CALCULATION OF NEAR-FIELD MOLECULAR INTERACTIONS IN POLYMERS

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The role of near-field and far-field interactions in determining the conformative mobility of macromolecules is analyzed here. An algorithm is proposed for finding the global minimum energy of near-field intramolecular interactions.

The calculation of transport processes in certain types of molecular structures is of great interest, as it relates to the problem of producing semipermeable membranes.

Transport processes in complex molecular structures such as polymers, for instance, are determined largely by the nature of interactions between molecules of the polymer and its conformation.

Intramolecular interactions, which determine the conformative stability of its various spatial structures, are usually classified according to the distance between the interacting groups along the principal valence chain. Effects within chain fragments containing 1-3 radicals are usually defined as near-field interactions. It is convenient to single out this class of interactions, from the interpretive point of view, inasmuch as the spatial structure of a molecule which variously combines stable conformations of its fragments has properties that greatly simplify many problems in the configuration statistics and the conformation analysis of such molecules, at least within the qualitative scope.

When considering the intramolecular energy of a polymer molecule in terms of monomer–monomer interactions, one can conveniently describe these in matrix form: the diagonal matrix elements u_{ii} represent energies determined by means of potential maps of the respective monomers, while the matrix elements $u_{i,i+1}$ represent energies of interaction between adjacent monomers, etc.

It is well known that conformations even by monomer elements in a row arrangement correlate very weakly, as a rule, because of coexisting stereostructures in the framework [1]. Thus, the contributions of interactions u_{ij} are almost completely determined by the nature of the contact between the i-th and j-th monomer elements. The relative location of i-th and j-th monomer elements is obviously becoming less constrained kinematically, meanwhile, as the indices i and j move farther apart in sequence.

This can be explained as follows. Let us assume that a small displacement R (Å) of the k-th functional group relative to the j-th conformation

$$\bar{\Phi} = \begin{pmatrix} \varphi_1 \\ \vdots \\ \varphi_n \end{pmatrix} \tag{1}$$

can be effected so that the sum of the squares of angular displacements due to internal rotations $(\bar{\Phi}-\bar{\Phi}')^2$ will be minimum.

With small displacements described by the expression [3]

$$R_{jk} = \sum_{n=j}^{k} (\bar{\theta}_n + \bar{\Xi}_n \times \bar{\rho}_k)\, \Delta\varphi_n \tag{2}$$

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and with

$$\Delta\bar{\Phi} = \bar{\Phi} - \bar{\Phi}', \tag{3}$$

we have

$$\bar{R}^2_{jk} \approx \Delta\bar{\Phi}T\Delta\bar{\Phi}, \tag{4}$$

where the elements of matrix T are

$$t_{ik} = \begin{cases} (\bar{\theta}_i + \bar{\Xi}_i \times \bar{\rho}_j)(\bar{\theta}_k + \bar{\Xi}_k \times \bar{\rho}_j) & \text{for } i > k, \\ 0 & \text{for } i < k. \end{cases} \tag{5}$$

The thus formulated condition can be written as

$$\nabla(\Delta\bar{\Phi}^2 - \mu\Delta\bar{\Phi}T\Delta\bar{\Phi}) = \Delta\bar{\Phi} - \mu T\Delta\bar{\Phi} = 0; \tag{6}$$

where μ is a Lagrangian multiplier.

The sought solution will be an eigenvector $\bar{Y}$ which corresponds to the eigenvalue $1/\mu$ of matrix T, where

$$\bar{Y}^2 = \frac{1}{\mu}\bar{Y}T\bar{Y} = \frac{1}{\mu}R^2_{ik} \tag{7}$$

and for a unitary R_{ik}

$$\sigma_{\Delta\varphi_i} = \sqrt{\frac{1}{\mu n}}\,. \tag{8}$$

On the assumption that μ does not depend on n, as in the case of a block-diagonal matrix T, for example, the mean "compensating" change in the rotation angle $\Delta\varphi_i$ is proportional to $1/\sqrt{n}$.

If T is a block matrix, then $1/\mu$ increases proportionally to n and

$$\sigma_{\Delta\varphi_i} \sim \frac{1}{n}\,. \tag{9}$$

In actual structures the relation should be somewhere intermediate.

If, instead of $\Delta\bar{\Phi}^2$, the deformation energy

$$\Delta U \approx \Delta\bar{\Phi}A\Delta\bar{\Phi} \tag{10}$$

is minimized (here A denotes the matrix of the second derivatives), then an analogous result will be obtained for matrix $A^{-1}T$.

Another estimate can be made using, instead of Eq. (6), the requirement that the sum of the squares of changes in the coordinates of many atoms be minimum for any given change of the i-th angle by $\Delta\varphi_i$. This quantity may be approximated by

$$P \approx \Delta\bar{\Phi}\,S'\Delta\,\bar{\Phi}, \tag{11}$$

where elements of matrix S' are defined as

$$S_{ij} = \sum_{k=1}^{i}\sum_{l=1}^{j}(\bar{\theta}_i + \bar{\Xi}_i \times \bar{\rho}_k)(\bar{\theta}_j + \bar{\Xi}_j \times \bar{\rho}_l). \tag{12}$$

On the basis of the concepts developed in [4], the magnitudes of the component vectors in parentheses are assumed to have a normal distribution with the dispersion σ^2.

From the condition

$$\nabla P = S\Delta\bar{\Phi} = 0 \tag{13}$$

we find

$$S\bar{F}_i = \Delta\varphi_i\bar{\Lambda}, \tag{14}$$

where

$$\bar{F}_i = \begin{pmatrix} \Delta\varphi_1 \\ \cdot \\ \cdot \\ \cdot \\ \Delta\varphi_p \\ \cdot \\ \cdot \\ \cdot \\ \Delta\varphi_n \end{pmatrix}; \; p \neq i; \; \bar{\Lambda} = \begin{pmatrix} \lambda_{1i} \\ \cdot \\ \cdot \\ \cdot \\ \lambda_{pi} \\ \cdot \\ \cdot \\ \cdot \\ \lambda_{ni} \end{pmatrix}; \; p \neq i,$$

and matrix S is obtained from matrix S' by deleting the i-th row and the i-th column. It is not difficult to ascertain that the diagonal elements S_{ii} have a χ^2 distribution with 3(n−i) degrees of freedom and with the mean value of S_{ii} equal to $3\sigma^2(n-i)$.

The dispersion of element S_{ij} is

$$\sigma^2_{S_{ij}} = \sigma^4 (n-i)(n-j), \tag{15}$$

and the dispersion of ratio $\Delta\varphi_k/\Delta\varphi_i$ is

$$\sigma^2_{\frac{\Delta\varphi_k}{\Delta\varphi_i}} \approx \frac{n-i}{9(n-k)} \tag{16}$$

by virtue of matrix S being a nearly diagonal one.

Expression (16) relates the distribution of $\Delta\varphi_k$ to the quantity $|k-i|$ and may be used in a feasibility study of "compensating" for a deformation of the spatial structure.

Concepts of this sort point to the feasibility of describing the said interactions thoroughly, without a loss of accuracy in the results; since it is the calculation of far-field interactions which takes up most of the machine time necessary for computing the conformations of a rather unwieldy object, on the other hand, it seems worthwhile to introduce here effective radical–radical potentials and, at the same time, to retain the former level of detailization in describing the near-field interactions.

According to the calculations in [4], widening the "zone" of accountable interactions along the principal valence chain, i.e., accounting for the type $i \longleftrightarrow i+1$ and $i \longleftrightarrow i+2$ effects will result in a significant change in the estimate of local spatial conditions, as compared to the map of a monomer element. Accounting for near-field interactions within oligomer fragments will bring out a new aspect of the situation, namely the partial overlapping of such fragments. By the same token, the conformations of all radicals appear interdependent and the energy of near-field interactions becomes a nontrivial characteristic of molecule conformations, unlike, for example, the sum of the energies of separate monomer elements which correspond to a given conformation.

Let $U_k(\bar{\Phi}_i, \bar{\Phi}_{i+1}, \ldots, \bar{\Phi}_{i+k-1})$ denote the conformation energy of a fragment containing k monomer elements in some sequence, beginning from the i-th, and let

$$\bar{\Phi}_j = \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \cdot \\ \cdot \\ \cdot \\ \varphi_p \end{pmatrix} \tag{17}$$

represent the set of internal-rotation angles corresponding to the j-th monomer element. The energy of near-field interactions will be expressed as

$$E(\bar{\Phi}_1, \bar{\Phi}_2, \ldots, \bar{\Phi}_n) = U_k(\bar{\Phi}_1, \bar{\Phi}_2, \ldots, \bar{\Phi}_k)$$

$$+ \sum_{j=2}^{k+1} \left[U_k(\bar{\Phi}_j, \bar{\Phi}_{j+1}, \ldots, \bar{\Phi}_{j+k-1}) - U_{k-1}(\bar{\Phi}_j, \bar{\Phi}_{j+1}, \ldots, \bar{\Phi}_{j+k-2}) \right]. \tag{18}$$

When k is small, the procedure for minimizing E with respect to all internal-rotation angles is rather simple. As in statistical physics of polymers, accounting for near-field interactions only has, analogously, made it possible to use the already available formalism of the Easing model, which appears to provide some concepts of dynamic programing [2] suitable here almost without any modification.

We seek the global minimum E, i.e., the quantity

$$
\begin{aligned}
&\min E(\bar\Phi_1, \bar\Phi_2, \ldots, \bar\Phi_n) \\
&= \min_{\bar\Phi_1} \min_{\bar\Phi_2} \ldots \min_{\bar\Phi_n} \Big\{ U_k(\bar\Phi_1, \bar\Phi_2, \ldots, \bar\Phi_k) \\
&\quad + \sum_{j=2}^{k+1} [U_k(\bar\Phi_j, \bar\Phi_{j+1}, \ldots, \bar\Phi_{j+k-1}) \\
&\quad - U_{k-1}(\bar\Phi_j, \bar\Phi_{j+1}, \ldots, \bar\Phi_{j+k-2})] \Big\} \\
&= \min_{\bar\Phi_1} \min_{\bar\Phi_2} \ldots \min_{\bar\Phi_{k-1}} \Big\{ U_k(\bar\Phi_1, \bar\Phi_2, \ldots, \bar\Phi_k) \\
&\quad + \min_{\bar\Phi_k} \min_{\bar\Phi_{k+1}} \ldots \min_{\bar\Phi_n} \sum_{j=2}^{k+1} [U_k(\bar\Phi_j \bar\Phi_{j+i} \ldots \bar\Phi_{j+k-1}) - U_{k-1}(\bar\Phi_j \ldots \bar\Phi_{j+k-2})] \Big\}. \qquad (19)
\end{aligned}
$$

We introduce the function

$$
\begin{aligned}
&\theta_i(\bar\Phi_{i+1}, \bar\Phi_{i+2}, \ldots, \bar\Phi_{i+k}) \\
&= \min_{\bar\Phi_1} \min_{\bar\Phi_2} \ldots \min_{\bar\Phi_i} \Big\{ U_k(\bar\Phi_1 \ldots \bar\Phi_k) \\
&\quad + \sum_{j=2}^{i} [U_k(\bar\Phi_j \ldots \bar\Phi_{j+k-1}) - U_{k-1}(\bar\Phi_j \ldots \bar\Phi_{j+k-2})] \Big\}. \qquad (20)
\end{aligned}
$$

It is not difficult to prove that

$$
\begin{aligned}
&\theta_{i+1}(\bar\Phi_{i+2} \ldots \bar\Phi_{i+k}) \\
&= \min_{\bar\Phi_1} \min_{\bar\Phi_2} \ldots \min_{\bar\Phi_{i+1}} \Big\{ U_k(\bar\Phi_1 \ldots \bar\Phi_k) \\
&\quad + \sum_{j=2}^{i+1} [U_k(\bar\Phi_j, \bar\Phi_{j+1}, \ldots, \bar\Phi_{j+k-1}) \\
&\quad - U_{k-1}(\bar\Phi_j \ldots \bar\Phi_{j+k-2})] \Big\} \\
&= \min_{\bar\Phi_1} \min_{\bar\Phi_2} \ldots \min_{\bar\Phi_{i+1}} \Big\{ U_k(\bar\Phi_1, \bar\Phi_2, \ldots, \bar\Phi_k) \\
&\quad + \sum_{j=2}^{i} [U_k(\bar\Phi_j \ldots \bar\Phi_{j+k-1}) - U_{k-1}(\bar\Phi_j \ldots \bar\Phi_{j+k-2})] \\
&\quad + U_k(\bar\Phi_{i+1} \ldots \bar\Phi_{i+k}) - U_{k-1}(\bar\Phi_{i+1} \ldots \bar\Phi_{i+k-1});
\end{aligned}
$$

i.e.,

$$
\begin{aligned}
\theta_{i+1} = \min \big[&\theta_i(\bar\Phi_{i+1} \ldots \bar\Phi_{i+k}) \\
&+ U_k(\bar\Phi_{i+1} \ldots \bar\Phi_{i+k}) - U_{k-1}(\bar\Phi_{i+1} \ldots \bar\Phi_{i+k-1}) \big]. \qquad (21)
\end{aligned}
$$

Obviously,

$$\theta_1 = \min_{\bar\Phi_1} U(\bar\Phi_1, \bar\Phi_2, \ldots, \bar\Phi_k). \qquad (22)$$

The authors propose to solve Eq. (19) by successive computations of functions θ_i.

The minimization requirement does formally limit the dimensionality of the problem of calculating any θ_i to a level which corresponds to the dimensionality of the potential function for a molecular fragment consisting of k monomer elements, but in a direct numerical implementation of each separate variational procedure this requirement is, apparently, irrelevant. An important merit of the algorithm described here is that, if the global minimum for a fragment consisting of n radicals differs only locally in the angles $\bar\Phi_1 \ldots \bar\Phi_n$ from the global minimum for a fragment consisting of n + 1 radicals, the final results of this computation will be the global minimum E.

It must be emphasized that we deal here with a situation where there is no interaction between conformations of monomer elements n and n + k through the framework or as a result of correlated changes in the conformations of the lateral radical groups in intermediate monomer elements. Already for k > 3 such effects appear improbable [3].

The described algorithm can be easily used for calculating the energy of near-field interactions with the aid of the following combinatorial scheme.

Suppose we have determined all stable conformations in relatively small fragments of a molecular chain by successive detaching from it k radicals. This procedure must then be repeated for all fragments of a molecule which contain one less monomer element. The energy of near-field interactions (up to $i \longleftrightarrow i+k-1$ interactions inclusively) in the entire molecule whose conformation is given on the potential map of each monomer element, accurately down to the local minimum, can be evaluated from (18) with the values for each U_k, U_{k-1} taken for stable oligomer conformations corresponding to one another (radical by radical) within the intersection range and within an accuracy down to the vicinity of the local minimum.

The following comment is in order here, with regard to the estimated error in calculating the near-field interactions in the approximate manner shown here. Let the internal-rotation angles

$$\bar{T}_a = \begin{pmatrix} \tau_1 \\ \cdot \\ \cdot \\ \cdot \\ \tau_k \end{pmatrix} \tag{23}$$

refer to the first of the overlapping fragments, let

$$\bar{T}_b = \begin{pmatrix} \tau_j \\ \cdot \\ \cdot \\ \cdot \\ \tau_m \end{pmatrix} \tag{24}$$

refer to the second one, and let

$$\bar{T}_{ab} = \begin{pmatrix} \tau_j \\ \cdot \\ \cdot \\ \cdot \\ \tau_k \end{pmatrix} \tag{25}$$

refer to their intersection.

At some local minimum, the energy of the first two fragments will be written as

$$\begin{gathered} U_0^a = U(\bar{T}_a^0), \\ U_0^b = U(\bar{T}_b^0). \end{gathered} \tag{26}$$

If $\bar{T}^0_{ab}$ denotes the conformation of the central fragment, close to $\bar{T}_a$ and $\bar{T}_b$, then the energy of near-field interactions will be

$$E = U_0^a + U_0^b - U(\bar{T}^0_{ab}) \tag{27}$$

accurately down to the effect of angles $\bar{T}_{ab} - \bar{T}_0$ on U_0^a and U_0^b.

It can be shown that, among any $\bar{T}^a_{ab}$, $\bar{T}^b_{ab}$ conformation pairs of intersecting fragments, the point $(\bar{T}^a_{ab} + \bar{T}^b_{ab})/2$ used for $\bar{T}^0_{ab}$ yields the smallest error. Indeed, with A denoting the matrix of second derivatives, the total error of the estimate made here is

$$\Delta E = (\bar{T}^a_{ab} - \bar{T}^0_{ab})\, A\, (\bar{T}^a_{ab} - \bar{T}^0_{ab}) + (\bar{T}^b_{ab} - \bar{T}^0_{ab})\, A\, (\bar{T}^b_{ab} - \bar{T}^0_{ab}). \tag{28}$$

Minimizing ΔE with respect to $\bar{T}^0_{ab}$, we obtain

$$\begin{gathered} (\bar{T}^a_{ab} - \bar{T}^0_{ab}) + (\bar{T}^b_{ab} - \bar{T}^0_{ab}) = 0; \\ \bar{T}^0_{ab} = \frac{1}{2}(\bar{T}^a_{ab} + \bar{T}^b_{ac}). \end{gathered} \tag{29}$$

Experience with calculations of this kind shows that satisfactory results are also obtained by an independent minimization of the intersection fragment.

A more thorough analysis of specific results obtained by this procedure will be made in subsequent articles.

LITERATURE CITED

1. S. G. Galaktionov, in: Conformation Calculations for Complex Molecules [in Russian], Minsk (1970), p. 8.

2. R. Bellman and T. Dreyfus, Application Problems in Dynamic Programing [Russian translation], Moscow (1961).
3. S. G. Galaktionov, M. B. Zamskaya, et al., Izv. Akad. Nauk BSSR, Ser. Biolog., No. 2 (1971).
4. S. G. Galaktionov, ibid., No. 3 (1970).