The order of the strength of counterion binding to these polycations was similar to the order for the Hofmeister series, acetate being the weakest and SCN$^-$ being the strongest binding ions.

The unperturbed dimensions of the vinylimidazole-containing polymers vary only slightly with the nature of solvent or quaternary side group on the imidazole site but vary greatly with the counterion. The characteristic ratio is the largest ($C_\infty = 28$) when acetate or propionate is the counterion. In the presence of a stronger binding counterion, such as chloride, the characteristic ratio decreases to 15–18.

Both viscosity and light scattering data suggest that these polymers are coillike in methanol or aqueous salt solutions. The persistence lengths, calculated on the basis of the wormlike-chain model using the Yamakawa–Fujii scheme, are q = 22–23 Å for PVI and q = 20 Å for QPVI in methanol/0.01 M TBABr.

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Symmetry Criteria in the Theory of Chain Polymer Hydrodynamics†

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ABSTRACT: The assumption that the motion of flexible-chain polymers can be modeled as that of a rigid body in certain stationary flows is examined. An explicit formula is derived for the center-of-mass velocity in sedimentary flow, based on several assumptions in the literature: (1) rigid-body motion, (2) coincidence of the axis of rotation with the direction of flow, and (3) isotropy of the unperturbed solution. An examination of the velocity formula shows that it fails to satisfy necessary symmetry requirements except in the special case where the angular velocity vanishes for all conformations. Since this condition on angular velocity will not be met unless hydrodynamic interaction is preaveraged, the set of assumptions is concluded to be generally inconsistent with the equations of diffusive motion for chain or other polymers. Quantitative estimates of the error are reached in an accompanying paper on the dynamical simulation of chains with hydrodynamic interaction.

I. Introduction

The assumption that flexible-chain polymers move as rigid bodies in sedimentary or simple shear flow has a long history. This examination of the hypothesis was stimulated by the recent work of Zimm,[1] who used the hypothesis to derived algorithms for the Monte Carlo calculation of the sedimentation constant and intrinsic viscosity of chain polymers. The purpose of his work was to eliminate the approximation of preaveraged hydrodynamic interaction (HI) in the calculation of these transport coefficients. Unfortunately, the hypothesis of rigid-body motion is here found to be inexact for flexible chains with fluctuating HI; with preaveraged HI the hypothesis is correct. This work can supply no estimates of the error that results from the hypothesis, but an accompanying dynamical simulation[2] indicates significant errors for sedimentary flow.

Our work is based on the diffusion equation for chain polymer motion and is unrestricted in the choice of chain potential. Any conventional HI is also allowed. We do assume that the HI interaction tensor is a function of chain coordinates and not of time. Thus solvent inertia as well as chain inertia is suppressed. Our intention has been to follow the assumptions used by Zimm, to obtain an explicit formula rather than an algorithm for the sedimentation constant, and to strengthen the appeal to symmetry. Examination of the explicit formula shows the contradictions inherent in the rigid-body hypothesis or, more precisely, in one particular form of that hypothesis: that the axis of rigid-body rotation coincides with the symmetry axis of the external force. This assumption is found to be defective even for truly rigid bodies.

The proper formulas for the sedimentation constant and intrinsic viscosity of a bead model without HI go back at least as far as Kramers.[3] Inclusion of HI makes for considerable difficulty. If the HI is preaveraged, formulas correct for any chain potential are available. For the in-

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trinsic viscosity in this approximation there is the formula of Gotlib and Svetlov[4,5] and for the sedimentation or diffusion constant several formulas due to Kirkwood.[2,6]

In section II the diffusion equations are reviewed and summarized. A transformation to internal and center-of-mass coordinates[5,7] is carried out to facilitate imposition of the explicit constraint that the center of mass is uniformly distributed. We take this to be an experimental constraint, but further study of the experiments is warranted. (The essence of the constraint is not the focus on the center of mass; given a translational invariance of the system, the singlet distribution of any bead position, or any linear combination of bead positions, would also be uniformly distributed. The problem is that typical experiments do not deal with uniform systems in the steady state but with nonuniform, time-dependent systems that may exhibit different aspects of the coupling between internal and translational degrees of freedom.)

We verify in section II that rigid-body motion of the kind assumed by Zimm gives *a* solution to the diffusion equation. In section III the sedimentation problem is considered, and an explicit formula for the sedimentation coefficient is derived. It is examined from the standpoint of symmetry requirements in section IV and rejected on that basis.

II. Equations of Motion

A. Basic Equations. The basic diffusion equations for polymer motion will be summarized in a form[6-8] suitable for the subsequent analysis.

The total force on the ith bead, $i = 0, ..., M$, is compounded of a frictional force $-\mathbf{F}_i$, an entropic force $-k_BT\nabla_i \ln \Psi$, an intramolecular force $-\nabla_i U$, and an external force $-\nabla_i X$. The sum of these forces is put equal to zero; i.e., chain inertia is neglected.

$$-\mathbf{F}_i - \nabla_i(k_BT \ln \Psi + U + X) = 0 \tag{2.1}$$

Ψ is the probability density for the bead position vectors $\mathbf{R}_i$. $\mathbf{F}_i$ is the frictional force that bead i exerts on the solvent:

$$\mathbf{F}_i = \beta_i(\mathbf{V}_i - \mathbf{V}_i') \tag{2.2}$$

where β_i is a friction constant and $\mathbf{V}_i'$ is the perturbed solvent velocity.

$$\mathbf{V}_i' = \mathbf{V}_i^0 + \sum_{j=0}^{M} \boldsymbol{T}_{ij}\cdot\mathbf{F}_j \qquad \boldsymbol{T}_{ii} = 0 \tag{2.3}$$

$\mathbf{V}_i^0$ is the unperturbed solvent velocity evaluated, like $\mathbf{V}_i'$, at the location of i, and $\boldsymbol{T}_{ij}$ is the HI tensor. $\boldsymbol{T}_{ij}$ may be given by the Oseen–Stokes form, or some modification of it, e.g., a smoothed form that eliminates the singularity.[2] $\boldsymbol{T}_{ij}$ is presumed to depend only on the relative coordinate vector $\mathbf{R}_{ij}$ from bead i to bead j. From eq 2.2 and 2.3 it follows that

$$\begin{aligned}\mathbf{V}_i &= \mathbf{V}_i' + \beta_i^{-1}\mathbf{F}_i \\ &= \mathbf{V}_i^0 + \sum_{j=0}^{M} \boldsymbol{H}_{ij}\cdot\mathbf{F}_j \end{aligned} \tag{2.4}$$

where

$$\boldsymbol{H}_{ij} \equiv \boldsymbol{T}_{ij} + \beta_i^{-1}\delta_{ij}\boldsymbol{1} \tag{2.5}$$

For brevity we adopt a matrix notation for bead indices; e.g., $\mathbf{V}$ is a column matrix with elements $\mathbf{V}_i$. Equation 2.4 becomes

$$\mathbf{V} = \mathbf{V}^0 + \boldsymbol{H}\cdot\mathbf{F} \tag{2.6}$$

and eq 2.1 becomes

$$\mathbf{F} = -\nabla(k_BT \ln \Psi + U + X) \tag{2.7}$$

The ith element of ∇ is $\partial/\partial\mathbf{R}_i$.

The conservation equation for the probability density Ψ is

$$\partial\Psi/\partial t + \sum_{i=0}^{M} \nabla_i\cdot(\mathbf{V}_i\Psi) = 0 \tag{2.8}$$

or

$$\partial\Psi/\partial t + \nabla^{\mathrm{T}}\cdot(\mathbf{V}\Psi) = 0 \tag{2.9}$$

The transpose symbol, superscript T, is used in conformity with matrix notation for the inner product of a row matrix ∇^{T} and a column matrix $\mathbf{V}\Psi$. Ψ is factored into an equilibrium part Ψ_e and a correction Φ:

$$\Psi = \Psi_e\Phi \tag{2.10}$$

Since

$$-k_BT\nabla \ln \Psi_e = \nabla U$$

eq 2.7 becomes

$$\mathbf{F} = -\nabla(k_BT \ln \Phi + X) \tag{2.11}$$

The analysis to follow is based on eq 2.6, 2.9, and 2.11. First a transformation of coordinates from the set $\mathbf{R}_i$ to center-of-mass and internal coordinates is made.

B. Change of Coordinates. The ith bond vector is

$$\mathbf{b}_i = \mathbf{R}_i - \mathbf{R}_{i-1} \qquad i = 1, ..., M \tag{2.12}$$

This set of M internal vector coordinates is supplemented with the center-of-mass coordinate $\mathbf{b}_0$ to make up a complete set:

$$\mathbf{b}_0 = (M + 1)^{-1}\sum_{i=0}^{M}\mathbf{R}_i \tag{2.13}$$

Since the Jacobian of the transformation from $\mathbf{R}$'s to $\mathbf{b}$'s is a constant, the symbol Ψ may be retained for the probability density of $\mathbf{b}$'s.

A corresponding transformation of the ∇_i operator is

$$\nabla_i = \sum_{k=0}^{M}(\nabla_i\mathbf{b}_k)\cdot\nabla_i{}^b \qquad \nabla_i{}^b \equiv \partial/\partial\mathbf{b}_i \tag{2.14}$$

Equations 2.12 and 2.14 give

$$\nabla_i = \sum_{k=0}^{M} A_{ik}\nabla_k{}^b \tag{2.15}$$

where

$$\begin{aligned} A_{ik} &\equiv \delta_{ik} - \delta_{i,k-1} \qquad k = 1, ..., M \\ A_{i0} &\equiv (M + 1)^{-1} \end{aligned} \tag{2.16}$$

and $i = 0, ..., M$. In matrix notation eq 2.15 is

$$\nabla = A\nabla^b \tag{2.17}$$

Likewise, eq 2.12 and 2.13 are

$$\mathbf{b} = A^{\mathrm{T}}\mathbf{R} \tag{2.18}$$

The basic eq 2.6, 2.9, and 2.11 may now be expressed in the new coordinates. The velocities $\mathbf{V}_i$ transform to bond velocities

$$\mathbf{v}_i = \mathbf{V}_i - \mathbf{V}_{i-1} \qquad i = 1, ..., M$$

and a center-or-mass velocity $\mathbf{v}_0$ in the same way that the $\mathbf{R}$'s transform to $\mathbf{b}$'s. So eq 2.6 gives

$$\mathbf{v} = A^{\mathrm{T}}\mathbf{V} = \mathbf{v}^0 + A^{\mathrm{T}}\boldsymbol{H}\cdot\mathbf{F} \tag{2.19}$$

The frictional force $\mathbf{F}$ is given by eq 2.11 as the gradient of scalar potentials, so eq 2.11 and 2.17 give

$$\mathbf{F} = A\mathbf{f} \tag{2.20}$$

where

$$\mathbf{f} = -\nabla^b(k_\mathrm{B}T \ln \Phi + X) \tag{2.21}$$

Therefore eq 2.19 becomes

$$\mathbf{v} = \mathbf{v}^0 + \hat{B}\cdot\mathbf{f} \tag{2.22}$$

where

$$\hat{B} \equiv A^\mathrm{T}\boldsymbol{H}A \tag{2.23}$$

The elements $\hat{B}_{ij}$ coincide for $i, j > 0$ with the $\boldsymbol{B}_{ij}$ used in earlier work.[5] But $\hat{B}$ is extended with a zeroth row and column that give the diffusional properties of the center of mass and its coupling with internal coordinates. The symbol B (the old $\boldsymbol{B}$), will be used for the matrix $\hat{B}$ with the zeroth row and column deleted. The distinction is important mainly for those formulas involving the inverse B^{-1}. The inverse of $\hat{B}$ will not be required.

The conservation eq 2.9 in the new coordinates is

$$\partial\Psi/\partial t + \nabla^{b\mathrm{T}}\cdot(A^\mathrm{T}\mathbf{V}\Psi) = \partial\Psi/\partial t + \nabla^{b\mathrm{T}}\cdot(\mathbf{v}\Psi) = 0 \tag{2.24}$$

C. Steady-State Sedimentation. We suppose that the system is very large and that the polymer concentration is uniform in the equilibrium state. An external force, the same for all beads, is turned on, and we assume that a large central portion of the system remains uniform in polymer concentration. That is, we assume that concentration heterogeneities develop on a very slow time scale in the central portion, and on that same time scale polymer molecules in the center rapidly acquire a quasi-steady-state distribution of conformations and velocities. We take the external force to be small and consider only first-order deviations from equilibrium. Under these conditions eq 2.24 becomes

$$\nabla^{b\mathrm{T}}\cdot(\mathbf{v}\Psi_\mathrm{e}) = 0 \tag{2.25}$$

Or more explicitly

$$\sum_{i=0}^{M}\nabla_i{}^b\cdot(\mathbf{v}_i\Psi_\mathrm{e}) = \sum_{i=0}^{M}(\mathbf{v}_i\cdot\nabla_i{}^b\Psi_\mathrm{e} + \Psi_\mathrm{e}\nabla_i{}^b\cdot\mathbf{v}_i) = 0 \tag{2.26}$$

A class of formal and partial solutions to eq 2.26 may readily be identified, namely, solutions corresponding to uniform rigid-body motion. Our intent is merely to demonstrate that the proposed solutions satisfy eq 2.26; the solutions will be found inadequate on other grounds.

The proposed solutions are characterized by a center-of-mass velocity $\mathbf{v}_0$ that is independent of center-of-mass position $\mathbf{b}_0$, and by rotational motion

$$\mathbf{v}_i = \mathbf{w} \times \mathbf{b}_i \qquad i > 0$$

$$\mathbf{w} = w\mathbf{e}_z \tag{2.27}$$

w is the magnitude and $\mathbf{e}_z$ is a unit vector in the direction of the angular velocity. $\mathbf{e}_z$ is presumed to coincide with the direction of the external force. w and $\mathbf{v}_0$ may depend on polymer conformation but not on $\mathbf{b}_0$. $\mathbf{e}_z$ is completely independent of polymer coordinates. These conditions may be contrasted with what is required by linearity in the external force, say $\mathbf{E}_0 = -\nabla_i X$:

$$\mathbf{w} = \boldsymbol{W}\cdot\mathbf{E}_0$$

where $\boldsymbol{W}$ is a dyadic determined by the $\mathbf{b}_i$, $i > 0$. For the assumed motion to be correct, we will have to find not only that $\boldsymbol{W}$ is proportional to the unit dyadic but that the proportionality constant w is completely independent of the direction of $\mathbf{E}_0$.

With eq 2.27, the first set of terms on the right-hand side of eq 2.26 vanishes because Ψ_e is invariant to rigid-body translation or rotation of the chain coordinates. This is evident for translation, $i = 0$. For rotation, $i > 0$, the sum

$$\sum_{i>0}\mathbf{v}_i\cdot\nabla_i{}^b\Psi_\mathrm{e} = \mathbf{w}\cdot\sum_{i>0}\mathbf{b}_i \times \nabla_i{}^b\Psi_\mathrm{e} \tag{2.28}$$

is w times $\partial\Psi_\mathrm{e}/\partial\varphi$, where φ is the angle of rotation about $\mathbf{e}_z$. This derivative vanishes because of the rotational isotropy of the unperturbed solution (this isotropy characterizes the orientation of a molecular frame with respect to a laboratory frame; the molecule itself may well be anisotropic with respect to the molecular frame). The second set of terms on the right-hand side of (2.26) vanishes because $\mathbf{v}_0$ is independent of $\mathbf{b}_0$ and w is independent of φ:

$$\sum_{i>0}\nabla_i{}^b\cdot\mathbf{v}_i = \sum_{i>0}\mathbf{b}_i\cdot(\nabla_i{}^b \times \mathbf{w}) = \mathbf{e}_z\cdot\sum_{i>0}\mathbf{b}_i \times \nabla_i{}^b w = 0 \tag{2.29}$$

It follows that motion of the indicated kind provides *a* solution to eq 2.26. Since the particular solutions will have to be rejected, other solutions must exist.

Equations 2.21 and 2.22 may now be formally solved by

$$k_\mathrm{B}T\hat{B}\cdot\nabla^b\Phi = \mathbf{v}^0 - \hat{B}\cdot\nabla^b X - \mathbf{v} \tag{2.30}$$

The solvent velocity field $\mathbf{v}^0$ will be suppressed in the following discussion. The polymer velocities $\mathbf{v}$ consist of a translational motion $\mathbf{v}_0$ and rotational motion $\mathbf{v}_i$ for $i > 0$. The remainder of the problem for sedimentary flow consists in the calculation of $\mathbf{v}_0$ from eq 2.30 and supplementary information about symmetry that permits elimination of $\nabla^b\Phi$ from the equations.

We remark that eq 2.30 is an identity that relates the bead velocities $\mathbf{v}$ to the perturbation in Φ. The new information is generated by the rigid-body assumptions about $\mathbf{v}$. These assumptions have two results: (1) the number of unknowns in $\mathbf{v}$ is much reduced and (2) the conservation eq 2.26 is satisfied.

III. Sedimentary Flow

In sedimentary flow caused by the weak force $\mathbf{E}_0$, Φ must be a scalar (because $\Psi_\mathrm{e}\Phi$ is a probability density) and linear in $\mathbf{E}_0$:

$$\Phi = 1 + (\sum_{i>0} I_i\mathbf{b}_i)\cdot\mathbf{E}_0 \tag{3.1}$$

The coefficients I_i may be functions of conformation, e.g., they may depend on $\mathbf{b}_k\cdot\mathbf{b}_l$, but are invariant with respect to rigid-body translations and rotations of the molecule. It follows that a rigid-body rotation of the molecule around $\mathbf{E}_0$, which does not affect the $\mathbf{b}_i\cdot\mathbf{E}_0$, leaves Φ invariant. That is

$$\partial\Phi/\partial\varphi \equiv \mathbf{e}_z\cdot\sum_{i>0}\mathbf{b}_i \times \nabla_i{}^b\Phi = 0 \tag{3.2}$$

So we proceed to solve eq 2.30 for $\nabla^b\Phi$ and substitute into (3.2) to get equations for the $\mathbf{v}_i$.

We write eq 2.30 first for the translational component and then for the internal coordinates:

$$k_\mathrm{B}T\sum_{j>0}\hat{B}_{0j}\cdot\nabla_j{}^b\Phi = \hat{B}_{00}\cdot\mathbf{E}_0 - \mathbf{v}_0 \tag{3.3}$$

$$k_\mathrm{B}T\sum_{j>0}B_{ij}\cdot\nabla_j{}^b\Phi = \hat{B}_{i0}\cdot\mathbf{E}_0 - \mathbf{v}_i \qquad i > 0 \tag{3.4}$$

Notice that the truncated $M \times M$ matrix (of dyadics) occurs in eq 3.4. In each equation $\nabla_0{}^b\Phi$ has been suppressed because Φ is independent of $\mathbf{b}_0$. Equations 3.2 and 3.4 give

$$\partial\Phi/\partial\varphi = \mathbf{e}_z\cdot\sum_i\sum_{k>0}\mathbf{b}_i \times (B^{-1})_{ik}\cdot(\hat{B}_{k0}\cdot\mathbf{E}_0 - \mathbf{v}_k) = 0 \tag{3.5}$$

With the assumed rotational form for the velocities $\mathbf{v}_i$, $i > 0$, given by eq 2.27, eq 3.5 is readily solved for w, the angular speed of rotation:

$$w = \frac{-\mathbf{e}_z\cdot[\sum_i \sum_{k>0} \mathbf{b}_i \times (B^{-1})_{ik}\cdot\hat{B}_{k0}]\cdot\mathbf{e}_z}{\mathbf{e}_z\cdot[\sum_i \sum_{k>0} \mathbf{b}_i \times (B^{-1})_{ik} \times \mathbf{b}_k]\cdot\mathbf{e}_z} E_0 \equiv w_0 E_0 \quad (3.6)$$

Since the rotational velocities are now known, eq 3.4 provides

$$k_B T \nabla_i^b \Phi = \sum_{k>0} (B^{-1})_{ik}\cdot[\hat{B}_{k0}\cdot\mathbf{E}_0 - w_0(\mathbf{E}_0 \times \mathbf{b}_k)] \quad (3.7)$$

for all $i > 0$. This equation together with (3.3) permits calculation of $\mathbf{v}_0$:

$$v_0^z/E_0 = \mathbf{e}_z\cdot\hat{B}_{00}\cdot\mathbf{e}_z - \sum_j \sum_{k>0} \mathbf{e}_z\cdot\hat{B}_{0j}\cdot(B^{-1})_{jk}\cdot[\hat{B}_{k0}\cdot\mathbf{e}_z - w_0(\mathbf{e}_z \times \mathbf{b}_k)] \quad (3.8)$$

The equilibrium average of eq 3.8 gives the sedimentation coefficient. The first term on the right-hand side gives the simplest Kirkwood approximation

$$\begin{aligned}\langle\hat{B}_{00}\rangle_e &= \boldsymbol{I}(\tfrac{1}{3}\,\mathrm{tr}\,\langle\hat{B}_{00}\rangle_e) \\ &= \boldsymbol{I}(M+1)^{-2}\sum_k \sum_{l\geq 0}[\delta_{kl}\beta_k^{-1} + (\tfrac{1}{3})\langle\mathrm{tr}\,\boldsymbol{T}_{kl}\rangle_e]\end{aligned} \quad (3.9)$$

and the other terms provide corrections that are discussed in the next section.

IV. Discussion

We should first observe that one of our symmetry criteria, that Φ is invariant to angular rotation around an axis oriented parallel to the direction of the sedimenting force, is equivalent to Zimm's requirement[1] that the torque around that axis vanishes. This equivalence follows from the relationship between the gradient of Φ and the frictional force given in eq 2.11. Indeed, all we have accomplished is the derivation of an explicit formal solution to Zimm's algorithm. Our remaining task is the application of another symmetry criterion that the formal solution fails to satisfy.

We have already alluded to the second symmetry requirement below eq 2.27. In a linear-response theory the angular velocity has to be linear in the external force $\mathbf{E}_0$. The coefficient matrix must be independent of the direction as well as the magnitude of the external force. But we have assumed the coefficient matrix to be a scalar, w_0, times the unit matrix and then found in eq 3.6 that w_0 depends on the direction $\mathbf{e}_z$ of the external force. We have to conclude that the algorithm fails to satisfy symmetry criteria that must be imposed on an isotropic system and that it is probably invalid even for most rigid bodies. One suspects this because the hypothesis that the coefficient matrix $\boldsymbol{W}$ is proportional to the unit matrix implies that the proportionality constant w_0 is a pseudoscalar. This follows from the requirement that the angular velocity is an axial or pseudovector; see eq 2.27 and below. So we have the anomaly of a body with angular velocity invariant to rotation of the body, but which changes sign when the coordinates of the body are inverted. There will not be many types of such bodies. The spherical body, with vanishing angular velocity, is one such. Possibly the isotropic helicoid[9] is another.

Wilemski and Tanaka[10] have recently discussed the intrinsic viscosity on the basis of closely related considerations. The assumption of constant rigid-body motion around the external symmetry axis is concluded to be correct for certain rigid bodies of high symmetry (rod, polygon, dumbbell) but is generally approximate.

It is probable that chain polymers, being nearly spherical, are treated nearly correctly by the algorithm. However, other means will have to be used for such quantitative purposes as estimates of the error in Kirkwood's formula for the sedimentation coefficient of chain polymers. Our preliminary work in the following paper[2] indicates that the errors in Kirkwood's formula are quite a bit smaller than Zimm's calculations[1] indicate. But the limited chain size and limited number of trajectories in our work precludes a confident statement.

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