Improved hydrodynamic interaction in macromolecular bead models

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The calculation of hydrodynamic properties of macromolecules in terms of bead models requires an adequate description of the hydrodynamic interaction between the spherical elements. For this purpose, the original or modified Oseen tensor are customarily used, although it has been shown that this simple description may lead to erroneous results, particularly for rotational coefficients. In this paper we study several more elaborate theories for multisphere systems. We apply those treatments to our problem of rigid bead models, implementing them in computer programs, and making calculations for various test structures. The comparison of the results from the various theories, and from other, presumably very accurate procedures, allow us to give some guidelines to improve the treatment of hydrodynamic interactions in macromolecular bead models. These advances are introduced in new versions of our public-domain computer software. © 1999 American Institute of Physics. [S0021-9606(99)52234-4]

I. INTRODUCTION

Bead models, composed of spherical elements, have been used for many years to calculate hydrodynamic properties of macromolecules. In their pioneering work, Kirkwood and Riseman (KR) developed a theory of macromolecular hydrodynamics, which was applied to the calculation properties of flexible or rodlike macromolecules modeled as random or straight chains of beads. Bloomfield et al. foresaw the possibility of applying bead models to rigid (mainly biological) macromolecules, represented as rigid arrays of spheres, and later, several authors developed further this possibility using more advanced versions of the KR theory. These advances have been described in reviews and implemented in computer programs, although the main motivation of the present work comes from the field of rigid macromolecules, it is also noteworthy that, in the so-called rigid-body treatment, hydrodynamic properties of flexible chain macromolecules can be calculated as useful, lower bound approximations.

The most important aspect of the hydrodynamics of bead models is the hydrodynamic interaction between beads. As it is well known, this effect falls off as the interbead distance is increased. Long chainlike structures that, as mentioned above, apply to straight, wormlike or random chains, are composed by many elements that are much smaller than the overall size, and typically the interbead distances are much larger than their radii. Thus, hydrodynamic interactions can be adequately described with the most simplified way based on the Oseen tensor, as in the primitive KR treatment.

In the field of rigid macromolecules, two different strategies can be employed. One of them is shell modeling, in which the surface of the particle is modeled as a shell composed of many small beads. Again, typical distances between beads are larger than bead sizes (indeed, this strategy includes an extrapolation to zero bead size), and correct results can be obtained with the simplest, Oseen hydrodynamic interactions. Regarding this technique, it is pertinent to mention that it is computationally intensive, and has been used in scarce (but successful) applications.

In a different strategy, the whole volume of the particle is filled with beads, equal or unequal, with the only requisite that the overall size and shape of the array are as close as possible to those of the modeled particle. In current terminology, the “bead model” term, in a strict sense, is reserved for this strategy. Examples range from the Bloomfield models for T-even viruses to polygonal or polyhedral arrays employed for oligomeric proteins, such as hexameric seed globulins. In the first example, the massive head of the virus is represented as a single bead, that accounts for most of the size of the particle. In the second example, there are few beads arranged in a very compact fashion. In all of these situations, the interbead distances are not necessary much larger than their radii, and the elementary KR-Oseen treatment may fail. The above-mentioned chainlike structures belong to this category, and a similar failure can happen in certain circumstances; for instance, evidently, when the chain is short, and in the particular situation of rotation around the long axis of a straight or weakly bending rod.

These considerations evidence the need, in some cases, of a more precise description of the hydrodynamics of a bead model. The hydrodynamics of a multispher system finds also essential applications in the dynamics of colloidal suspensions and some recent advances come from that field. Nowadays, several theories are available, such as those proposed by Reuland, Felderhof and Jones, Mazur and van Saarloos, and Goldstein. The purposes of the present paper are: (i) a comparative analysis of these theories; (ii) their application to rigid bead models; (iii) a search of simple improvements of the KR treatment; and (iv) a numerical study of the performance of the various approaches in typical bead models.
II. THEORY FOR A MULTISPERSE SYSTEM

A. General case

The system considered in this work consists of \( N \) spherical particles with radii \( a_i, i = 1, \ldots, N \) immersed in a fluid of viscosity \( \eta \). The motion of the spheres is given by the linear velocities, \( u_{P_j} \), of each of them referred to an arbitrary point \( P_j \), which for simplicity can be the sphere’s center, and their angular velocities, \( \omega_i \). When the spheres move, they will experience frictional forces, \( F_j \), and frictional torques, \( T_{P_j} \), referred to point \( P_j \).

In the viscous (noninertial) regime, the relationship between forces and torques, on the one hand, and linear and angular velocities, on the other hand, are linearly related. The relationship can be written,

\[
F_i = \sum_{j=1}^{N} \xi_{ij}^u \mathbf{u}_{P_j} + \sum_{j=1}^{N} \xi_{ij}^r \mathbf{r}_{P_j} \cdot \omega_j,
\]

\[
T_{P_j} = \sum_{i=1}^{N} \xi_{ij}^u \mathbf{u}_{P_i} + \sum_{i=1}^{N} \xi_{ij}^r \mathbf{r}_{P_j} \cdot \omega_j,
\]

where the \( \xi_{ij}^u \)’s are the 3×3 friction matrices for translation \((tt)\), rotation \((rr)\) and translation-rotation coupling \((tr,rt)\). If we define ‘supervectors’ of dimension \( 3N \times 3 \),

\[
\mathcal{F} = \begin{pmatrix} F_i \\ \vdots \\ \vdots \end{pmatrix}, \quad \mathcal{T} = \begin{pmatrix} T_{P_i} \\ \vdots \\ \vdots \end{pmatrix}, \quad \mathcal{U} = \begin{pmatrix} \mathbf{u}_{P_i} \\ \vdots \\ \vdots \end{pmatrix}, \quad \mathcal{O} = \begin{pmatrix} \omega_i \\ \vdots \\ \vdots \end{pmatrix},
\]

then the linear relationship is formulated as

\[
\begin{pmatrix} \mathcal{F} \\ \mathcal{T} \end{pmatrix} = \begin{pmatrix} \xi_{ij}^u & \xi_{ij}^r \\ \xi_{ij}^r & \xi_{ij}^{tr} \end{pmatrix} \begin{pmatrix} \mathcal{U} \\ \mathcal{O} \end{pmatrix}.
\]

The arrays \( \xi_{ij}^u, \xi_{ij}^r, \) and \( \xi_{ij}^{tr} \) are of dimension \( 3N \times 3N \), and the grand friction matrix is \( 6N \times 6N \). Important symmetry relationships are \( \xi_{ij}^u = \xi_{ji}^u \), \( \xi_{ij}^r = \xi_{ji}^r \) and \( \xi_{ij}^{tr} = \xi_{ji}^{tr} \), so that the grand friction matrix is symmetric.

The relationship in Eq. (5) can be inverted to express the dependence of the velocities on the forces, in terms of a grand mobility matrix with the same block structure as the grand friction matrix,

\[
\begin{pmatrix} \mathcal{U} \\ \mathcal{O} \end{pmatrix} = \begin{pmatrix} \mu_{ij}^u & \mu_{ij}^r \\ \mu_{ij}^r & \mu_{ij}^{tr} \end{pmatrix} \begin{pmatrix} \mathcal{F} \\ \mathcal{T} \end{pmatrix},
\]

with

\[
\begin{pmatrix} \mu_{ij}^u & \mu_{ij}^r \\ \mu_{ij}^r & \mu_{ij}^{tr} \end{pmatrix} = \begin{pmatrix} \xi_{ij}^u & \xi_{ij}^r \\ \xi_{ij}^r & \xi_{ij}^{tr} \end{pmatrix}^{-1},
\]

or, more simply

\[
\xi_{ij}^{tr} \equiv (\mu_{ij}^u - \mu_{ij}^r \cdot \mu_{ij}^{tr})^{-1}.
\]

B. A rigid bead model

In the next step, we particularize further for the specific case in which we are concerned in this paper; 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 \( \omega \). The angular velocity of all the beads is \( \omega_i = \omega \), and the linear velocity of their centers are \( \mathbf{u}_i = \mathbf{u}_O + \omega \times \mathbf{r}_i \). The characteristic point \( P_i \) of each sphere, and \( \mathbf{r}_i = \mathbf{r}_{P_i} \) is its position vector from origin \( O \). Then Eqs. (1) and (2) now read

\[
F_i = \sum_{j=1}^{N} \xi_{ij}^u \mathbf{u}_O + \omega \times \mathbf{r}_j + \sum_{j=1}^{N} \xi_{ij}^r \mathbf{r}_j \cdot \omega_j,
\]

\[
T_{P_i} = \sum_{j=1}^{N} \xi_{ij}^u \mathbf{u}_O + \omega \times \mathbf{r}_j + \sum_{j=1}^{N} \xi_{ij}^r \mathbf{r}_j \cdot \omega_j.
\]

The vectorial products \( \mathbf{r}_i \times (\cdots) \) and \((\cdots) \times \mathbf{r}_i \), where \((\cdots)\) is any vector can be expressed conveniently in terms of dot products, in the forms \( \mathbf{A}_i \cdot (\cdots) \) and \((\cdots) \cdot \mathbf{A}_j \), where

\[
\mathbf{A}_i = \begin{pmatrix} 0 & -z_i & y_i \\ z_i & 0 & -x_i \\ -y_i & x_i & 0 \end{pmatrix}.
\]

Next, the total force \( \mathbf{F} \), and the total torque at a common origin, \( O \), can be obtained by summation of Eqs. (11) and (12) over all the beads,

\[
\mathbf{F} = \sum_{i=1}^{N} \mathbf{F}_i = \sum_{i=1}^{N} \left( \sum_{j=1}^{N} \xi_{ij}^u \mathbf{u}_O + \sum_{j=1}^{N} \xi_{ij}^r \mathbf{u}_j - \sum_{j=1}^{N} \xi_{ij}^r \mathbf{A}_j \right),
\]

\[
\mathbf{F} = \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ \xi_{ij}^u \mathbf{u}_O - \xi_{ij}^r \mathbf{A}_j + \xi_{ij}^r \mathbf{r}_j \cdot \omega \right],
\]

\[
\mathbf{T}_O = \sum_{i=1}^{N} \left( \mathbf{r}_i \times (\mathbf{F}_i + \mathbf{F}_j) \right) = \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ \xi_{ij}^r \mathbf{u}_O - \xi_{ij}^r \mathbf{A}_j + \xi_{ij}^r \mathbf{r}_j \cdot \omega + \xi_{ij}^r \mathbf{r}_i \cdot \omega \right],
\]

These expressions for the rigid bead models are to be compared with the general expressions for a general rigid body,

\[
\mathbf{F} = \Xi^u \cdot \mathbf{u}_O + \Xi^r \cdot \omega,
\]

\[
\mathbf{T}_O = \Xi^r \cdot \mathbf{u}_O + \Xi^r \cdot \omega.
\]

Factoring out \( \mathbf{u}_O \) and \( \omega \) in Eqs. (15) and (16) and comparing with (17) and (18) we arrive at the final results for the friction tensors.
From the symmetry relationships indicated above, we find
\[ \Xi'' = \sum_{i=1}^{N} \sum_{j=1}^{N} \xi_{ij}^{''}, \]
\[ \Xi''_0 = \sum_{i=1}^{N} \sum_{j=1}^{N} (-\xi_{ij}^{''} \cdot A_j + \xi_{ij}^{''}), \]
\[ \Xi''_l = \sum_{i=1}^{N} \sum_{j=1}^{N} (\xi_{ij}^{''} + A_i \cdot \xi_{ij}^{''}), \]
\[ \Xi''_n = \sum_{i=1}^{N} \sum_{j=1}^{N} (\xi_{ij}^{''} \cdot A_j + A_i \cdot \xi_{ij}^{''} - A_i \cdot \xi_{ij}^{''} \cdot A_j). \]

From the symmetry relationships indicated above, we find that
\[ \Xi''_0 = (\Xi''_0)^T, \] as required for the symmetry of the grand resistance matrix [Eq. (6)].

### III. DESCRIPTION OF THE HYDRODYNAMIC INTERACTION

As commented in the Introduction, a number of different treatments have been proposed for the friction or mobility matrices. Here we describe several advanced theories, and compare them with the simpler, more frequently used descriptions based on the Kirkwood–Riseman theory.

#### A. Hydrodynamic interaction theories of Reuland et al. (RFJ), Mazur-van Saarlos (MVS), and Goldstein (GOL)

In this work we consider three detailed theoretical descriptions of the hydrodynamic interaction in a multisphere system, proposed by Reuland, Felderhof, and Jones (RFJ), Mazur and van Saarlos (MVS), and Goldstein (GOL). The expressions for the mobility tensors in each of these theories are given in the Appendix. Here, we just intend to describe and compare the main features of the three treatments, and for this purpose, we have made a synthesis, noticing that the theoretical results of the three theories can be recast in a common form, in which the mobility matrices are expressed, in a compact and schematic manner, as

\[ \pi \eta_0 \mu_{ij}'' = \delta_{ij} \frac{1}{6a_i} \left( 1 + \delta_{ij} \right) \left[ \frac{1}{8r_{ij}} (I + P_{ij}) + \frac{(a_i^2 + a_j^2)}{8r_{ij}^3} (I - 3P_{ij}) + \frac{25a_i^3a_j^3}{8r_{ij}^5} P_{ij} \right] + \sum_{k \neq i,j} \sum_{s=1}^{N} \frac{a_i^{s-1}}{r^s} S_s(\hat{r}_{ik}, \hat{r}_{kj}) + \sum_{k \neq i,j} \sum_{l \neq i,j} \sum_{q=1}^{N} \frac{a_i^{q-1}}{r^q} Q_q(\hat{r}_{ik}, \hat{r}_{kl}, \hat{r}_{lj}), \]

\[ \pi \eta_0 \mu_{ij}'' = - (1 - \delta_{ij}) \frac{1}{8r_{ij}} \epsilon \cdot \hat{r}_{ij} + \sum_{k \neq i,j} \sum_{w=1}^{N} \frac{a_i^{w-2}}{r^w} W_w(\hat{r}_{ik}, \hat{r}_{kj}), \]

where \( a_i \) is the radius of the bead \( i \), \( r_{ij} \) is the vector from the center of bead \( i \) to the center of bead \( j \), \( r_{ij} \) is the center-to-center distance, \( \hat{r}_{ij} = r_{ij}/r_{ij} \) is the unitary center-to-center vector, \( I \) is the identity matrix, and

\[ P_{ij} = \hat{r}_{ij} \hat{r}_{ij} = \frac{r_{ij}^2}{r_{ij}^2}. \]

In Eq. (24), \( \epsilon \) is the Levi-Civita tensor, and the product \( \epsilon \cdot \mathbf{r} \), where \( \mathbf{r} \) is any vector with Cartesian coordinates \((x, y, z)\), is given by

\[ \epsilon \cdot \mathbf{r} = \begin{pmatrix} 0 & z_{ij} & -y_{ij} \\ -z_{ij} & 0 & x_{ij} \\ y_{ij} & -x_{ij} & 0 \end{pmatrix}. \]

In Eqs. (23)–(25), \( \delta_{ij} \) is the Kronecker’s delta, so that the terms with a \( \delta_{ij} \) factor take place in the \( \mu_{ii} \)'s only and those with \((1 - \delta_{ij})\) in the \( \mu_{ij} \)'s with \( i \neq j \) only. The mobility tensors \( \mu_{ij} \) contain, first, two-body terms depending on the radii, \( a_i \) and \( a_j \), and the distance vector \( r_{ij} \), that are followed by three-body terms, and even four-body terms representing how the hydrodynamic interaction between \( i \) and \( j \) is influenced by other individual beads, \( k \), or bead pairs, \((k,j)\). These terms are indicated, respectively, as sums \( \Sigma_{k \neq i,j} \) and \( \Sigma_{k \neq i,j} \Sigma_{l \neq i,j} \). The contributions from bead \( k \) or bead pair \( k,j \) contain one or more terms and are therefore indicated as sums such as \( \Sigma_{s=1,2,\ldots} \), where \( s_1 \) is the lowest index. The terms to be summed have the form, for example, \( r^{-s} a_i^{-n} S_s(\hat{r}_{ik}, \hat{r}_{kj}) \), \( r^{-n} \) stands for a product such as \( r_{ik}^{-n_1} r_{kj}^{-n_2} \cdots \) with \( n_1 + n_2 + \cdots = n \) and, similarly, \( a^m \) stands for a product \( a_i^{m_1} a_j^{m_2} a_k^{m_3} \cdots \) with \( m_1 + m_2 + m_3 + \cdots = m \). The tensorial functions that appear in the two body and three body terms, such as \( S_s(\hat{r}_{ik}, \hat{r}_{kj}) \) depend on the unitary distance vectors, i.e., on their orientation but not on the scalar distances.

The form in which we have synthesized the three theories allows an analysis of the dependence of the various terms on the intersphere distances, which appear as powers \( r^{-n} \) or \( r^{-m} \). One may envision a situation in which a given multisphere structure is uniformly expanded, keeping constant the radii, \( a_i \), increasing the distances \( r_{ij} \), and preserving the initial geometry, so that the unitaries \( \hat{r}_{ij} \) remain unchanged. The solvent would drain more and more freely within the structure, and the hydrodynamic interactions fall to zero as \( r^{-n} \), approaching the completely free draining limit.
TABLE I. Powers of \( r_{ij} \) or \( r \) in the expressions of the mobility matrices. Values between parentheses and double parentheses are, respectively, for three-body and four-body terms.

<table>
<thead>
<tr>
<th></th>
<th>MVS</th>
<th>RFJ</th>
<th>GOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_{ii}^m )</td>
<td>0, (−4, −6),((−7))</td>
<td>0, (−4)</td>
<td>0, (−4) *</td>
</tr>
<tr>
<td>( \mu_{jj}^m )</td>
<td>−1, −3, (−4, −6),((−7))</td>
<td>−1, −3, −7</td>
<td>−1, −3</td>
</tr>
<tr>
<td>( \mu_{ij}^m )</td>
<td>0, (−6)</td>
<td>0, (−6, −8)</td>
<td>0, (−6) *</td>
</tr>
<tr>
<td>( \mu_{ij}^r )</td>
<td>−3, (−6)</td>
<td>−3, −9</td>
<td>−3</td>
</tr>
<tr>
<td>( \mu_{ij}^r )</td>
<td>−2, (−5, −7)</td>
<td>−2</td>
<td>(−6) *</td>
</tr>
<tr>
<td>( \mu_{ij}^r )</td>
<td>−2, (−5, −7)</td>
<td>−2</td>
<td>−2</td>
</tr>
</tbody>
</table>

*Lowest order in a series expansion.

The theory of Reuland, Felderhof, and Jones (RFJ) (Ref. 32) is formulated in principle for a pair of beads but can be generalized for a multispher system. Thus, the \( \mu_{ij} \) tensors with \( i \neq j \) do not contain two-body terms. However, contributions from the second bead appear in the \( \mu_{ii} \)’s, that give rise to three-body terms in the generalization. The theory of Mazur and van Saarlos (MVS) (Ref. 33) is the most extensive; it was devised to derive many-body interactions; these authors report up to four-body terms in \( \mu_{ij}^m \). In both the RFJ and MVS theories, the various terms contain explicitly the \( r^{-n} \) powers. On the contrary, in the theory of Goldstein (GOL), which differs form the RFJ and MVS in being based on the variational calculation (see Ref. 35 for a discussion of variational methodology), the various terms are not only \( r^{-n} \) powers but contain also terms such as \( \ln[1 + a_j/(1 - a_j)] \), \( a_j/(1 - a_j^2) \), etc., where \( a_j = a_i/r_{ij} \). Making the necessary Taylor series expansion, these functions can be replaced by polynomials in \( a_j \) and subsequently the GOL expressions could be recast as the sum of terms containing \( r^{-n} \). We have made only the first stage of such replacement, just to find the lowest values of the exponents \( s_1, q_1, w_1 \), etc. in Eqs. (23)–(25).

The two-body terms in all the \( \mu_{ij} \)’s up to \( r_{ij}^{-3} \) are the same for RFJ, MVS, and GOL theories. (This observation suggests the proposal, in this work, of a simplified third-order treatment, as described below.) The two-body terms indicated as \([\ldots]\) in \( \mu_{ij}^m \) and \( \mu_{ij}^r \) appear exclusively in the RFJ theory. RFJ and GOL give three-body terms of the order of \( r^{-4} \) in \( \mu_{ij}^m \), but not in \( \mu_{ij}^r \), while in MVS there are \( r^{-4} \) and \( r^{-6} \) three-body terms and \( r^{-7} \) four-body terms in both \( \mu_{ij}^m \) and \( \mu_{ij}^r \). In \( \mu_{ij}^r \), GOL and RFJ predict \( r^{-6} \) three-body terms, but not in \( \mu_{ij}^r \), while MVS gives \( r^{-6} \) three-body terms in both \( \mu_{ij}^m \) and \( \mu_{ij}^r \). Finally, \( \mu_{ij}^r \) has no two-body contributions, and contains three-body terms of the order of \( r^{-7} \) (see Table I).

B. Quasiexact results for two spheres

The problem of translational and rotational dynamics of a pair of spheres has been the subject of considerable attention by various workers. Numerical results for the two translational and two rotational diffusion coefficients of a pair of identical spheres can be obtained from quasiexact treatments.36–39 For two spheres of arbitrary size, a convenient source is the study of Jeffrey and Onishi (JON) (Ref. 40) on dimensionless, translational, and rotational mobility functions, \( x \)’s and \( y \)’s that, in the notation of these authors, are defined so that

\[
\mu_{ij}^m = \frac{1}{3 \pi (a_i + a_j)} \left[ x_{ij}^d P + y_{ij}^d (I - P) \right],
\]

\[
\mu_{ij}^r = \frac{1}{\pi (a_i + a_j) \rho} j y_{ij}^b \cdot \hat{r}_{ij},
\]

\[
\mu_{ij}^r = \frac{1}{\pi (a_i + a_j)^3} \left[ x_{ij}^e P + y_{ij}^e (I - P) \right].
\]

Jeffrey and Onishi have reported very accurate results (obtained, in some cases, by summation of series up to terms of \( r_{12}^{-220} \)) for the \( x \)’s and \( y \)’s in Eqs. (28)–(30), expressed as functions of the parameters \( S = 2 r_{12} / (a_1 + a_2) \) (\( S = 2 \) for touching beads) and \( \lambda = a_2/a_1 \) (\( \lambda = 1 \) for identical beads). Their results can be found in Tables 13–15 and 17–20 of their paper.

C. The Kirkwood–Riseman and related treatments

The original Kirkwood–Riseman (KRO) treatment of macromolecular bead models consists of assigning a translational friction coefficient \( \zeta_i = 6 \pi n \eta a_i \), to each bead, and representing the hydrodynamic interaction by means of the Oseen tensor. It can be easily shown that this is equivalent to taking the first term, of order \( r_{ij}^{-1} \) in \( \mu_{ij}^m \),

\[
\mu_{ij}^m = \delta_{ij} (6 \pi n \eta a_i)^{-1} I + (1 - \delta_{ij}) (8 \pi n \eta r_{ij}^{-1}) (I + P_{ij}).
\]

In the original KRO treatment \( \mu_{ij}^{rr} \) are taken as zero.

A common modification of the KRO treatment consists of using a modified Oseen tensor, given by the Rotne–Prager–Yamakava expression for identical beads, or, more generally, the García de la Torre–Bloomfield expression for nonidentical beads. In the Kirkwood–Riseman treatment with a modified tensor (KRM), the translational mobility matrix is formulated as

\[
\mu_{ij}^m = \delta_{ij} (6 \pi n \eta a_i)^{-1} I + (1 - \delta_{ij}) (8 \pi n \eta r_{ij}^{-1}) (I + P_{ij}) + (8 \pi n \eta r_{ij}^{-3}) (a_i^2 + a_j^2) (I - 3 P_{ij}),
\]

and \( \mu_{ij}^{rr} \) are, again, neglected.

It has been pointed out that the KR treatment so formulated contains a deficiency that affects the calculation of rotational properties and intrinsic viscosity. This problem was not evident in the earliest applications of the KR treatment because it was applied to long, straight or random chains with many elements.45–47 That deficiency was corrected by including the so-called volume correction. Now, in terms of the mobility tensors and functions, that deficiency is clearly seen; there is an inconsistency in representing \( \mu_{ij}^m \) with terms of the order of \( R^{-1} \) or \( R^{-3} \) and missing a zeroth order contribution to the rotational function, which should be (at least)

\[
\mu_{ij}^{rr} = (8 \pi n \eta a_i^3)^{-1} I.
\]
When Eq. (33) is employed along with Eq. (31) [or Eq. (32)], the Garcia de la Torre–Rodes volume correction is found. It consists of adding $6 \eta_0 V_m I$ to the diagonal components of the rotational friction tensor, $\Xi'_0$, with $V_m = \sum_i (4 \pi a_i^3 / 3)$ being the volume of the bead model. This correction can be applied to values from the original or modified interaction tensors; these two cases will be denoted, respectively, as KROV and KR MV.

In these KR-based treatments including those with volume correction, the main computational task is the inversion of the $3 \times 3$ translational mobility matrix, $\mu^{rr}$. We note now that, for consistency with the introduction in Sec. IV, the rotational friction tensor, $\mu^{rr}$, and $\mu^{tt}$, terms up to $r_{ij}^{-3}$, one may wish to include the $r_{ij}^{-2}$ and $r_{ij}^{-3}$ terms that take place in the $rt$ and $rr$ matrices. Up to order $r_{ij}^{-3}$, we have

$$\mu^{rr}_{ij} = -(1 - \delta_{ij})(8 \pi \eta_0 a_i^3)^{-1} \hat{r}_{ij}, \tag{34}$$

and

$$\mu^{rt}_{ij} = \delta_{ij}(8 \pi \eta_0 a_i^3)^{-1} + (1 - \delta_{ij})(16 \pi \eta_0 a_i^3)^{-1}(3 P_{ij} - I). \tag{35}$$

This will be denoted as the third-order treatment (3RD), and it involves the inversion of full $6N \times 6N$ grand mobility matrix.

### D. Other strategies: Cubic substitution and shell model

When the failure of the standard KR procedure for rotational diffusion was described, the first remedy put forward by Wilson and Bloomfield consisted of replacing some or all the beads in the primary model by a cubic array of smaller beads. Then a KRO or KR M calculation is carried out to obtain the properties. Thus, in this cubic substitution (CBS) the frictional force at the primary bead is moved away from its center, being instead distributed closer to the surface of the parent sphere, where it actually acts. This is of little effect for the total force that determines the translational coefficients, but has a very beneficial influence in the calculation of the torques that determine the rotational quantities. This modeling strategy has the obvious inconvenience of increasing the computer times, since the number of frictional elements, $N$, is increased to $8N$ after the cubic substitution. Anyhow, for moderate $N$’s this increase can be afforded; such is the case in the study of properties of oligomeric arrays or chains.

The cubic substitution is a modeling strategy intermediate between the bead modeling in strict sense and the shell modeling. In shell modeling (SHM), as originally proposed by Bloomfield and Riseman, the arbitrarily shaped surface of the hydrodynamic particle is described as a shell of many small frictional elements, to which the standard Kirkwood–Riseman–Oseen treatment is applied; indeed, its computational requirements are notoriously large. The results are extrapolated to the limit of zero element size. As described elsewhere, this modeling strategy must be differentiated from bead modeling since it avoids the representation of the particle as a discrete set of spherical subunits. However, for the purpose of the present study we can take the straightforward step of remodeling the bead model as a shell model, simply replacing each bead by a spherical shell.

### IV. NUMERICAL RESULTS

We have applied the various treatments, from the simple Oseen-tensor description, to the most elaborated treatments of HI to various rigid structures described below, that serve as test cases. In the presentation of results (Table II) we chose as a reference for each case a HI treatment that is presumably quasiexact, giving the numerical values of the solution property for this treatment, while for all the other treatments we just give the relative, percent deviation, i.e., 100 (value-reference/reference). All these structures are axially symmetric and therefore the set of primary hydrodynamic properties reduce to two translational coefficients, $D_t^i$ and $D_t^r$, and two rotational coefficients, $D_r^i$ and $D_r^r$, which are the diagonal components of the corresponding translational and rotational diffusion tensors, $D_i$ and $D_r$, calculated from the friction tensors $\Xi^{ii}, \Xi^{rr}$, and $\Xi^{ir}$ in the general way described elsewhere. Although for the test structures to be considered here, that have an axis and a center of symmetry, we simply have $D_i = k_B T (\Xi^{ii})^{-1}$ and $D_r = k_B T (\Xi^{rr})^{-1}$, where $O$ is the particle’s center.

The experimentally observable properties are combination of the parallel and perpendicular coefficients. The overall translational diffusion coefficient is $D_t = (D_t^i + 2D_t^r)/3$, while the rotational dynamics depends on up to three relaxation times, of which we just consider here the longest and shortest ones, given by $\tau_r = 1/(6D_r^r)$ and $\tau_5 = 1/(4D_r^r + 2D_r^r)$. The numerical values in Table II are for the dimensionless quantities $(6 \pi \eta_0 a^3 / k_B T) D_i, (6 \pi \eta_0 a^3 / k_B T) D_r$, and $(k_B T / 6 \pi \eta_0 a^3 / \tau)$, where $u$ is some convenient unit of length.

A simple but significant case is a rigid dimer ($N = 2$). The influence of hydrodynamic interactions on the hydrodynamic property of the dimer is greatest when the two spheres are identical ($a_1 = a_2$) and touching each other ($r_{21} = a_1 + a_2$). As described above, nearly results are available for this case. We choose for reference the same set of values or quasiexact values as in our previous work, although the Jeffrey–Onishi results are also practically exact. For the diverse HI treatments, the deviations from the reference values are given in Table II, both for the primary coefficients as well as for the observable properties.

We have also considered a dimer of unequal spheres. Hydrodynamic interaction effects will be less influential, but it is convenient to run calculations with different spheres to check the computer algorithms. For this case we take the two-spheres results of Jeffrey and Onishi as the reference. The numerical values are in Table II.

We have also considered cases with more spheres, that may be representative of the structures that we find in modeling biological macromolecules. Particularly, we have made calculations for two structures with $N = 6$ beads. One of them is a straight array in which the beads are touching and collinear, that is representative of various biological macromolecules that have a rigid rodlike shape of moderate aspect ratio. The other hexameric array is an octahedron, which has
V. DISCUSSION

The discussion of the results for translational quantities is simple because even the more primitive methods are well behaved. It is interesting to note that the KRO results are not necessarily better than the KRO results. The main virtue of the modified Oseen tensor is not a general (and anyhow moderate) improvement in numerical results, but essentially the removal of singularities that may appear in some circumstances and produce large errors.51,52 Some noteworthy features displayed by the translational results in Table II are the high performance of the cubic substitution and, among the higher-order-HI treatments, that of the Goldstein theory.

An important antecedent of this work is the study of higher-order HI effects in translational properties of bead models, carried out by Phillips53 employing a hydrodynamic tensor based on the Mazur–van Saarlos $\mu_0^{ij}$ mobilities. Phillips noticed that when successive, higher-order terms are added in the two-body interactions, or when one goes from two-body to three-body and four-body interaction, no clear improving trend is found; instead, the successive results fluctuate and the values obtained with high-order, many-body interaction are not essentially better than with just the modified Oseen tensor. As this author was mainly concerned with translational properties, the calculation of rotational mobilities was avoided making the assumption $\xi^{ii}=(\mu^{ij})^{-1}$, instead of Eq. (8). The influence of this assumption on the conclusions may be marginal. Indeed, in our results we observe a similar trend; the translational results of what we propose as a third-order two-body treatment [Eqs. (31)–(35)] present deviations of about 2% only, even somewhat better than those of some higher-order treatments.

The above commented peculiarities of the results of the various treatments for translational diffusion are less relevant than the discussion of rotational diffusion properties, where the main deficiencies of the old treatments were found, and where the most substantial improvements might be expected.

### Table II. Deviations of the calculated properties from the various methods, from the indicated values of a reference method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Exact (Ref.)</th>
<th>JO</th>
<th>SHM</th>
<th>CBS</th>
<th>KRO</th>
<th>KRM</th>
<th>KROV</th>
<th>KRMV</th>
<th>RFJ</th>
<th>MVS</th>
<th>GOL</th>
<th>3RD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_1$</td>
<td>1.5504</td>
<td>0.7</td>
<td>0.3</td>
<td>1.1</td>
<td>12.9</td>
<td>4.8</td>
<td>4.7</td>
<td>4.7</td>
<td>1.9</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_2$</td>
<td>1.3803</td>
<td>0.1</td>
<td>0.2</td>
<td>-0.6</td>
<td>-0.4</td>
<td>4.1</td>
<td>-0.4</td>
<td>4.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>$D_3$</td>
<td>1.4370</td>
<td>0.3</td>
<td>0.2</td>
<td>0.0</td>
<td>4.4</td>
<td>4.4</td>
<td>4.4</td>
<td>1.8</td>
<td>1.8</td>
<td>1.1</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>$D_4$</td>
<td>3.3708</td>
<td>-1.4</td>
<td>-2.7</td>
<td>0.4</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>-11.0</td>
<td>-11.0</td>
<td>-0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>$\tau_s$</td>
<td>0.1044</td>
<td>1.0</td>
<td>-0.3</td>
<td>0.9</td>
<td>-36.1</td>
<td>-29.0</td>
<td>17.0</td>
<td>24.1</td>
<td>0.3</td>
<td>-0.4</td>
<td>-0.9</td>
<td>-1.4</td>
</tr>
<tr>
<td>$D_5$</td>
<td>1.5957</td>
<td>-1.0</td>
<td>0.3</td>
<td>-0.6</td>
<td>57.5</td>
<td>40.9</td>
<td>-14.5</td>
<td>-19.4</td>
<td>-0.3</td>
<td>0.4</td>
<td>0.9</td>
<td>1.4</td>
</tr>
<tr>
<td>$\tau_c$</td>
<td>0.0601</td>
<td>1.4</td>
<td>0.2</td>
<td>-0.1</td>
<td>-100.0</td>
<td>-100.0</td>
<td>13.2</td>
<td>14.4</td>
<td>0.8</td>
<td>-0.2</td>
<td>0.1</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

**Notes:**
- **Dimer, $a_1=0.5$, $a_2=0.5$, $r_{12}=1.0$**
- **Linear hexamer, touching beads, $a=0.5$**
- **Octahedral hexamer, touching beads, $a=0.5$**

On the other hand, the octahedron is the preferred structure of important (hexameric) multisubunit proteins such as the seed globulins, whose hydrodynamic modeling have been described elsewhere. Results for the linear and octahedral hexamers are given in Table II.
Prior to the analysis of the more advanced descriptions of HI, it seems pertinent to make some remarks on the previous, primitive or ad hoc methods. The failure of the original Oseen or modified Oseen treatments for rotational diffusion is evident, as it yields abnormal values for $D_r^{zz}$ and an unphysical, zero value for $D_r^{rr}$ in the cases of linear structures. When the zeroth order term of $\mu^r_{ii}$ is introduced as the so-called volume correction in the KROV and KRMV methods, the rotational diffusion coefficients are clearly overestimated but, anyhow, the results are more meaningful than in the bare KRO or KRM treatments. The cubic substitution and the shell models always give results quite close to the exact or advanced procedures. The shell model is computationally expensive and, as commented above, its scope is different from that of bead models in strict sense. For the latter models, the ad hoc procedure was the cubic substitution, which is found in Table II to give excellent results for all the properties of all the test particles. This gives support to the use made in previous work of this procedure to model oligomeric structures.\footnote{15,28}

Of more importance, within the context of the present work, is the performance of the higher-order procedures, which varies slightly from one property to the other, or from one structure to another, although some trends can be inferred from the results in Table II. Thus, the results from MVS treatment appear to be somewhat more deviated from the rest of treatments. One may suspect that the inclusion of many-body interactions may not be reflected in improved results, as concluded for translational properties by Phillips.\footnote{53} The RFJ procedure yields values very close to those from the GOL procedure, although the latter includes three-body interactions that are not included in the former.

While the KR-based procedures, including those with volume correction, are based on a grand friction of diffusion tensor of dimension $3N\times3N$, with $N\times N \times 3$ blocks, all the higher-order procedures (3RD, MVS, RFJ, and GOL) include the pure rotational, $rr$, and coupling $tr$ blocks, and the grand friction and diffusion tensors are $6N\times6N$ [Eq. (7)]. This implies some increase in computer requirements, mainly due to the need of inverting three $3N\times3N$ matrices \[\text{[Eqs. (8)–(10)]}\] rather than only one. Roughly speaking, the computer needs for a higher-order calculation with $N$ beads, are similar to that of a KR calculation with $2N$ beads. A factor of 2 in the number of beads may be unimportant; rather, actual improvements in the representativity of a bead model, either for compact or for chainlike macromolecules, may require to increase $N$ by an order of magnitude. Therefore, higher-order procedures are seemingly affordable. Furthermore, the numerous, elaborate calculations required in three-body and four-body treatments (GOL and MVS) are replaced by simpler computations in two-order treatments (RFJ and 3RD). Particularly, the calculations are simplest for the 3RD procedure, which still is able to predict translational and rotational properties with expected deviations of just a few percent, within the range of typical experimental errors.

VI. CONCLUDING REMARKS

When bead models have a moderate number of beads, or when one or a few of the beads are large and dominate the frictional properties of the whole particle, the original KR treatment fails. In this paper we have shown that this failure can be avoided with improved descriptions of hydrodynamic interaction, some of which present a very good balance between effectiveness and computational cost. This conclusion adds further merits to the bead modeling methodology.

It should be mentioned that the bead modeling approach is not the only method available to study the transport properties of complex, rigid particles. An alternative procedure is the boundary element method,\footnote{54} pioneered by Youngren and Acrivos.\footnote{55,56} This method is powerful since it allows the consideration of various hydrodynamic behaviors (stick and slip conditions) and makes it possible to include, within an unified treatment, electrostatic and other physical aspects, which allows treating complex phenomena such as electrophoresis.\footnote{57} On the other hand, bead models are, in the opinion of many workers, more intuitive and simpler to build, particularly when the object is not compact and very irregular. The idea of using spherical elements for modeling, is appealing for molecular biologists, because parts of the macromolecule (subunits) can be represented individually. Also, from a chemical point of view, it is interesting to employ beads to represent molecular entities such as repeating units or even atoms. Also, the methodologies (like the treatments for hydrodynamic interactions, studied in this paper) developed for bead models can be applied not only to rigid particles, but also to flexible or semiflexible macromolecules, which are customarily modeled as chains of beads.

In the present work we have assumed that the beads in the model obey the stick boundary conditions, which is applicable to particles of macromolecular size. We have also restrict our study to the case when there are no external forces in the surrounding fluid, as it happens for translational and rotational friction or diffusion in a quiescent solvent, which are the properties considered in our study. However, we think that the treatment could be extended to cover both aspects. The formalism can be applied using mobility matrices for spheres with slip boundary conditions. The consideration of solvent flows will require a much more complex formalism to include stresslets and gradients, but we hope that this is under our reach, so that the improvements could be extended to the intrinsic viscosity and rheological properties.

VII. COMPUTER PROGRAMS

The computer algorithms developed for this work will be publicly available in the form of Fortran source code, and can be freely downloaded from our web site, http://leonardo.fcu.um.es/macromol, where the latest versions of our public-domain programs HYDRO (Ref. 17) and SOLPRO (Refs. 58–60) are deposited. Now HYDRO includes and option to carry out the calculation of translational and rotational coefficients using the third-order procedure (3RD) as suggested in this work. A separate file (bldall.x.f, where x is a version number), will contain the subroutines that implement the JON (for two beads), GOL, MVS, and RFJ methods. The user may easily replace the 3RD subroutine implemented in HYDRO by any of the other methods.
ACKNOWLEDGMENTS

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APPENDIX A: GOLDSTEIN EXPRESSIONS

\[
\mu^{\sigma\sigma}_{ii} = \frac{1}{6 \pi \eta_0 a_i} \mathbf{I} + \frac{1}{64 \pi \eta_0 r_{ij}} \left[ \mathbf{I} \left\{ \left( \frac{9}{2} + 3 \alpha_j^2 \right) \ln \frac{1 + \alpha_j}{1 - \alpha_j} - 3 \alpha_j - \frac{6 \alpha_j}{1 - \alpha_j} + \alpha_j^2 \left( \frac{16 \alpha_j}{3(1 - \alpha_j)^3} - \frac{28 \alpha_j}{3(1 - \alpha_j)^2} + \frac{2 \alpha_j}{1 - \alpha_j} \right) \right\} + \mathbf{P}_{ij} \left[ 9 \alpha_j - \frac{6 \alpha_j}{1 - \alpha_j} \left( \frac{9 \alpha_j^2}{2} + \frac{3}{2} \ln \frac{1 + \alpha_j}{1 - \alpha_j} \right) \right] + \left( \frac{1}{1 - \alpha_j} \right)^2 \right] \]  
\[
+ \left( \frac{1}{1 - \alpha_j^2} \right)^2 \right] + \mathbf{P}_{ij} \left[ 24 \alpha_j \left( \frac{1}{1 - \alpha_j^2} \right)^3 - \frac{9 \alpha_j}{1 - \alpha_j^{1/2}} \right], \quad (A1)
\]

\[
\mu^{\sigma\sigma}_{ij} = \frac{1}{8 \pi \eta_0 a_i} \sum_{j \neq i} \frac{1}{256 \pi \eta_0 r_{ij}} \left[ \mathbf{I} \left( -\frac{40 \alpha_j}{1 - \alpha_j} + \frac{34 \alpha_j}{1 - \alpha_j^2} + \frac{3 \alpha_j^2}{2} \ln \frac{1 + \alpha_j}{1 - \alpha_j} \right) \right] \]  
\[
+ \mathbf{P}_{ij} \left( \frac{24 \alpha_j}{1 - \alpha_j^2} - \frac{6 \alpha_j}{1 - \alpha_j^{1/2}} - \frac{9 \alpha_j}{1 - \alpha_j^{1/2}} \right), \quad (A2)
\]

\[
\mu^{\sigma\sigma}_{i\bar{i}} = \frac{1}{8 \pi \eta_0 r_{ij}} \left[ \mathbf{I} \left( 1 + \frac{\alpha_i^2 + \alpha_j^2}{3} \right) + \mathbf{P}_{ij} \left( (1 - (\alpha_i^2 + \alpha_j^2)) \right) \right], \quad (A3)
\]

\[
\mu^{\sigma\sigma}_{i\bar{j}} = \frac{1}{16 \pi \eta_0 r_{ij}} (-\mathbf{I} + 3 \mathbf{P}_{ij}), \quad (A4)
\]

\[
\mu^{\sigma\sigma}_{\bar{i}\bar{j}} = \frac{1}{8 \pi \eta_0 r_{ij}} e \cdot \mathbf{r}_{ij}, \quad (A5)
\]

where \( \alpha_i = a_i/r_{ij} \) and \( \alpha_j = a_j/r_{ij} \).

APPENDIX B: MAZUR-VAN SAARLOS EXPRESSIONS

\[
\mu^{\sigma\sigma}_{ij} = \frac{1}{6 \pi \eta_0 a_i} \left[ \delta_{ij} \mathbf{I} + \frac{3}{4} \mathbf{A}_{ij} \mathbf{P}_{ij} - \frac{3}{4} \mathbf{A}_{ij}(a_i^2 + a_j^2) \left( \mathbf{P}_{ij} - \frac{1}{3} \mathbf{I} \right) \right] + \sum_{k \neq i, j} \frac{3}{8 \pi r_{ik}^2 r_{kj}} \left[ a_i a_j \left( 5 a_i^2 + 3 a_j^2 \right) \left( 1 - \frac{3 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2}{5} \right) \mathbf{r}_{ik} \mathbf{r}_{kj} \right]  
\]
\[
+ \frac{3}{8 \pi r_{ik}^2 r_{kj}} \left[ a_i a_j \left( 49 - 117 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2 \right) \left( 1 - \frac{3 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2}{5} \right) \mathbf{r}_{ik} \mathbf{r}_{kj} \right] + \frac{3}{8 \pi r_{ik}^2 r_{kj}} \left[ a_i a_j \left( 49 - 117 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2 \right) \left( 1 - \frac{3 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2}{5} \right) \mathbf{r}_{ik} \mathbf{r}_{kj} \right]  
\]
\[
+ \frac{3}{8 \pi r_{ik}^2 r_{kj}} \left[ a_i a_j \left( 49 - 117 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2 \right) \left( 1 - \frac{3 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2}{5} \right) \mathbf{r}_{ik} \mathbf{r}_{kj} \right] + \frac{3}{8 \pi r_{ik}^2 r_{kj}} \left[ a_i a_j \left( 49 - 117 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2 \right) \left( 1 - \frac{3 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2}{5} \right) \mathbf{r}_{ik} \mathbf{r}_{kj} \right]  
\]
\[
\times (1 - 3 (\mathbf{r}_{ik} \cdot \mathbf{r}_{kj})^2), \quad (B1)
\]
\[ \mu_{ij}^{rr} = \frac{1}{12 \pi \eta \eta_0 a_i^2} \left[ -\frac{3}{2 r_{ij}} a_i^2 \epsilon \cdot r_{ij} + \sum_{k \neq i, j} \frac{45}{4 r_{ik} r_{kj}} a_i^2 a_j^3 (r_{ik} \cdot r_{kj}) (r_{jk} \cdot r_{ik}) - \frac{3}{4 r_{ik} r_{kj}} a_i^2 a_j^3 (3a_k^2 + 5a_j^2) (5 (r_{ik} \cdot r_{kj}) (r_{jk} \cdot r_{ik})) \\
\times (r_{ik} \cdot r_{kj}) - (r_{ij} \cdot r_{kj}) (r_{jk} \cdot r_{ik}) + (r_{ik} \cdot r_{kj}) \epsilon \cdot r_{jk} + (r_{ik} \cdot r_{kj}) (r_{ik} \cdot r_{ij}) \epsilon \cdot r_{jk} + \frac{9}{32 r_{ik} r_{kj}} a_i^2 a_j^5 (25 (1 - 7 (r_{ik} \cdot r_{kj})) (r_{jk} \cdot r_{ik}) r_{ij} + 50 (r_{ik} \cdot r_{kj}) (r_{jk} \cdot r_{ik}) r_{ij} - 16 (r_{ik} \cdot r_{kj}) (r_{jk} \cdot r_{ij}) \epsilon \cdot r_{kj} - 3 (1 - 5 (r_{ik} \cdot r_{kj})^2) \epsilon \cdot r_{jk}) \right] , \]

\[ \mu_{ij}^{rr} = \frac{1}{8 \pi \eta \eta_0 a_i^3} \left[ \frac{15}{3} a_j^3 (r_{jk} \cdot r_{ik}) (r_{jk} \cdot r_{ij}) \\
+ (r_{ik} \cdot r_{kj}) r_{ik} r_{jk} - (r_{ik} \cdot r_{jk})^2 \right] . \]

APPENDIX C: REULAND–FELDERHOF–JONES EXPRESSIONS

The Reuland–Felderhof–Jones expressions, for stick conditions, are

\[ \mu_{ij}^{rr} = \frac{1}{8 \pi \eta_0} \left[ \frac{4}{3 a_j} + \sum_{j \neq i} \left[ -5 a_j^3 P_{ij} - 10 a_j^2 a_i^3 P_{ij} \right] r_{ij} \right] \\
- \frac{7}{20} a_j^2 P_{ij} - a_j P_{ij} - \frac{1}{10} \left( \frac{2}{3 a_j^2} \right) \left( I + 3 P_{ij} \right) r_{ij} \left( a_j \right) \\
+ 3 a_j P_{ij} r_{ij} \right] , \]

\[ \mu_{ij}^{rr} = \frac{1}{8 \pi \eta_0} \left[ \frac{I}{a_j} - \sum_{j \neq i} \left( \frac{15}{4} a_j I P_{ij} r_{ij}^2 + \frac{35}{4} a_j^5 I P_{ij} r_{ij}^3 \right) \right] , \]

\[ \mu_{ij}^{rr} = \frac{1}{8 \pi \eta_0} \left[ I + 2 P_{ij} \right] r_{ij} \left( a_j \right) \\
+ a_j^2 I - 2 P_{ij} r_{ij} \right] , \]

\[ \mu_{ij}^{rr} = \frac{1}{8 \pi \eta_0} \left[ \frac{I + P_{ij}}{r_{ij}} + \left( a_j^2 + a_i^2 \right) \frac{I - 3 P_{ij}}{r_{ij}} + 25 a_j^3 a_i^3 P_{ij} r_{ij} \right] , \]

\[ \mu_{ij}^{rr} = \frac{1}{8 \pi \eta_0} \left[ \frac{1}{r_{ij}} + \frac{75}{8} a_j^3 a_i P_{ij} r_{ij} \right] . \]

\[ \mu_{ij}^{rr} = \frac{1}{8 \pi \eta_0} \left[ \frac{-1 + 3 P_{ij}}{2 r_{ij}^3} + 75 a_j^3 a_i P_{ij} r_{ij} \right] . \]


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