Notes

Double-Sum Formulas for the Hydrodynamic Properties of Macromolecular Structures

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Received May 5, 1982

The translational diffusion coefficient of a macromolecular structure composed of N identical hydrodynamic units can be calculated from the expression[1-3]

$$D_t = (k_B T / \zeta) \sum_{i=1}^{N} \sum_{j=1}^{N} [(\mathbf{H}^{-1})_{ij}]^{-1} \qquad (1)$$

$k_B T$ is the Boltzmann factor, ζ is the friction coefficient of the units, and $\mathbf{H}$ is the hydrodynamic interaction matrix, whose elements are defined as[4]

$$H_{ij} = 1 \qquad \text{for } i = j \qquad (2a)$$

$$H_{ij} = (\zeta / 6\pi\eta_0) R_{ij}^{-1} \qquad \text{for } i \neq j \qquad (2b)$$

where η_0 is the solvent viscosity and R_{ij}^{-1} is the reciprocal distance between units i and j.

Equation 1 was derived as an approximation from the general Kirkwood–Riseman theory by preaveraging the hydrodynamic interaction tensor, or Oseen tensor, over the orientations of the molecule with respect to the velocity field and, as written, is valid only for rigid structures. In the case of flexible polymer chains simple calculations can be performed by also introducing a conformational preaveraging of $\mathbf{H}$ through the substitution of R_{ij}^{-1} by the mean reciprocal average $\langle R_{ij}^{-1} \rangle$ in eq 2.

The practical use of eq 1 is limited by the numerical inversion of matrix $\mathbf{H}$. However, the translational diffusion coefficient can be calculated from the double-sum formula proposed by Kirkwood in 1953[5]

$$D_{t,K} = (k_B T / N^2 \zeta) \sum_{i=1}^{N} \sum_{j=1}^{N} H_{ij} \qquad (3)$$

Equation 3 comes from the approximate solution of the hydrodynamic interaction equations in terms of a truncated series expansion (see ref 4, section 32) and is independent of the form (original or preaveraged) used for the interaction tensor.

Other hydrodynamic properties can be also obtained from the Kirkwood–Riseman theory. Thus, if orientational preaveraging is introduced, the theory yields the following formula for the intrinsic viscosity of a rigid structure:[2,6,7]

$$[\eta] = (N_A \zeta / 6 M \eta_0) \sum_{i=1}^{N} \sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij} B_{ij} \qquad (4)$$

In eq 4 N_A is the Avogadro number, M is the molecular weight, and B_{ij} is an element of matrix $\mathbf{B}$, defined as

$$B_{ij} = \mathbf{R}_i \cdot \mathbf{R}_j \qquad (5)$$

where $\mathbf{R}_i$ and $\mathbf{R}_j$ are the positions of units i and j referred to some hydrodynamic center,[6] which coincides with the center of masses in the case of highly symmetric, rigid particles. In most cases the hydrodynamic center can be

substituted by the center of masses as a reasonable approximation. For flexible chains a conformational preaveraging for $\mathbf{H}$ and $\mathbf{B}$ should be introduced through the mean quantities $\langle R_{ij}^{-1} \rangle$ and $\langle \mathbf{R}_i \cdot \mathbf{R}_j \rangle$.

A double-sum formula for $[\eta]$ was derived 12 years ago by Tsuda,[9-11] namely, eq 21 of ref 10 (in fact, using the "shell-model" idea of Bloomfield et al.,[12] Tsuda obtained a second formula, which will not be considered here owing to its complexity). Although Tsuda's treatment contained approximations, the preaveraging of the interaction tensor was avoided. Garcia de la Torre and Bloomfield[13] have presented an alternate derivation of Tsuda's formula using a series-expansion approximation equivalent to that leading to eq 3 from eq 1 for the diffusion coefficient.

While Tsuda's formula does not require the inversion of matrix $\mathbf{H}$, it still has a complex form, which complicates the numerical calculations for macromolecular models and makes it very difficult to arrive at limiting analytical expressions. Consequently, a further simplification of Tsuda's formula may be useful for these purposes. Such a simplification is performed following Tsuda's procedure and introducing the additional approximation of taking the orientationally preaveraged Oseen tensor

$$\langle \mathbf{T}_{ij} \rangle = H_{ij} \mathbf{I} \qquad (6)$$

instead of the nonpreaveraged tensor used by Tsuda. $\mathbf{I}$ in eq 6 is the 3×3 unity matrix. With this approximation, eq 21 of ref 10 reduces to

$$[\eta]_{app} = (N_A \zeta / 6 M \eta_0) [\sum_{i=1}^{N} B_{ii}]^2 [\sum_{i=1}^{N} \sum_{j=1}^{N} H_{ij} B_{ij}]^{-1} \qquad (7)$$

We are currently exploring the performance of the double-sum formulas, eq 3 and 7, and the more rigorous preaveraged formulas, eq 1 and 4, with respect to the values obtained with still more rigorous nonpreaveraged expressions. We intend to publish numerical results on this matter in the near future. In the course of this investigation, extended to many different molecular structures, we have noticed that eq 3 and 7 are equivalent to eq 1 and 4 for some symmetric arrangements of units. In this note we will show these equivalences for several simple cases.

Defining $\mathbf{R}$ as the matrix whose elements are the distances between the different pairs of units, R_{ij}, we will consider structures whose units are disposed so that all the rows in $\mathbf{R}$ have the same elements, arranged in different orders. It happens so, for instance, when the units are placed at the vertices of regular polygons or polyhedra. As a consequence of such a situation it follows that

$$\sum_{j=1}^{N} R_{ij}^{s} = \sum_{j=1}^{N} R_{kj}^{s} \qquad i \neq k \qquad (8)$$

for any arbitrary s. Equation 8 with $s = -1$ and $s = 2$, together with the definitions of $\mathbf{H}$ and $\mathbf{B}$, eq 2 and 5, lead to

$$\sum_{j=1}^{N} H_{ij} = \sum_{j=1}^{N} H_{kj} \qquad i \neq k \qquad (9a)$$

$$\sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij} = \sum_{j=1}^{N} (\mathbf{H}^{-1})_{kj} \qquad i \neq k \qquad (9b)$$

and

$$\sum_{j=1}^{N} H_{ij}B_{ij} = \sum_{j=1}^{N} H_{kj}B_{kj} \qquad i \neq k \qquad (10a)$$

$$\sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij}B_{ij} = \sum_{j=1}^{N} (\mathbf{H}^{-1})_{kj}B_{kj} \qquad i \neq k \qquad (10b)$$

From eq 1, 3, and 9 we get

$$D_{t,K}/D_t = (\sum_{j=1}^{N} H_{ij})[\sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij}] \qquad (11)$$

for any i. Since matrix $\mathbf{H}$ is symmetric

$$\sum_{i=1}^{N}(\sum_{j=1}^{N} H_{ij})[\sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij}] = \sum_{j=1}^{N} \sum_{l=1}^{N} \sum_{i=1}^{N} H_{ji}(\mathbf{H}^{-1})_{il} \qquad (12)$$

and, consequently, for structures satisfying eq 8

$$D_{t,K}/D_t = (1/N)\sum_{j=1}^{N} \sum_{l=1}^{N} \delta_{jl} = 1 \qquad (13)$$

In order to show easily the equivalence between eq 4 and 7, we should add some other conditions. Thus we will be restricted to structures for which

$$|\mathbf{R}_i| = |\mathbf{R}_k| \qquad i \neq k \qquad (14)$$

Then all the elements B_{ii} are identical. Taking also into account eq 4, 7, and 10 and noticing that $B_{ij} = B_{ii} \cos \alpha_{ij}$, where α_{ij} is the angle defined by vectors $\mathbf{R}_i$ and $\mathbf{R}_j$, we find

$$[\eta]/[\eta]_{app} = \sum_{j=1}^{N} \sum_{l=1}^{N} H_{ij}(\mathbf{H}^{-1})_{il} \cos \alpha_{ij} \cos \alpha_{il} \qquad (15)$$

or

$$[\eta]/[\eta]_{app} = (1/2)\sum_{j=1}^{N} \sum_{l=1}^{N} \{[\cos(\alpha_{ij} + \alpha_{il}) + \cos(\alpha_{ij} - \alpha_{il})]H_{ij}(\mathbf{H}^{-1})_{il}\} \qquad (16)$$

Many symmetrical structures have C_2 symmetry axes defined by the center of masses and each one of the hydrodynamic units. In all these cases

$$\sum_{j=1}^{N} H_{ij} \sin \alpha_{ij} = 0$$

$$\sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij} \sin \alpha_{ij} = 0$$

and

$$\sum_{j=1}^{N} \sum_{l=1}^{N} H_{ij}(\mathbf{H}^{-1})_{il} \sin \alpha_{ij} \sin \alpha_{il} = 0 \qquad (17)$$

Equations 16 and 17 lead to

$$[\eta]/[\eta]_{app} = \sum_{j=1}^{N} \sum_{l=1}^{N} \cos(\alpha_{ij} - \alpha_{il})H_{ij}(\mathbf{H}^{-1})_{il} \qquad (18)$$

For planar structures satisfying eq 8, 14, and 17 the simplification $\alpha_{ij} - \alpha_{il} = \alpha_{jl}$ gives

$$[\eta]/[\eta]_{app} = (1/N)\sum_{j=1}^{N} \sum_{l=1}^{N} \cos \alpha_{jl} \sum_{i=1}^{N} H_{ij}(\mathbf{H}^{-1})_{il} = 1 \qquad (19)$$

Equation 19 is applicable to structures formed by units placed at the vertices of regular polygons.

Some structures satisfying eq 8, i.e., with $D_{t,K} = D_t$, do not yield $[\eta]/[\eta]_{app} = 1$. This is the case of a rectangular structure (for which eq 17 is not valid) or a nonplanar flexible ring composed by N units joined through statistical segments. Another interesting instance is the straight rod with large N. In this structure eq 8 holds asymptotically

while the two formulas for the intrinsic viscosity are not equivalent.

Nevertheless, the equivalence between eq 4 and 7 applies for some nonplanar structures of higher symmetry. Thus in the very simple case of four units disposed at the vertices of a tetrahedron the elements of matrices $\mathbf{H}$ and $\mathbf{H}^{-1}$ have only two different values since off-diagonal terms are all identical. Then

$$\sum_{j=1}^{N} H_{ij}(\mathbf{H}^{-1})_{ij} = H_{ii}(\mathbf{H}^{-1})_{ii} + 3H_{ik}(\mathbf{H}^{-1})_{ik} = 1 \qquad (20)$$

and

$$\sum_{j=1}^{N} H_{ij}(\mathbf{H}^{-1})_{kj} = H_{ii}(\mathbf{H}^{-1})_{ik} + H_{ik}(\mathbf{H}^{-1})_{ii} + 2H_{ik}(\mathbf{H}^{-1})_{ik} = 0 \qquad (21)$$

for any $k \neq i$. On the other hand, since $\cos \alpha_{ik} = -^1/_3$ for $i \neq k$

$$\sum_{j=1}^{N} \sum_{l=1}^{N} H_{ij} \cos \alpha_{ij}(\mathbf{H}^{-1})_{il} \cos \alpha_{il} = H_{ii}(\mathbf{H}^{-1})_{ii} - H_{ii}(\mathbf{H}^{-1})_{ik} - H_{ik}(\mathbf{H}^{-1})_{ii} + H_{ik}(\mathbf{H}^{-1})_{ik} \qquad (22)$$

Subtracting eq 21 from eq 20, comparing the result with eq 22, and taking into account eq 15 lead to $[\eta]/[\eta]_{app} = 1$. Similar, though considerably more elaborate demonstrations could be worked out for other regular polyhedral structures.

References and Notes

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Alternating Copolymerization of 7,7,8,8-Tetracyanoquinodimethane with Methyl Methacrylate in Acetonitrile

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In previous papers, we reported spontaneous alternating copolymerizations of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in acetonitrile with donor monomers such as styrene (St), 2-chloroethyl vinyl ether (CEVE), phenyl vinyl ether (PhVE), and vinyl acetate (VAc),[1,2] indicating that TCNQ acts as a powerful electron-acceptor monomer. Moreover, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄),[3] a much stronger electron acceptor than TCNQ, was found to copolymerize in an alternating