with the normalized distribution function equation (8). The two beads are separated by m links along the chain. As $\beta = 0$, the averages $I_m^{(N)}$ are independent of N and are given by equation (1).

We define R_m^{-1} by the identity:

$$R_m^{-1} = \left(\frac{\pi}{2} \right)^{1/2} \int_0^{\infty} \exp\left(-\frac{1}{2} t^2 R_m^2 \right) dt \tag{13}$$

Now, the interbead position vector $\vec{R}_m$ is

$$\vec{R}_m = \vec{r}_j - \vec{r}_k = \sum_{e=1}^{N} (Q_{je} - Q_{ke}) \vec{u}_e = \sum_{e=1}^{N} f_e\ \vec{u}_e \tag{14}$$

where Q_{je} are the matrix elements of the transformation matrix Q for a given rate of shear β. We omit the term with $e = 0$ because the first column of Q is a constant and the difference vanishes.

The squared distance R_m^2 gives

$$R_m^2 = \sum_{e,e'=1}^{N} \sum_{\alpha,\alpha'=1}^{3} f_e f_{e'}\ \delta_{\alpha\alpha'}\ u_e^{\alpha}\ u_{e'}^{\alpha'} \tag{15}$$

The introduction of the sums on α and α' allows this quadratic form in the space of the normal coordinates to be written as

$$R_m^2 = \vec{U}^T F \vec{U} \tag{16}$$

where F is a $3N \times 3N$ matrix with matrix elements $F_{ee'}^{\alpha\alpha'}$ defined:

$$F_{ee'}^{\alpha\alpha'} = F_{ee'}\ \delta_{\alpha\alpha'} = f_e f_{e'}\ \delta_{\alpha\alpha'} \tag{17}$$

The identity (equation 13) reads now

$$R_m^{-1} = \left(\frac{\pi}{2} \right)^{1/2} \int_0^{\infty} dt\ \exp\left\{ -\frac{t^2}{2} \sum_{e,e'=1}^{N} \sum_{\alpha,\alpha'=1}^{3} F_{ee'}^{\alpha\alpha'}\ u_e^{\alpha}\ u_{e'}^{\alpha'} \right\} \tag{18}$$

This integral is a realization of the non-linear dependence of the inverse distance R_m^{-1} on the normal modes $\vec{U}$.

When we introduce this representation of R_m^{-1} in the expression (12) for the averages and interchange the order of integration, we get

$$I_m^{(N)} = \left(\frac{\pi}{2} \right)^{1/2} C \int_0^{\infty} dt \left\{ \int d\vec{U}\ \exp\left(-\frac{1}{2} \sum\sum_{e,e'\alpha\alpha'} \theta_{ee'}^{\alpha\alpha'} u_e^{\alpha} u_{e'}^{\alpha'} \right) \right\} \tag{19}$$

where

$$\theta_{ee'}^{\alpha\alpha'} = S_{ee'}^{\alpha\alpha'} + t^2\ F_{ee'}^{\alpha\alpha'} \tag{20}$$

are the matrix elements of $\theta_m = S + t^2 F$. The first term in equation (20) mixes two of the components of each normal mode, and the second one mixes the *same* cartesian component of the normal modes. The assumed isotropy of the hydrodynamic interaction is responsible for this simplification in the structure of the matrix θ_m.

Table 1 The zeroth-order averages $I_{0,m}^{(N)}$ ($m = 1, 2, \ldots, N$) computed as functions of the reduced rate of shear β, for $N = 2$

	β										
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
m											
1	1.382	1.350	1.262	1.135	0.988	0.841	0.703	0.581	0.477	0.391	0.320
2	0.977	0.953	0.886	0.791	0.683	0.576	0.477	0.391	0.318	0.258	0.210

Table 2 As *Table 1*, for $N = 4$

	β										
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
m											
1	1.382	1.256	0.972	0.682	0.455	0.298	0.194	0.127	0.083	0.055	0.037
2	0.977	0.882	0.672	0.460	0.300	0.192	0.122	0.078	0.051	0.033	0.022
3	0.798	0.715	0.538	0.363	0.233	0.147	0.093	0.059	0.038	0.025	0.016
4	0.691	0.617	0.463	0.311	0.200	0.126	0.079	0.051	0.032	0.021	0.014

Table 3 As *Table 1*, for $N = 6$

	β					
	0	0.1	0.2	0.3	0.4	0.5
m						
1	1.382	1.087	0.622	0.320	0.162	0.082
2	0.977	0.760	0.424	0.211	0.103	0.051
3	0.798	0.613	0.333	0.162	0.077	0.038
4	0.691	0.525	0.281	0.134	0.064	0.031
5	0.618	0.470	0.247	0.118	0.055	0.027
6	0.564	0.427	0.226	0.107	0.051	0.024

Table 4 As *Table 1*, for $N = 8$

	β					
	0	0.1	0.2	0.3	0.4	0.5
m						
1	1.382	0.869	0.350	0.133	0.051	0.020
2	0.977	0.607	0.236	0.086	0.032	0.012
3	0.798	0.487	0.183	0.065	0.024	0.009
4	0.691	0.415	0.151	0.052	0.019	0.007
5	0.618	0.365	0.130	0.044	0.016	0.006
6	0.564	0.330	0.116	0.039	0.014	0.005
7	0.522	0.303	0.106	0.036	0.013	0.005
8	0.489	0.284	0.099	0.033	0.012	0.004

The $3N$-dimensional integral on the normal modes can be explicitly performed since the argument of the exponential is a real, symmetric quadractic form in the integration variables $\vec{U}$. The result is

$$\int d\vec{U} \exp\left(-\frac{1}{2}\vec{U}^T\theta_m\vec{U}\right) = (2\pi)^{3N/2}[\det \theta_m]^{-1/2} \qquad (21)$$

Finally, our main result is achieved: the averages $I_m^{(N)}$ may be computed from one-dimensional integrals, as

$$I_m^{(N)}(\beta) = \left(\frac{\pi}{2}\right)^{1/2} (2\pi)^{3N/2} C \int_0^\infty dt[\det \theta_m]^{-1/2} \qquad (22)$$

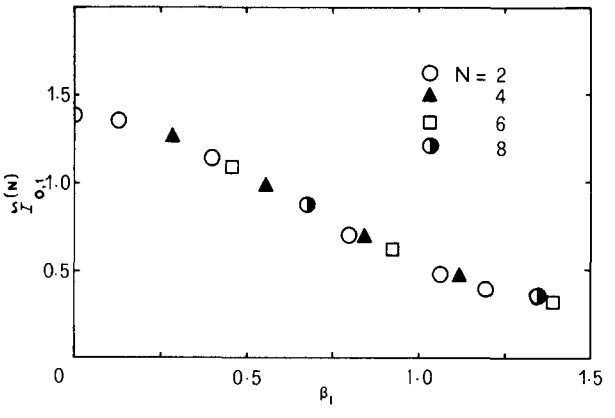

Figure 1 The zeroth-order averages $I_{0,1}^{(N)}$ plotted as functions of the scaled rate of shear β_1.. The lowest non-zero eigenvalues $\lambda_{1,N}^{(0)}$ are 0.75, 0.3569, 0.2161 and 0.1482 for $N = 2$, 4, 6 and 8, respectively

The last equation, together with equations (9) and (11), define a set of non-linear coupled equations for the unknown eigenvalues $\lambda_k (k = 1, 2, \ldots, N)$ and can be solved self-consistently for each value of the parameter β.

NUMERICAL RESULTS

The evaluation of the mean values (22) requires the knowledge of the eigenvectors of the non-symmetrical matrix HA. In the literature, there are several procedures to find them when the averages $I_m^{(N)}$ are given by equation (1). The reader is referred to a recent discussion by Zimm[7] on this subject. A method is followed that was proposed by Fong and Peterlin[2], where the eigenvalues of the matrix A are uhity and $\lambda_k^{(0)} = \mu_k^{(0)}$ for any k. (The superscript refers to the limit $\beta = 0$).

The set of equations (9), (11) and (22) can be solved by successive approximations starting from the solution of the eigenvalue problem (9) and (11) for $\beta = 0$. From the eigenvalues and eigenvectors, one constructs the matrices S and F, respectively, for a given value of the parameter β. The determinant of the θ_m matrix is then evaluated for each point of the integration variable t, and the integrations are performed with the usual quadrature

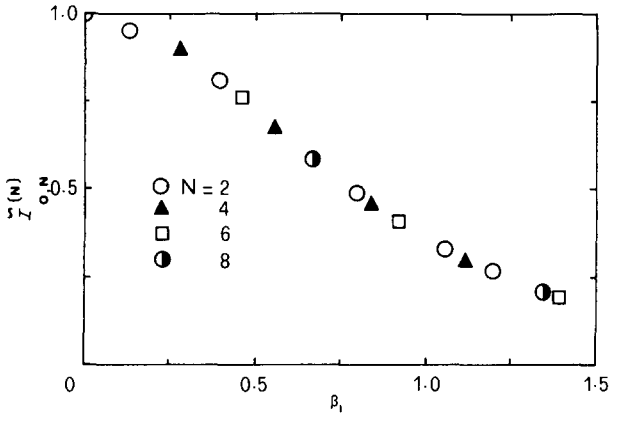

Figure 2 The zeroth-order normalized averages $I_{0,N}^{(N)}$ plotted as functions of the scaled rate of shear β_1

Table 5 The averages $I_1^{(2)}$, $I_2^{(2)}$ and the non-zero eigenvalues λ_1, λ_2 computed with increasing number of iterations, for $\beta = 0.3$, 0.6, 0.9 and 1.2. The first column includes the zeroth-order approximation

		Zeroth-order	Number of iterations		
			1	2	3
$\beta = 0.3$	$I_{0,1}$	1.1347	1.1619	1.1592	1.1594
	$I_{0,2}$	0.7914	0.8113	0.8093	0.8095
	λ_1	0.7975	0.7924	0.7929	0.7929
	λ_2	2.0413	2.0186	2.0208	2.0206
$\beta = 0.6$	$I_{0,1}$	0.7029	0.8355	0.8132	0.8171
	$I_{0,2}$	0.4768	0.5710	0.5550	0.5578
	λ_1	0.8780	0.8539	0.8580	0.8573
	λ_2	2.4027	2.2910	2.3098	2.3066
$\beta = 0.9$	$I_{0,1}$	0.3909	0.5778	0.5468	0.5521
	$I_{0,2}$	0.2583	0.3866	0.3651	0.3687
	λ_1	0.9339	0.9011	0.9066	0.9057
	λ_2	2.6660	2.5076	2.5338	2.5293
$\beta = 1.2$	$I_{0,1}$	0.2148	0.3908	0.3663	0.3698
	$I_{0,2}$	0.1393	0.2567	0.2401	0.2424
	λ_1	0.9644	0.9343	0.9386	0.9380
	λ_2	2.8158	2.6657	2.6866	2.6836

formulas. These results define the zeroth-order averages $I_{0,m}^{(N)}$. The substitution of these quantities in equations (9) and (11) starts an iterative procedure.

The zeroth-order averages $I_{0,m}^{(N)}$ $(m = 1, 2, \ldots, N)$ was computed for chains with $N = Z - 1 = 2$, 4, 6 and 8 links as functions of β. The hydrodynamic interaction parameter was chosen: $h^* = 0.25$. All the integrals were performed with 12-points Gauss-Laguerre quadrature routine and the results are collected in *Tables* 1–4. The averages $I_{0,1}^{(N)}$ are plotted in *Figure* 1 as a function of the scaled rate of shear $\beta_1 = \beta/\lambda_{1,N}^{(0)}$, where $\lambda_{1,N}^{(0)}$ is the lowest non-zero eigenvalue of HA for a given number of links N. The normalized averages

$$\tilde{I}_{0,N}^{(N)}(\beta) = \frac{I_{0,N}^{(N)}(\beta)}{I_{0,N}^{(N)}(0)} \qquad (23)$$

that are related to the inverse end-to-end distances are also shown in *Figure* 2. To this order, all the averages exhibit universal behaviour-independence with $N =$ when plotted in terms of the scaled variable β_1.

The effect of successive approximations is reported here for the simplest case $N = 2$. In *Table* 5, we reproduce the zeroth-order calculation, the resulting values of $I_1^{(2)}$, $I_2^{(2)}$, and the non-zero eigenvalues λ_1 and λ_2 obtained up to three iterations for $\beta = 0.3$, 0.6, 0.9 and 1.2.

Table 5 shows that, for low values of β, the zeroth-order approximation and the exact results agree within 2%. As β increases, the relative error in the averages grows up to 50% in extreme conditions ($\beta = 1.2$), but the approximate eigenvalues λ_1, λ_2 differ from the exact ones by less than 5%. This behaviour is also present in chains with a higher number of links, and make the zeroth-order approximation a good starting point to study the gradient dependence of the intrinsic viscosity of polymer solutions[8].

CONCLUSIONS

A method was developed to evaluate inverse interbead distances in the frame of the elastic necklace model with a finite number of beads, but the inclusion of the internal viscosity offered no difficulty. As stated earlier, the author was only interested in the influence of a transverse gradient flow on a polymer chain with *scalar* hydrodynamic interactions. Any consideration of the actual anisotropy of the interactions is beyond the scope of this paper. A full discussion on the gradient dependence of the dynamic properties of polymer solutions with the necklace model will be published elsewhere.

ACKNOWLEDGMENTS

The author thanks Professor A. Peterlin for calling his attention to this problem and stimulating correspondence. He has benefitted from many discussions with H. Fanchiotti and H. Vucetich. The computer facilities from C.E.S.P.I. of University of La Plata are also acknowledged.

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