Eur Biophys J (1998) 27: 549–557

ARTICLE

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Intrinsic viscosity and rotational diffusion of bead models for rigid macromolecules and bioparticles

Received: 15 October 1997 / Accepted: 19 February 1998

Abstract The conventional Kirkwood-Riseman (K-R) treatment of the intrinsic viscosity of macromolecular bead models shows a deficiency when it is applied to models with few beads, whose sizes are not much smaller than of the modelled particle. We present a complete derivation of the intrinsic viscosity up to first order in interbead distances (Oseen-type hydrodynamic interaction), finding that a term that belongs to the zeroth-order contribution is missing in the usual description. This term is simply proportional to the total volume of the bead model. The nature of this correction for viscosity is similar to a previously described correction for rotational coefficients. We discuss the performance of these corrections for various simple models, including ellipsoids as well as oligomeric structures in rodlike, chainlike and polyhedral conformations.

Key words Intrinsic viscosity · Rotational diffusion · Rigid macromolecules · Friction tensors · Hydrodynamic theory

1 Introduction

1.1 Antecedents

Among the various hydrodynamic properties of rigid macromolecules in solution (or rigid particles in dilute suspension), the intrinsic viscosity, [η], offers an excellent balance between sensitivity to size and shape and ease of determination. A recent review by Harding (1998) summarizes many years of measurement and applications of [η]. It is noteworthy that one of the main drawbacks of [η] measurement, namely the need to work at a moderately high concentration, is being removed by modern instrumentation (Haney 1985).

The Kirkwood-Riseman theory of hydrodynamic properties, including intrinsic viscosity, of rodlike and flexible-chain macromolecules modelled as strings of spherical beads (Kirkwood and Riseman 1948; Riseman and Kirkwood 1950; Yamakawa 1971), treated the frictional forces as vectors acting at the bead centers, while they are in fact distributed over the spherical surfaces. Thus, for a shear flow with fluid velocity $v_x^o = \dot{\gamma} y$ at a point with coordinates (x, y, z), the intrinsic viscosity of the macromolecule is calculated as

$$[\eta] = -\frac{N_A}{M\eta_0\dot{\gamma}} \sum_{i=1}^{N} \left\langle y_i F_i^x \right\rangle \tag{1}$$

where N_A is Avogadro's number, M is the molecular weight of the solute, η_0 is the viscosity of the solvent, F_i^x is the x component of the frictional force at the center of bead i with coordinate y_i. The sum is extended to the N elements composing the bead model, and the angular brackets denote averaging over all the possible orientations of the particle with respect to the velocity field.

The problem of predicting hydrodynamic properties of rigid macromolecules or particles of arbitrarily complex shape was attacked in the pioneering work of Bloomfield et al. (1967 a, b), as an extension of the Kirkwood-Riseman theory. Later, improvements in the description of hydrodynamic interaction and in computational aspects were introduced by García de la Torre and Bloomfield (GT-B) (1977 a, b; 1978), with particular application to the viscosity (García de la Torre and Bloomfield 1978). The GT-B expression for [η] is

$$[\eta]^{uncorr} = \frac{N_A}{M\eta_0} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\frac{1}{15} \sum_{\alpha} r_i^\alpha C_{ij}^{\alpha\alpha} r_j^\alpha + \frac{1}{20} \sum_{\alpha \neq} \sum_{\beta} r_i^\alpha C_{ij}^{\beta\alpha} r_j^\beta - \frac{1}{30} \sum_{\alpha \neq} \sum_{\beta} r_i^\alpha C_{ij}^{\alpha\beta} r_j^\beta + \frac{1}{20} \sum_{\alpha \neq} \sum_{\beta} r_i^\alpha C_{ij}^{\beta\beta} r_j^\beta \right) \tag{2}$$

In Eq. (2), the $\mathbf{r}_i$'s vectors are the position vectors of bead i with respect to a particular hydrodynamic centre (the

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viscosity centre) which, for centrosymmetric particles coincide with the symmetry. The $\mathbf{C}_{ij}$ tensors, with components $C_{ij}^{\alpha\beta}\,(\alpha, \beta = x, y, z)$, are the 3×3 ij-blocks of a $3N \times 3N$ supermatrix, $\mathcal{C} = \mathcal{B}^{-1}$, where the $3N \times 3N$ supermatrix $\mathcal{B}$ is composed by 3×3 blocks $\mathbf{B}_{ij} = \mathbf{T}_{ij}$ if $i \neq j$ and $\mathbf{B}_{ii} = (1/\zeta_i)\mathbf{I}$, where $\zeta_i = 6\pi\eta_0\sigma_i$ is the Stokes' law friction coefficient of bead i, with radius σ_i. Both vectors $\mathbf{r}_i$ and matrices $\mathbf{C}_{ij}$ are referred to an arbitrary chosen system of axes fixed to the particle.

In the above expressions, $\mathbf{T}_{ij}\,(i, j = 1,\ldots N)$ represents the 3×3 hydrodynamic interaction tensors between beads i and j, which can be directly calculated from the Cartesian coordinates and radii of the N beads in the model. To order R_{ij}^{-1} in the interbead distances, R_{ij}, this tensor has the form originally given by Oseen. An alternative that includes terms up to R_{ij}^{-3} is the modified Oseen tensor, derived by Rotne and Prager (1969) and Yamakawa (1970) for interacting elements of equal size and generalized by García de la Torre and Bloomfield (1977 a) for elements of different radii. For more details, the reader is referred to the original references and available reviews (García de la Torre and Bloomfield 1981; García de la Torre 1981; García de la Torre 1989). We note that, instead of the $\mathbf{S}_{ij}$ employed in the original works (García de la Torre and Bloomfield 1978), we alternatively employ $\mathbf{C}_{ij}$ (García de la Torre 1989) which has the virtue of making supermatrix $\mathcal{C}$ symmetric, which brings about some computational advantages.

1.2 The problem and its preliminary solutions

From Eq. (1) or (2), it is evident that for one bead placed at the particle's center, $\mathbf{r}_i = \mathbf{0}$ and it would not contribute to the intrinsic viscosity. This is not numerically relevant in typical cases in which the macromolecular model is composed of many beads of similar sizes, since none of them dominates the hydrodynamic behavior. This was indeed the situation contemplated in the original K-R theory (Kirkwood and Riseman 1948; Riseman and Kirkwood 1950) corresponding to strings of N beads in the limit of $N \to \infty$. On the other hand, for a model of a few beads, one of them may be at the centre and its missing contribution to $[\eta]$ may introduce an important error. An extreme but illustrative situation is that of a single bead, i.e., with N = 1 and $\mathbf{r}_i = \mathbf{0}$; the application of Eq. (1) or (2) to this case yields the nonphysical results $[\eta] = 0$ instead of the correct Einstein value $[\eta] = (10/3)(N_A\pi\sigma^3/M)$.

This deficiency was detected and recognized from the beginning in the GT-B treatment (García de la Torre and Bloomfield 1978), along with a similar problem for rotational coefficients. Actually, the same problem affects the rotational friction tensor and the coefficients derived from it (*vide infra*). A remedy was soon proposed (Wilson and Bloomfield 1979; García Bernal and García de la Torre 1980): each 'mother' bead in the model (or at least some of them) can be replaced by a cubic arrays of smaller spheres. Thus the frictional resistance at the mother bead is displaced from the center toward its surface, and the mathematical singularity disappears. This modelling strategy, known as the cubic substitution has been successfully applied to various structures (García Bernal and García de la Torre 1981; Allison and McCammon 1984) including ologomeric arrays of spheres. The evident drawback is that as the number of elements increases by a factor of 8, the computing time of the rigorous hydrodynamic calculations increases by up to $8^3 = 512$. This is unimportant for bead models with a few subunits but it may pose a serious problem for other types of models.

In the context of hydrodynamics of flexible-chain polymers in solution, this problem was noticed for the first time in a paper by Bianchi and Peterlin (1968). These authors undertook a K-R calculation of intrinsic viscosities of short flexible chains, modelled by a small number of identical beads, and proposed in an *ad hoc* manner that the K-R prediction for $[\eta]$ should be corrected by adding a term equal to $[\eta]_1$, the intrinsic viscosity of the bead monomer. Later, Yamakawa et al. (Yoshizaki et al. 1988; Abe et al. 1991) arrived at the same conclusion. Thus, the volume correction for viscosity would be

$$[\eta] = [\eta]_1 + [\eta]^{uncorr} \tag{3}$$

where $[\eta]_1 = 5N_AV_1/2M_1$ is the intrinsic viscosity of a single bead (monomer) with volume V_1 and molecular mass M_1.

In the context of models for rigid macromolecules composed of beads of varying sizes, a similar correction was suggested and published by one of the present authors (García de la Torre 1989). The reasoning was as follows. If the hydrodynamic interactions are turned off, setting $\mathbf{T}_{ij} = \mathbf{0}$ for the interaction tensor, Eq. (2) reduces to a particularly simple form:

$$[\eta]^{uncorr} = (10/3)(N_A\pi/M)\sum_{i=1}^{N}\sigma_i r_i^2 \tag{4}$$

This hypothetical (not practical) case, has been studied in detail by Abdel-Kalik and Bird (1975) who obtained the result:

$$[\eta] = (10/3)(N_A\pi/M)\sum_{i=1}^{N}(\sigma_1^3 + \sigma_i r_i^2) \tag{5}$$

Comparing the uncorrected results with theirs, we see that we are missing an additive term equal to

$$(10\pi N_A/3M)\sum_{i=1}^{N}\sigma_i^3 = 5N_AV/2M \tag{6}$$

Accordingly we proposed, without further justification, that the intrinsic viscosity should be corrected as

$$[\eta] = \frac{5N_AV_m}{2M} + [\eta]^{uncorr} \tag{7}$$

where V_m is the volume of the model, equal to

$$V_m = \frac{4}{3}\pi\sum_{i=1}^{N}\sigma_i^3 \tag{8}$$

and σ_i's are the individual bead radii. We emphasize that V is the total volume of the *bead model*, understood as the sum of the volumes of all the spheres. This must be kept in mind when one uses shell-type models in which it is just the surface of the particle that is covered by a thin shell of many small beads, and V_m is very different (smaller) from the true particle volume, V_p.

It is clear that Eq. (7)–(8) reduce to Eq. (3) for identical beads, and yield the Abdel-Khalik (Eq. (5)) result if hydrodynamic interactions are neglected.

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2 Theory

In this section we provide a theoretical justification of the volume correction for the intrinsic viscosity. In a shear flow, the hydrodynamic treatment must consider not only translational and rotational contributions to friction (forces and torques), but also the stresslet associated to the shear (Brenner and O'Neil 1972; Brenner 1974). We will show that, if hydrodynamic interaction is truncated at the first order in interbead separations (at the Oseen level) for the three contributions, then the result includes naturally the volume correction in the zero-th order term. Thus, the volume correction is not just an *ad hoc* patch but instead it forms an integral part of the expression for $[\eta]$ of a bead model at the Oseen level.

2.1 Solvent flow and viscosity

We first consider a simple fluid, namely the solvent in the absence of suspended particles, which is undergoing a linear shear flow with a velocity field:

$$\mathbf{v}^o(\mathbf{r}) = \mathbf{v}_O^o + \boldsymbol{\Omega} \times \mathbf{r} + \mathbf{S} \cdot \mathbf{r} \tag{9}$$

$\mathbf{v}^o(\mathbf{r})$ and $\mathbf{v}_O^o$ are the unperturbed velocities at a general point with position vector $\mathbf{r}$ with respect to an arbitrary origin, O. $\boldsymbol{\Omega}$ is the fluid spin and $\mathbf{S}$ is the symmetric part of the velocity gradient, $\mathbf{G}$, i.e., $\mathbf{S} = \frac{1}{2}(\mathbf{G} + \mathbf{G}^T)$.

We recall that the viscosity of such a simple fluid, η_0, is related to the rate of energy dissipation per unit volume, W_0 (Happel and Brenner 1973; Zhou 1995):

$$W_0 = 2\eta_0 \mathbf{S} : \mathbf{S} \tag{10}$$

In Eq. (10) we employ the double dot product of second-rank tensors, defined as $\mathbf{A} : \mathbf{B} = Tr(\mathbf{A} \cdot \mathbf{B})$.

2.2 Multiparticle system

Next, we consider a particle suspension under linear shear flow. In the absence of suspended particles the fluid would have a velocity field given by Eq. (9).

Our primary problem is the calculation of the viscosity of the solution or suspension, η. By analogy with Eq. (10), this is given by:

$$W = 2\eta \mathbf{S} : \mathbf{S} \tag{11}$$

We can formulate $W = W_0 + \delta W$, where δW is the excess energy dissipation per unit volume over that due to the solvent particles. Furthermore, we write $\delta W = n_p \delta w_1$, δw_1 being the rate of energy dissipation per suspended particle. $n_p = c_p N_A / M$ and c_p are, respectively, the number concentration and mass concentration of particles. If the excess viscosity is expressed in terms of the intrinsic viscosity, $[\eta] = (\eta - \eta_0)/(\eta_0 c_p)$, then we have:

$$[\eta] = \frac{N_A}{M\eta_0} \frac{\delta w_1}{2\mathbf{S} : \mathbf{S}} \tag{12}$$

Let us assume that N particles are suspended in the fluid. Each particle, i, has a translational velocity $\mathbf{u}_{P_i}$ measured at some point P_i in the particle, and rotates with angular velocity ω_i. We define the following arrays:

$$\mathcal{F} = \begin{pmatrix} \mathbf{F}_1 \\ \vdots \\ \mathbf{F}_N \end{pmatrix} \quad \mathcal{T} = \begin{pmatrix} \mathbf{T}_{P,1} \\ \vdots \\ \mathbf{T}_{P,N} \end{pmatrix} \quad \mathcal{A} = \begin{pmatrix} \mathbf{A}_{P,1} \\ \vdots \\ \mathbf{A}_{P,N} \end{pmatrix} \tag{13}$$

$$\mathcal{U} = \begin{pmatrix} \mathbf{u}_{P,1} - \mathbf{v}^o(\mathbf{r}_{P,1}) \\ \vdots \\ \mathbf{u}_{P,N} - \mathbf{v}^o(\mathbf{r}_{P,N}) \end{pmatrix} \quad \mathcal{O} = \begin{pmatrix} \omega_1 - \Omega \\ \vdots \\ \omega_N - \Omega \end{pmatrix} \quad \mathbf{S} = \begin{pmatrix} \mathbf{S} \\ \vdots \\ \mathbf{S} \end{pmatrix} \tag{14}$$

$\mathbf{F}_i$ and $\mathbf{T}_{P,i}$ are, respectively, the force and torque exerted by particle i on the fluid, when the particles are moving with relative linear and angular velocities $\mathbf{u}_{P,i} - \mathbf{v}^o(\mathbf{r}_{P,i})$ and $\omega_i - \boldsymbol{\Omega}$. $\mathcal{S}$ contains N copies of $\mathbf{S}$ and $\mathcal{A}$ contains the values of the stresslets, $\mathbf{A}_{P,i}$ exerted by particle i on the fluid. All these arrays are of dimension $3N \times 1$, except $\mathcal{S}$, which is $3N \times 3$.

The linearity between, $\mathcal{F}$, $\mathcal{T}$ and $\mathcal{A}$, on the one hand and $\mathcal{U}$, $\mathcal{O}$ and $\mathbf{S}$, on the other (Brenner and O'Neil 1972), can be formulated in terms of a grand resistance matrix (Schmitz and Felderhof 1982a) or a grand mobility matrix (Schmitz and Felderhof 1982b). We choose the latter representation, writing:

$$\begin{pmatrix} \mathcal{U} \\ \mathcal{O} \\ \mathcal{A} \end{pmatrix} = \begin{pmatrix} \mu^{tt} & \mu^{tr} & \mu^{ts} \\ \mu^{rt} & \mu^{rr} & \mu^{rs} \\ \mu^{st} & \mu^{sr} & \mu^{ss} \end{pmatrix} \begin{pmatrix} \mathcal{F} \\ \mathcal{T} \\ \mathcal{S} \end{pmatrix} \tag{15}$$

The μ matrices in Eq. (15) are of dimension $3N \times 3N$ and contain 3×3 blocks, μ_{ij}, with $i,j = 1,\ldots,N$.

We now particularize to the case of spherical particles. For the mobility matrix we can employ results available in the literature for the many-sphere and the two-sphere problems (Mazur and van Saarlos 1982; Schmitz and Felderhof 1982b), which are usually expressed as expansions in powers of the reciprocals of interparticle separations, R_{ij}^{-1}. To the first, lowest orders in R_{ij}^{-1}, many-body hydrodynamic interactions do not appear; rather, one can consider the problem as a superposition of pairwise interactions, and the results of the two-sphere problem, including shear (Schmitz and Felderhof 1982b) can be used.

In the spirit of the Oseen approximation, as it is customarily assumed in the K-R and GT-B theories, only terms of the order R_{ij}^{-1} are retained. Thus, Eq. (15) is greatly simplified since $\mu^{tr} = \mu^{rt} = \mu^{ts} = \mu^{st} = \mu^{rs} = \mu^{sr} = 0$. The remaining mobility matrices have the same structures:

$$\mu^{tt} = \mathscr{B} = \begin{pmatrix} \mathbf{B}_{11} & \cdots & \mathbf{B}_{1N} \\ \vdots & & \vdots \\ \mathbf{B}_{N1} & \cdots & \mathbf{B}_{NN} \end{pmatrix} \tag{16}$$

where $\mathbf{B}_{ii} = (1/\zeta_i)\mathbf{I}$ and $\mathbf{B}_{ij} \equiv \mathbf{T}_{ij}$, the latter being the hydrodynamic interaction tensor. For consistency in a first-order approach, the Oseen tensor should be used for $\mathbf{T}_{ij}$, rather than the modified tensor, that includes a third-order contribution. μ^{rr} has only the diagonal blocks, i.e. $\mu_{ij}^{rr} = 0$ for $i \neq j$ and $\mu_{ii}^{rr} = (1/f_i)\mathbf{I}$, where $f_i = 8\pi\eta_0\sigma_i^3$. Finally, the μ_{ij}^{ss} terms are fourth-rank tensors, with $\mu_{ij}^{ss} = 0$ for $i \neq j$ and μ_{ii}^{ss} satisfies $\mu_{ii}^{ss} : \mathbf{S} = 5\eta_0 V_i$, where $V_i = \frac{4}{3}\pi\sigma_i^3$ is the volume of the sphere.

The partial inversion of Eq. (15), required to express $\mathscr{F}$, $\mathscr{T}$ and $\mathscr{A}$ in terms of $\mathscr{U}$, $\mathbb{O}$ and $\mathscr{S}$ is rather easy after the reduction in order R_{ii}^{-1} described above. We find

$$\mathscr{F} = \mathscr{C} \cdot \mathscr{U};$$

$$\begin{pmatrix} \mathbf{F}_1 \\ \vdots \\ \mathbf{F}_N \end{pmatrix} = \begin{pmatrix} \mathbf{C}_{11} & \cdots & \mathbf{C}_{1N} \\ \vdots & & \vdots \\ \mathbf{C}_{N1} & \cdots & \mathbf{C}_{NN} \end{pmatrix} \begin{pmatrix} \mathbf{u}_{P,1} - \mathbf{v}^o(\mathbf{r}_{P,1}) \\ \vdots \\ \mathbf{u}_{P,N} - \mathbf{v}^o(\mathbf{r}_{P,N}) \end{pmatrix} \tag{17}$$

$$\mathbf{T}_{P,i} = f_i(\omega_i - \Omega) \tag{18}$$

$$\mathbf{A}_i = 5\eta_0 V_i \mathbf{S} \tag{19}$$

where the $3N \times 3N$ resistance matrix, $\mathscr{C}$ is the inverse of $\mathscr{B}$,

$$\mathscr{C} = \mathscr{B}^{-1} \tag{20}$$

2.3 Rigid assembly of spheres in shear flow

In the next step of this derivation we particularize further for the case of a rigid assembly of spheres, in which all move with overall translational velocity $\mathbf{u}_O$ referred to some origin O within the array, and rotational velocity ω. The angular velocity of all the beads is $\omega_i = \omega$, and the linear velocity of their centers are $\mathbf{u}_{P_i} = \mathbf{u}_O + \omega \times \mathbf{r}_i$. The characteristic point P_i of each sphere, and $\mathbf{r}_i \equiv \mathbf{r}_{P_i}$ is its position vector from origin O. At these points, the unperturbed fluid velocity is $\mathbf{v}_i^o \equiv \mathbf{v}^o(\mathbf{r}_{P_i}) = \mathbf{v}_O^o + \Omega \times \mathbf{r}_i + \mathbf{S} \cdot \mathbf{r}_i$.

The rigid assembly is immersed in the shear flow, given by Eq. (9). Pushed by the flow, the rigid particle acquires velocities $\mathbf{u}_O$ and ω. At the center of sphere i, $\mathbf{u}_{P_i} = \mathbf{u}_O + \omega \times \mathbf{r}_i$. The relative velocities in Eq. (17) are

$$\mathbf{u}_{P_i} - \mathbf{v}^o(\mathbf{r}_{P_i}) = \Delta\mathbf{v}_O + \Delta\omega \times \mathbf{r}_i + \mathbf{S} \cdot \mathbf{r}_i \tag{21}$$

where $\Delta\mathbf{v}_O = \mathbf{u}_O - \mathbf{v}_O^o$ and $\Delta\omega = \omega - \Omega$ are the slip velocities.

The rate of energy dissipation due to a single particle (a rigid assembly of beads) is a sum over beads

$$\delta w_1 = \sum_{i=1}^{N} \left\{ \left[\mathbf{u}_{P_i} - \mathbf{v}^o(\mathbf{r}_{P_i}) \right]^T \cdot \mathbf{F}_i + (\omega - \mathbf{\Omega})^T \cdot \mathbf{T}_{P,i} + \mathbf{A}_i : \mathbf{S} \right\} \tag{22}$$

Here $\mathbf{u}^T \cdot \mathbf{F}$ and $\omega^T \cdot \mathbf{T}$ denote the scalar product of vectors.

Now we use the previous results for the multisphere system in the Oseen approximation, given by Eqs. (17), (18) and (19). We obtain

$$\begin{aligned} \delta w_1 = 5\eta_0 V_m \mathbf{S} : \mathbf{S} + \sum_{i=1}^{N}\sum_{j=1}^{N} \left[\Delta\mathbf{v}_O + \Delta\omega \times \mathbf{r}_i' + \mathbf{S} \cdot \mathbf{r}_i' \right]^T \cdot C_{ij}' \\ \cdot \left[\Delta\mathbf{v}_O + \Delta\omega \times \mathbf{r}_j' + \mathbf{S} \cdot \mathbf{r}_j' \right] + \sum_{i=1}^{N} f_i (\Delta\omega)^2 \end{aligned} \tag{23}$$

This result corresponds to an instantaneous orientation of the rigid assembly. Actually we employ a prime in $\mathbf{C}_{ij}'$ to denote that this tensor is referred to the laboratory fixed system of coordinates at which $\mathbf{S}$ is also referred. The position vectors of the bead centers, $\mathbf{r}_i'$, are also primed to denote that they are also referred to the laboratory axes. The value that we must use in Eq. (12) is $\langle \delta w_1 \rangle$, where $\langle \ldots \rangle$ is an average over orientations. Thus, we are faced with the evaluation of

$$\begin{aligned} \langle \delta w_1 \rangle = 5\eta_0 V_m \mathbf{S} : \mathbf{S} + \sum_{i=1}^{N} f_i (\Delta\omega)^2 \\ + \left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \left[\Delta\mathbf{v}_O + \Delta\omega \times \mathbf{r}_i' + \mathbf{S} \cdot \mathbf{r}_i' \right]^T \right. \\ \left. \cdot \mathbf{C}_{ij}' \cdot \left[\Delta\mathbf{v}_O + \Delta\omega \times \mathbf{r}_j' + \mathbf{S} \cdot \mathbf{r}_j' \right] \right\rangle \end{aligned} \tag{24}$$

In the treatment of the intrinsic viscosity in the Kirkwood-Riseman theory (Yamakawa 1971; Kirkwood and Riseman 1948; Riseman and Kirkwood 1950), it is assumed that the macromolecule moves with the same linear and angular velocity as the fluid. Thus, $\mathbf{u}_O = \mathbf{v}_O^o$ and $\omega = \Omega$, so that the slip velocities are zero, $\Delta\mathbf{v}_O = 0$ and $\Delta\omega = 0$.

This hypothesis was employed by García de la Torre and Bloomfield (1978) in their derivation of the intrinsic viscosity of rigid bead models. Later, Wegener (1984) pointed out that the assumption is strictly correct only for bodies of high symmetry. However, its effect on the resulting $[\eta]$ is very small. Harding et al. (1981) had already noticed this for triaxial ellipsoids, finding differences of only 1%. Wegener (1984) has examined a number of other cases, including bead models, and the differences remained about 1% or less.

Accordingly, we adopt the zero-slip assumption, and Eq. (24) is greatly simplified. We are just left with

$$\langle \delta w_1 \rangle = 5\eta_o V_m \mathbf{S} : \mathbf{S} + \left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} (\mathbf{S} \cdot \mathbf{r}_i')^T \cdot \mathbf{C}_{ij}' \cdot (\mathbf{S} \cdot \mathbf{r}_j') \right\rangle \tag{25}$$

From Eq. (12) and (25) we obtain

$$[\eta] = \frac{5N_A V_m}{2M\eta_0} + \frac{N_A}{2M\eta_0 \mathbf{S} : \mathbf{S}} \left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \mathbf{r}_i'^T \cdot \mathbf{S} \cdot \mathbf{C}_{ij}' \cdot \mathbf{S} \cdot \mathbf{r}_j' \right\rangle \tag{26}$$

We consider a simple shear flow with shear rate $\dot{\gamma}$. The fluid velocities are along the lab-fixed x axis and the gradient is along axis y. Thus we have $\mathbf{G} = \dot{\gamma}$ and $\mathbf{S} = \frac{1}{2}\dot{\gamma}\mathbf{E}$,

$$\mathbf{D} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \mathbf{E} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{27}$$

and $\mathbf{S} : \mathbf{S} = \dot{\gamma}^2/2$ since $Tr(\mathbf{E} : \mathbf{E}) = 2$.

Thus, we obtain

$$[\eta] = \frac{5N_A V_m}{2M\eta_0} + \frac{N_A}{4M\eta_0}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \mathbf{r}_i'^T \cdot \mathbf{E} \cdot \mathbf{C}'_{ij} \cdot \mathbf{E} \cdot \mathbf{r}'_j \right\rangle \tag{28}$$

Now, as $\mathbf{C}'_{ij}$ is a symmetric matrix, it follows that $\mathbf{E} \cdot \mathbf{C}'_{ij} = \mathbf{2}\mathrm{D} \cdot \mathbf{C}'_{ij}$. Therefore,

$$[\eta] = \frac{5N_A V_m}{2M\eta_0} + \frac{N_A}{2M\eta_0}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \mathbf{r}_i'^T \cdot \mathbf{D} \cdot \mathbf{C}'_{ij} \cdot \mathbf{E} \cdot \mathbf{r}'_j \right\rangle \tag{29}$$

It is easily verified that the second term in the right-hand side of Eq. (29) is the same as the result derived by García de la Torre and Bloomfield (1978), and the first term is the volume correction.

The rest of the derivation is as described by García de la Torre and Bloomfield. The orientational average is carried out and the final result for $[\eta]$ is that corresponding to Eqs. (7) and (8) in the Introduction section.

2.4 The related problem for rotational coefficients and the radius of gyration

The related problem for rotational dynamics has been described and solved in previous work. Here, we just recall the main results. The uncorrected form of the rotational friction tensor referred to an arbitrary origin, O, is given by

$$\Xi_{rr}^{uncorr} = -\sum_{i=1}^{N}\sum_{j=1}^{N} \mathbf{r}'_i \times \mathbf{C}_{ij} \times \mathbf{r}'_j \tag{30}$$

where r'_i are the coordinate vectors of the beads, now referred to O and the cross denotes the dyadic product. The proper origin for rotational diffusion and the way of calculating observable rotational quantities are described elsewhere (García de la Torre 1989).

If equation (30) is applied to a single bead, with O at its center, $\mathbf{r}' = \mathbf{0}$ and obviously $\Xi_{rr}^{uncorr} = \mathbf{0}$, with the erroneous result that the rotational friction coefficient is $f_r = 0$, (while the correct result is $f_r = 8\pi\eta_0\sigma^3$) which also results in a zero rotational time. In a model with a few beads, or if one of the beads is dominant and O is placed at or near its center, with $\mathbf{r}_i \cong \mathbf{0}$ then it turns out that its contribution to Ξ_{rr} is null.

This problem was pointed out (García de la Torre and Bloomfield 1977b) and solved by cubic substitution (Wilson and Bloomfield 1979; García Bernal and García de la Torre 1981) along with that for $[\eta]$. García de la Torre and Rodes (1983) presented a rigorous Kirkwood-Riseman formalism up to first order in hydrodynamic interaction. It was noted that a contribution to the zeroth-order term was missing. When it is included, the rotational friction tensor reads:

$$\Xi_{rr} = \Xi_{rr}^{uncorr} + 6V_m\eta_0\mathbf{I} \tag{31}$$

where $\mathbf{I}$ is the unitary tensor. Thus the correction consists just of adding $6V_m\eta_0$ to the diagonal components of Ξ_{rr}. The García de la Torre-Rodes correction for rotation has inspired the correction for viscosity presented in the present paper.

For the sake of completeness, we finally mention that a similar situation occurs for the radius of gyration. The square radius, R_g^2, is usually computed, for a set of N identical elements as

$$R_g^2(uncorr) = \frac{1}{N}\sum_{i=1}^{N} d_i^2 = \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} r_{ij}^2 \tag{32}$$

where d_i is the distance from the center of mass to element i, and r_{ij} is the distance from i to j. Strictly speaking, Eq. (32) is only valid for pointlike elements; actually, for a single element Eq. (32) gives $R_g(uncorr) = 0$.

In the context of bead models, one wishes to consider that the mass of the particle is not concentrated at some points but is distributed throught the spherical beads.

It can be easily demonstrated (see for instance Sólvez et al. 1988) that, for an array of spheres, the correct result for the square radius of gyration is given by

$$R_g^2 = \sum_{i=1}^{N} f_i\,(S_i^2 + d_i^2) = \sum_{i=1}^{N} f_i\,S_i^2 + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} f_i\,f_j\,r_{ij}^2 \tag{33}$$

where $f_i = V_i/V_m = \sigma_i^3/\Sigma\sigma_i^3$ is the volume fraction of bead i in the model, and $S_i^2 = 3\sigma_i^2/5$ is its individual radius of gyration (the model is assumed to be uniform in the sense of having the same mass or electron density in all beads). As above, d_i is the distance from the center of mass, C, to the center of bead i. This point satisfies the condition that its position vector $\mathbf{r}_{OC}$ with respect to an arbitrary origin O

$$\mathbf{r}_{OC} = \sum_{i=1}^{N} f_i\,\mathbf{r}'_i \tag{34}$$

Thus, the square radius of gyration of a bead model with elements of different sizes can be written as

$$R_g^2 = \sum_{i=1}^{N} f_i\,S_i^2 + R_g^2\,(uncorr) \tag{35}$$

where

$$R_g^2\,(uncorr) = \sum_{i=1}^{N} f_i\,d_i^2 = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} f_i\,f_j\,r_{ij}^2 \tag{36}$$

The first term on the right-hand side of Eq. (35) can be regarded as the volume correction for the radius of gyration. We recall that the correct result, as expressed by Eq. (35) and Eq. (36) is *exact*, as follows immediately from the definition of *Rg* (Sólvez et al. 1988). We note that Eq. (35) and Eq. (36) reduce to Eq. (32) for identical beads. For models composed of many small beads, $d_i^2 \gg \sigma_i$ or $r_{ij} \gg \sigma_i$, σ_j in most instances, and R_g^2 will be very close to $R_g^2(uncorr)$. Conversely, for models with few beads R_g^2 $(uncorr)$ will deviate significantly from the exact value. Finally Eqs. (35) and (36) predict correctly $R_g^2 = 3\sigma^2/5$ for a single sphere.

3 Results and discussion

3.1 Ellipsoidal models

The bead model for a prolate ellipsoid has been customarily employed since the work of Bloomfield et al. (1967a) as a benchmark for testing hydrodynamic theories and modelling procedures. The revolution ellipsoid is the only particle for which the hydrodynamic properties can be calculated from simple, analytical expressions. Particularly, $[\eta]$, can be determined by the equations of Simha (1940) and Scheraga (1955).

Bead models for prolate ellipsoids can be easily constructed. The model originally proposed by Bloomfield et al. (1967a) consists of a string of colinear spheres, whose radii decrease from the center to the end, and are interiorly tangent ot the surface of the original ellipsoid. The volume of the resulting bead model is appreciably smaller than that of the true ellipsoid.

A modified model with equalized volume was proposed by García de la Torre and Bloomfield (1977a). For an ellipsoid of semiaxes *a* and *b*, the bead model is constructed, as described above, for an ellipsoid of semiaxes *a* and *b′* adjusted so that the volume of the model, V_m, equals the volume of the ellipsoid, $V = 4\pi ab^2/3$. The two versions of the bead model for a prolate ellipsoid are displayed in Fig. 1.

The modified ellipsoidal model, treated with rigorous hydrodynamics, was shown to give an excellent prediction of translational friction coefficients; the deviation of the bead-model results from the exact values is less that 1% for the whole range of axial ratios (García de la Torre and Bloomfield 1977a). On the other hand, the failure of the bead-model calculation for ellipsoids at values of $p = a/b$ close to $p = 1$, for both rotational coefficients (García de la Torre and Bloomfield 1977b) and intrinsic viscosity (García de la Torre and Bloomfield 1978) was employed to illustrate the failure of such calculations in the sphere limit.

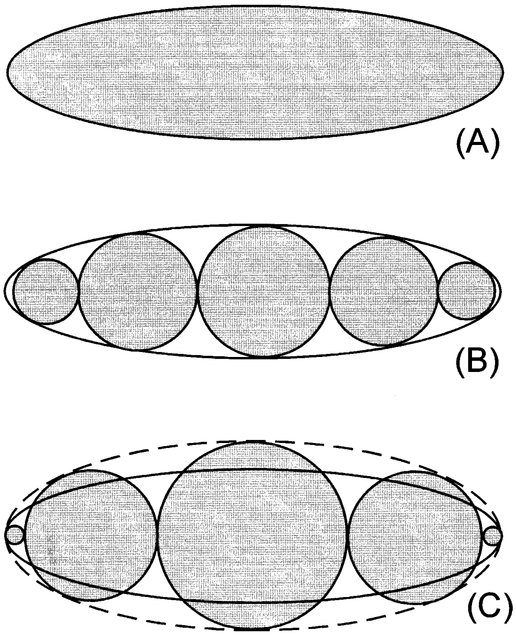

Fig. 1A–C Schemes for bead models of ellipsoids (planar sections). **A** The original ellipsoid; **B** the primary bead model; **C** the modified model with equalized volume

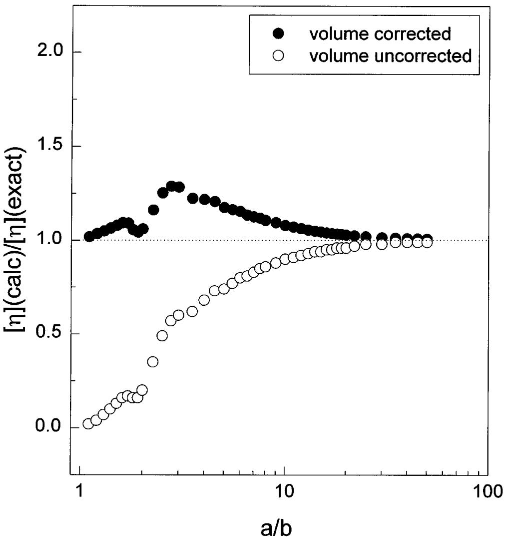

Fig. 2 Ratio of calculated to exact intrinsic viscosity plotted vs. the axial ratio, *p*. Calculated values are for the modified model, without and with the volume correction

In the present work we have determined how the volume correction influences the intrinsic viscosity of ellipsoidal bead models. The ratio $[\eta](calc)/[\eta](exact)$, for values calculated with the rigorous procedure, with and without volume correction, are plotted in Fig. 2. The volume correction gives an overestimation of $[\eta]$, while uncorrected viscosity gives an underestimation. The corrected results are correct for $p \simeq 1$ (as they should), while the uncorrected calculation gives the erroneous result, $[\eta] \simeq 0$. At very large *p*, the volume correction is insignificant and the results of both procedures tend to the exact value. At intermediate *p*, the results from the volume correction are not very precise; indeed, the deviation may reach +30% for *p* approximately 3. However, it is clear that the results with correction are always better than those without it; the ratio is closer to unity, for any *p*, when the volume correction is included.

Table 1 Intrinsic viscosity and rotational coefficients for a dimer

	$[\eta]_2/[\eta]_1$	$f^{\parallel}_2/f^{\parallel}_1$	$f^{\perp}_2/f^{\perp}_1$
Oseen uncorrected	0.77	0.00	2.40
Oseen corrected	1.77	2.00	4.40
K-R uncorrected	0.64	0.00	2.67
K-R corrected	1.64	2.00	4.67
Cubic substitution	1.34	1.77	3.79
Exact	1.38	1.78	3.76

Table 2 Intrinsic viscosity and rotational coefficients for different models

	Tetrahedron		Octahedron		Cube	
	$\frac{f_4}{f_1}$	$\frac{[\eta]_4}{[\eta]_1}$	$\frac{f_6}{f_1}$	$\frac{[\eta]_6}{[\eta]_1}$	$\frac{f_8}{f_1}$	$\frac{[\eta]_8}{[\eta]_1}$
Oseen modified uncorrected	4.57	0.97	6.66	1.03	9.93	1.18
Oseen modified corrected	8.57	1.97	12.66	2.03	17.93	2.18
Cubic substitution	6.05	1.38	8.80	1.39	13.19	1.52

3.2 Dimer

The case of a dimer, composed of two identical, touching spheres is theoretically important and useful in practice. Numerical values of the hydrodynamic properties are available from very fundamental treatments. These results are nearly exact, and can be used for comparison with our bead-model calculations.

Table 1 contains the results obtained for viscosity and rotational coefficients with and without volume correction, compared to nearly exact results. The numerical values in Table 1 are the ratios of the properties of a dimer of spheres of radius σ to those for a single sphere of radius σ, given by $[\eta]_1 = 10\pi N_A\sigma^3/(3M_1)$, and $f_1 = 8\pi\eta_0\sigma^3$. The coefficients for rotation around the center-to-center axis and perpendicular to it are denoted as $f^{\parallel}$ and $f^{\perp}$, respectively. The exact values are from Davis (1969) for rotation and from Brenner and Wakiya for $[\eta]$ (Brenner and O'Neil 1972; Wakiya 1971). We also include results from the cubic substitution method, from García Bernal and García de la Torre (1981).

It is clear from Table 1 that the volume correction improves the results for the dimer. The corrected $[\eta]$ and f overestimated the exact result while the uncorrect properties were underestimated, but it is clear that the corrected results are closer to the exact ones. By the way, we note the excellent performance of the cubic substitution procedure, although it has, as mentioned above, the drawback of requiring very long computer time.

3.3 Rodlike and flexible-chain structures

Two useful linear models with open ends are the straight array of beads, employed to represent rodlike structures, and the flexible chain of beads, which represents random coil conformations. In both cases the volume corrections must vanish in the limit of large N; however, it is interesting to determine their influence for small N, i.e. for oligomeric structures.

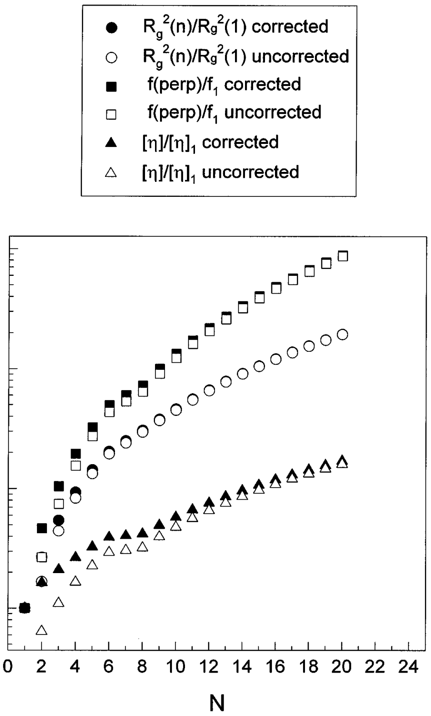

Fig. 3 Ratios of uncorrected and corrected values of the properties, to the (correct) properties of a single sphere: $f_1 = 8\pi\eta_0\sigma^3$, $[\eta]_1 = (10\pi N_A\sigma^3)/(3M_1)$ and $R_g^2(1) = 3\sigma^2/5$. Results for rods modeled as straight strings of touching beads as a function of the number of beads

For a straight, rodlike array of N identical touching beads, the corrected and uncorrected properties are presented in Fig. 3. We appreciate the large influence of the volume correction for small N (say $N \le 5$) while the large N its importance decreases significantly. Thus, for $N = 20$, the volume corrections are of only 2.3%, 0.5% and 5.9% for rotational friction, square radius and viscosity, respectively.

The calculation of properties of flexible chains of beads can be made using rigid-particle hydrodynamics. A simple Monte Carlo method is employed to generate instantaneous coil conformations, and for each conformation the hydrodynamic properties are computed as if it were a rigid particle. The final results are the averages over the Monte Carlo sample. This is the so-called 'rigid body' treatment of flexible structures, which has been successfully used for flexible-chain macromolecules (García de la Torre et al. 1982; García de la Torre et al. 1984; García Bernal et al. 1991). In the present study, we include a hard-sphere excluded-volume interaction: conformations with overlapping beads ($r_{ij} < 2\sigma$) are rejected. The results for flexible chains with up to 20 beads are plotted in Fig. 4. We note that the relative effect of the volume correction decreases very slowly with N. For $N = 20$, the correction still amounts

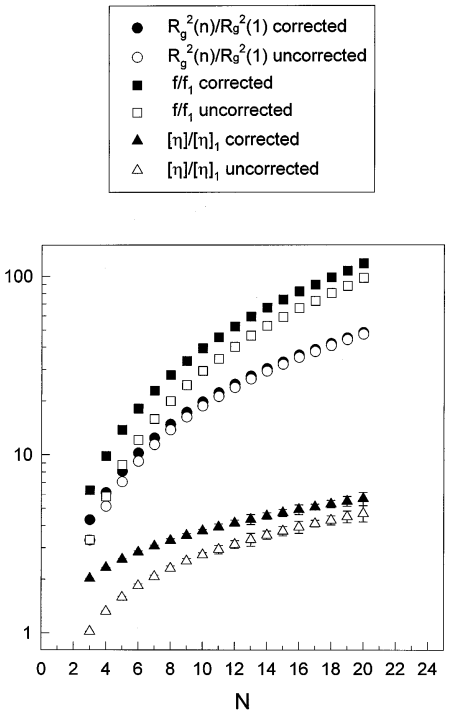

Fig. 4 The same as in Fig. 3 for flexible chains of non-overlapping beads. The *errors bars* are the standards errors of the Monte Carlo averages; when no shown, the error bar is of the same size as the symbol

to 17.0%, 2.1% and 17.6% for *f*, R^2g and $[\eta]$ respectively. At very large *N* the correction must be insignificant, but this may not be the case for shorter chains, as pointed out by some authors (Abe et al. 1991; Yoshizaki et al. 1988).

3.4 Compact, polyhedral oligomers

An important type of model, with features opposite to those of the linear, straight or coil-like chains considered above, is that of very compact oligomeric structures with a regular polyhedral shape, such as tetrahedrons, octahedrons or cubes. These structures have a wide applicability in the analysis of the properties of many system, of which multisubunit oligomeric proteins are a typical example (García de la Torre and Bloomfield 1978; García Bernal and García de la Torre 1981). From the theoretical point of view, these structures are also of great interest since, owing to their maximum compactness, hydrodynamic interactions are stronger than in any other structure with the same number of beads. Thus, peculiarities not exhibited by other structures can be expected in this case.

We have detected a first anomalous circumstance in the hydrodynamics of compact polyhedral structures in the calculations with the Oseen interaction tensor: The $3N \times 3N$ diffusion matrix, $\mathcal{B}$ in Eq. (16) is singular. The existence of singularities of this kind in Kirkwood-Riseman calculations with Oseen-type hydrodynamic interactions was reported years ago by some authors (Zwanzig 1968). This finding prompted the development of the modified-Oseen tensor (Rotne and Prager 1969; Yamakawa 1970; García de la Torre and Bloomfield 1977 a) which has been shown to remove the singularity (Yamakawa and Tanaka 1972) in some cases.

To our knowledge this situation had not been reported before for compact oligomers, although the situation could be expected since hydrodynamic interactions are strongest for such structures. In the García de la Torre-Bloomfield (1978) results for oligomers this was not noted since the modified Oseen tensor was used in the calculations.

Thus, for the present purpose, the Kirkwood-Riseman results (without volume correction) are obtained with the modified Oseen tensor although this amounts to the above noted slight inconsistency of using R_{ij}^{-3} term when other terms of the same order are missing. Then, the volume corrections are added to these results.

We expect that, as noted for the dimer, the results from the cubic substitution procedure will be very close to the exact ones (which are not available for $N > 2$), and therefore we use them as the reference for the other procedures. Then, we note that while the uncorrected values are below the reference, when we add the volume correction the corrected results clearly overestimate the properties. Apart from the sign, the absolute values of the deviation are even larger for the corrected values.

Thus, the case of the these very compact oligomeric structures is an exception to the improvement introduced by the volume correction for the other structures. This finding and the above commented anomaly in the Oseen calculations are probably related to the particularity high strength of hydrodynamic interactions. For these particular cases, the results from cubic substitution procedure are, at the present time, more reliable and should be the choice for the analysis of experimental results.

4 Computer program

The volume corrections were included in the first version of the HYDRO computer program (García de la Torre et al. 1994). In the latest version of HYDRO the volume corrections are optional (although they are recommended in most cases). The FORTRAN source code, in files hydrod_v.for or hydrox_v.for, with v ≥ 5, as well as the related program SOLPRO (García de la Torre et al. 1997) can be downloaded from our WWW page (http://leonardo.fcu.um.es/macromol) or requested by e-mail to jgt@fcu.um.es.

Acknowledgements This work was funded by grant PB96-1106 from the Direccion General de Investigacion Cientifica y Tecnica, MEC. B. C. is the recipient of a predoctoral award from the same agency. Support was also provided by grant FI-CON96/9 from Direccion General de Universidad e Investigacion, CARM.

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