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ORIGINAL PAPER

Intrinsic viscosity of bead models for macromolecules and nanoparticles

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Abstract The calculation of the intrinsic viscosity by means of classical treatments of bead models, typically composed of a number of identical beads, presents some problems when applied to models where the beads are unequal and their number is not very large. A correction to this problem was proposed 10 years ago (García de la Torre and Carrasco in Eur Biophys J 27:549–557, 1998). This so-called volume correction, which consisted of adding a term proportional to the volume of the model, was proved to be rigorous in physico-mathemathical terms, and produced improved results in some circumstances, but not always. Recently, the volume correction is being reconsidered so that with some deduced or empirical modifications, it can allow for safer predictions of the intrinsic viscosity. This paper contributes a discussion and further improvements of that correction for the intrinsic viscosity.

Introduction and theory

Since the early years of physical biochemistry and polymer science, it is well known that macromolecules in solution have the important effect, in some case remarkably intense, of increasing the viscosity of the solute. The quantity that characterizes this effect, namely, the intrinsic viscosity $[\eta]$, depends in a sensitive manner on the size, shape or flexibility of the macromolecular solute, and it is therefore informative about those aspects (Serdyuk et al. 2007). Until the 1980s, it was profusely used as a tool of macromolecular characterization. Inconveniences of the measurement of $[\eta]$, which is determined by the solution viscosities at various concentrations, and advantages of other hydrodynamic techniques like dynamic light scattering or modern analytical ultracentrifugation, caused a decline in the usage of $[\eta]$ measurements. However, as reviewed by Harding (1997), the study of $[\eta]$ of bio-macromolecular solutions is having a renaissance because of advances in instrumentation, like the differential viscometer (Longman et al. 2006), the microfluidic "viscometer-on-a-chip" (Lee and Tripathi 2005), or the coupling of on-line viscometers to separation (GPC or AFFF) techniques that allow the measurement for several components in a sample (Longman et al. 2006). Also, the repeated measurements at varying concentration may be replaced by single-concentration determinations (Solomon and Ciuta 1962; Pamies et al. 2008).

In contrast to the past and present importance of the determination of $[\eta]$, its theoretical description and computational prediction for rigid bead models representing particles of arbitrary shape, has presented various difficulties. The classical bead model theories of Kirkwood and Riseman (KR) (Kirkwood and Riseman 1948; Riseman and Kirkwood 1950; Yamakawa 1971) were devised for models, representing long rigid rods or flexible chains having a large number N of identical beads. Thus, the bead size would be much smaller than the overall size of the particle, and the frictional forces at each bead—which really act distributed all over its surface—could be applied at the bead center. Thus, the general Kirkwood–Riseman expression for $[\eta]$ of bead models are sum of terms contain terms of the form $y_i F^x{}_i$, where $F^x{}_i$ is the component along the shearing direction of the force at the center of bead i, and y_i is the component of the position vector from the

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hydrodynamic center to the center of the bead in the direction of the velocity gradient. García de la Torre and Bloomfield implemented the KR treatment for rigid bead models of arbitrary shape, in a rigorous manner in aspects referred to hydrodynamic interactions and numerical treatments; indeed, the finite size of the elements was considered for the representation of hydrodynamic interactions by means of a modified Oseen tensor (García de la Torre and Bloomfield 1977) but their result for the intrinsic viscosity (García de la Torre and Bloomfield 1978, 1981), which will be hereafter named as "uncorrected" and denoted as $[\eta]_{\mathrm{KRM}}$, still was affected by the above mentioned assumption of point-like elements of the Kirwood-Riseman theory. The first version of the HYDRO computer program García de la Torre et al. 1994) was based on that treatment. However, the results of such calculations were doubtful for models with few beads, and for the trivial case of a single sphere gave the absurd result $[\eta]_{\mathrm{KRM}}$=0 ($y_1 F^x{}_1 = 0$ because $y_1 = 0$ since the center of the bead is the hydrodynamic center). Such deficiency had been noted also by other workers in studies of short, oligomeric molecules García de la Torre et al. 1994).

Ten years ago, in this Journal, García de la Torre and Carrasco (1998) presented an extended version of the Kirkwood–Riseman theory that considered the finite size of the beads, arriving at the conclusion that the correct result should be

$$[\eta]_{\mathrm{KRV}} = [\eta]_{\mathrm{KRM}} + \frac{10\pi N_A}{3M}\sum_{i=1}^{N}\sigma_i^3 = [\eta]_{\mathrm{KRM}} + \frac{5N_A V}{2M} \qquad (1)$$

where M is the molecular weight and σ_i are the bead radii, and $V = (4\pi/3)\sum\sigma_i^3$ is the volume of the array of (non-overlapping) beads. This result generalizes a previous one from Yamakawa and coworkers for identical beads (Yoshizaki et al. 1988; Abe et al. 1991). Thus, it is seen that the correction is related to the volume of the model. The subscript KRV stands for full volume correction. It is evident that for a single bead with $[\eta]_{\mathrm{KRM}} = 0$, Eq. 1 gives the Einstein result, $[\eta]_{\mathrm{KRV}} = 5N_A V/2M$ for a spherical particle.

The defect of point-like sources of friction in the KR theory can be circumvented by a modeling strategy, namely, the cubic substitution, in which each bead in the original model is replaced by a cubic array of smaller "minibeads" Wilson and Bloomfield 1979; García Bernal and García de la Torre 1981). Thus, the frictional force does not act at the center of the bead but is distributed through eight points (the centers of the minibeads) that are close to the bead surface. This strategy increases the number of beads by a factor of 8, and the computing time is subsequently increased by a factor or $8^3 = 512$, but it is still affordable for models with a few hundred beads and, in cases when exact result from rigorous fluid-mechanical theories are available, the cubic substitution has been found to be practically exact (García de la Torre and Carrasco 1998; García de la Torre et al. 2007). Therefore, we will take the results from this procedure as the reference values $[\eta]_{\mathrm{REF}}$ for the evaluation of results of the other methods.

García de la Torre and Carrasco (1998) presented results of the volume correction for some structures, finding that $[\eta]_{\mathrm{KRV}}$ was generally better than the uncorrected, $[\eta]_{\mathrm{KRM}}$. Actually $[\eta]_{\mathrm{KRM}}$ was always a lower bound to the exact result, which meant that some correction should be added, indeed. However $t[\eta]_{\mathrm{KRV}}$ was always larger than the exact one (although usually closer to it than $[\eta]_{\mathrm{KRM}}$. Then, this suggested (García de la Torre et al. 2007) the possibility an empirical, fractional or intermediate volume correction, that would produce a value, $[\eta]_{\mathrm{KRI}}$, given by

$$[\eta]_{\mathrm{KRI}} = [\eta]_{\mathrm{KRM}} + f_\eta \frac{5N_A V}{2M} \qquad (2)$$

with $0 \le f_\eta \le 1$. Recently, we (García de la Torre et al. 2007) have examined the f factor needed to bring the uncorrected $[\eta]$ in agreement with the exact one:

$$f_\eta = \frac{[\eta]_{\mathrm{REF}} - [\eta]_{\mathrm{KRM}}}{[\eta]_{\mathrm{KRV}} - [\eta]_{\mathrm{KRM}}} = \frac{[\eta]_{\mathrm{REF}} - [\eta]_{\mathrm{KRM}}}{(5N_A V/2M)} \qquad (3)$$

As it was hinted in the previous work (García de la Torre and Carrasco 1998), we noticed that when one bead accounts for a large part of the whole volume (e.g., for a model with a large bead surrounded by some number of much smaller beads, the correction needed was near the full one, with $f_\eta \approx 1$. We say that the degree of fragmentation of such structures is small. One possible way of quantifying the fragmentation could be as follows. Suppose that the beads are indexed so that $i = 1$ is the largest one, $i = 2$ the second largest and so on. Let ϕ_i be the volume fraction of the bead (referred to the total volume). Define the cumulative amounts (which forms a monotonously increasing series) $S_i = \sum_{k=1}^{i}\phi_k$, with $S_0 = 0, S_1 = \phi_1$ and $S_N = 1$. Then, the quantity defined as:

$$S = N - \frac{1}{2} - \sum_{i=1}^{N}\frac{S_i + S_{i-1}}{2} \equiv N - \sum_{i=1}^{N} S_i \qquad (4)$$

has the following properties: (a) for a model with identical beads, it takes the maximum value, $S = N/2-1/2 = (N-1)/2$ (b) In a model in which the largest bead is dominant, with $\phi_1 \approx 1$, $S \approx 0$ and $S = 0$ for $N = 1$, i.e., the result for a single sphere. Here, we have introduced a change with respect to the previous work (García de la Torre et al. 2007), where we defined a very similar quantity (we previously used a definition for the fragmentation degree that was $S + 1/2$, with a value of 1/2 for the single sphere).

We also noticed that, for a given degree of fragmentation, as it happens for an array of N identical spheres with $S = (N-1)/2$, the f_η factor needed to match the uncorrected value to the exact one depended on the conformation, and particularly in the more or less elongated aspect, of the bead models. Thus, for globular, nearly isometric structures, f was close to zero (indicating that the uncorrected $[\eta]$ was practically exact), while larger f_η values were found, for instance, for strings of beads. As we needed an indicator of particle anisometry, we took a quantity based on a hydrodynamic tensor: the translational diffusion tensor, $\mathbf{D}_{tt}$. This choice was motivated by the fact that the HYDRO methods calculate translational diffusion jointly with intrinsic viscosity (because both properties come from, and require the inversion of the $3N \times 3N$ hydrodynamic interaction supermatrix. If $D_t^{(1)}$, $D_t^{(2)}$, $D_t^{(3)}$ are the eigenvalues of $\mathbf{D}_{tt}$ the tensor anisotropy can be expressed by

$$\Delta = [(D_t^{(1)})^2 + (D_t^{(2)})^2 + (D_t^{(3)})^2 - D_t^{(1)}D_t^{(2)} - D_t^{(1)}D_t^{(3)} - D_t^{(2)}D_t^{(3)}]^{1/2} \quad (5)$$

and a relative anisotropy can be formulated as $A_D = \Delta/D_t$, where $D_t = (1/3)(D_t^{(1)} + D_t^{(2)} + D_t^{(3)})$ is the translational diffusion coefficient. For a globular, approximately isometric particle, $\Delta \approx 0$ and $A_D \approx 0$. At another extreme, for a long rod, $D_t^{(1)} = D_t^{(2)} = \frac{1}{2}D_t^{(3)}$, and $A_D = 3/4$.

In this work, we consider an alternative to express a geometric asphericity instead of a hydrodynamic one. There are procedures to evaluate the intrinsic viscosity, like Fixman's bounds (Fixman 1983; Freire and Rey 1990) which do not require the evaluation of the full diffusion tensor, $\mathbf{D}_{tt}$. The Fixman procedure has been employed for models of dendrimer molecules (Rodríguez et al. 2007; Freire and Rubio 2008; Freire 2008), which due to their compactness require some degree of volume correction for the viscosity. There is even the possibility of an approximate evaluation of the diffusion coefficient, using the Kirkwood–Bloomfield formula (Bloomfield et al. 1967) which do not need $\mathbf{D}_{tt}$. A geometric asphericity, usually applied to random chains, but useful for any other shape, can be obtained from the Eigenvalues of the gyration tensor, $\mathbf{G}$. For an array of N non-overlapping spherical elements, the α, β components of this tensor (α, $\beta = x, y, z$) is evaluated as

$$\mathbf{G} = \sum_{i=1}^{N} f_i \left(s_i^\alpha s_i^\beta + (3/5)\sigma_i^2 \delta_{\alpha\beta} \right) \quad (6)$$

where $f_i = \sigma_i^3/\sum_i \sigma_i^3$ is the volume fraction of bead i, and $\delta_{\alpha,\beta}$ is a Kronecker's delta. The second term, which is the radius of gyration of the individual spheres, equal to (3/5) $\sigma_i^2 \delta_{\alpha\ \beta}$, is usually omitted for models composed of many identical, small beads, but it must be included so that Eq. 6 is valid for any distribution of bead sizes. If G_1, G_2, G_3 are the three eigenvalues of $\mathbf{G}$, an asphericity can be defined (Wei and Eichinger 1990) as

$$A_G = \frac{(G_2 - G_1)^2 + (G_3 - G_1)^2 + (G_3 - G_2)^2}{2(G_1 + G_2 + G_3)^2} \quad (7)$$

so that for isometric particles (not necessarily spherical) with $G_1 = G_2 = G_3$, we have $A_G = 0$, while for very elongated particles, with $G_1 \gg G_2$, G_3 the result is $A_G = 1$.

We seek some function $f_\eta(S, A; p_1, p_2, p_3, \ldots)$ relating the viscosity correction to the fragmentation, S, and the shape, the latter determined by A_D of A_G of the bead models. This function would be used to estimate to obtain, from $[\eta]_{\mathrm{KRM}}$ and V, an improved result, with an intermediate correction $[\eta]_{\mathrm{KRI}}$, by means of Eq. 3. Such function will contain some numerical parameters. As in our previous paper, we proceed in a semi-empirical manner, seeking the best set of parameters. To do so, for a great variety of bead models (as described below) we have evaluated the intrinsic viscosity with the three schemes, obtaining $[\eta]_{\mathrm{KMR}}$, $[\eta]_{\mathrm{KMV}}$ and $[\eta]_{\mathrm{REF}}$. For each structure, an adjusted f_η value is obtained from $[\eta]_{\mathrm{KMR}}$ and $[\eta]_{\mathrm{REF}}$ using Eq. 2.

In the determination of the optimum parameters, we introduce another difference from our previous work. Then, the parameters was obtained by a non-linear least-squares fit of the f_η's of the various structures to the fitting equation $f_\eta(S, A; p_1, p_2, p_3, \ldots)$. Now, we seek to determine the parameters by minimizing the deviations of the $[\eta]$ values with the intermediate volume correction (Eq. 2) for the whole set of test structures. The overall deviation is characterized by a percent typical relative difference, indicated as 100 Δ, given by

$$100\Delta = 100 \left\langle \left[\frac{[\eta]_{\mathrm{KRI}} - [\eta]_{\mathrm{REF}}}{[\eta]_{\mathrm{REF}}} \right]^2 \right\rangle^{1/2} \quad (8)$$

More specifically, 100 Δ is the root-mean-square value of the relative error of the KRI result with respect to the exact, REF value. This way puts the emphasis not in how well the $f_\eta(S, A; p_1, p_2, p_3, \ldots)$ fits the empirical f_η values, but on how well it gives better results for $[\eta]_{\mathrm{KRI}}$ from Eq. 3.

Results

As indicated above, we have made the empirical estimation of f_η for many different structures. Most of them are described in our previous paper (García de la Torre et al. 2007): dimers of unequal spheres, linear, polygonal and polyhedral arrays of identical beads, some models representing dendrimers, other models with unequal beads having peculiar shapes (e.g., "lollipops", etc.).

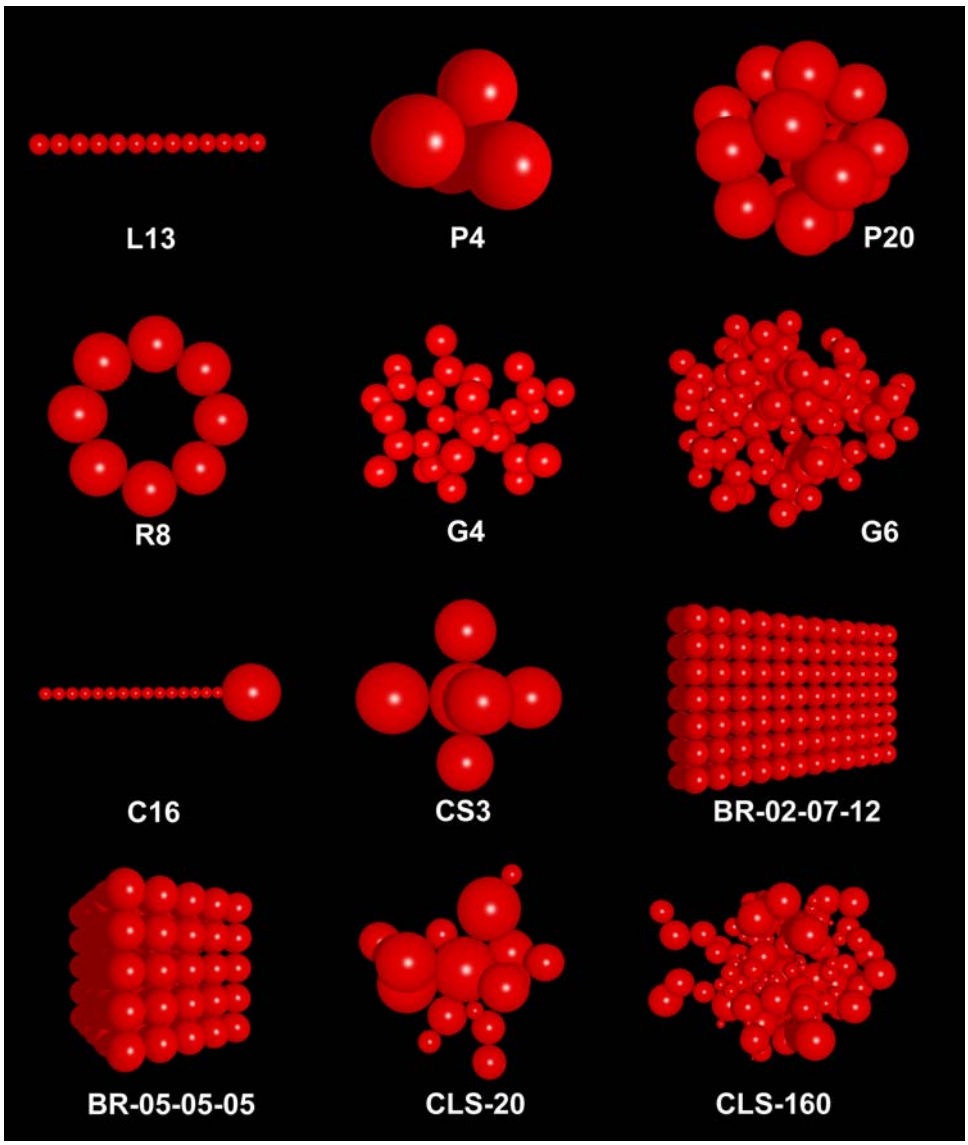

Fig. 1 Some of the models used in this study. Codes are those used in Table 1, and described in García de la Torre et al. (2007) or in the main text

We have included in the present study other structures that are motivated by the way in which some authors construct bead models for compact shapes like those of globular proteins.

The new structures are:

- Parallelipipedic arrays, or "bricks", with densely packed, identical touching beads arranged in a cubic lattice, having N_1, N_2, and N_3 beads on each side, with a total number of beads $N = N_1N_2N_3$. Structures will be denoted as BR-N1-N2-N3
- "Clusters" constructed as follows: one bead of radius σ is placed at the origin. Successive beads, up to a total of N, with random values for the radius between 0 and σ are added to the cluster, approaching towards the origin in a random direction until the new bead touches one of the existing ones. This results in an array of non-densely packed beads or unequal sizes. Structures will be denoted as CLS-N

Some selected models are depicted in Fig. 1. The whole set of results is presented in Table 1, where the notation for the various structures is that described in our previous paper (García de la Torre et al. 2007) and that indicated above for the new structures. We report the REF values normalized to the intrinsic viscosity of a sphere of the same volume as the model $[\eta]^*_{\mathrm{REF}} = [\eta]_{\mathrm{REF}}/(5N_AV/2M)$ (in this way the numerical values are not too different and do not depend on the actual size of the model). For the KMR, KRV and KRI values, we just give the percent difference $\%\mathrm{diff} = 100\ ([\eta] - [\eta]_{\mathrm{REF}})/[\eta]_{\mathrm{REF}}$ which indicates the deviation from the exact value, and is used for the estimation of the global error, in Eq. 8 (Fig. 2).

Table 1 Results for the empirical estimation of f_η for the models used in this study

Structure	N	REF[a]	errKRM %	errKRV %	A_G	S	f_η (obs)	f_η (cal)	errKRI %
M1	1	1.780	−100.0	0.0	0.000	0.000	1.000	1.000	0.0
D1	2	2.458	−53.1	20.1	0.391	0.500	0.726	0.739	1.0
D2	2	6.348	−68.1	17.0	0.623	0.111	0.801	0.834	2.8
D3	2	13.500	−80.4	13.0	0.756	0.036	0.861	0.833	−2.7
L3	3	3.292	−40.1	14.6	0.666	1.000	0.733	0.701	−1.7
L4	4	4.294	−30.9	11.1	0.797	1.500	0.736	0.704	−1.3
L6	6	6.608	−20.2	7.1	0.905	2.500	0.740	0.718	−0.6
L8	8	9.440	−15.0	4.1	0.945	3.500	0.786	0.727	−1.1
L10	10	12.690	−11.7	2.4	0.965	4.500	0.828	0.731	−1.4
L13	13	18.310	−8.8	1.0	0.979	6.000	0.894	0.735	−1.6
L20	20	34.750	−5.5	−0.3	0.991	9.500	1.067	0.738	−1.7
P4	4	2.542	−30.0	40.8	0.001	1.500	0.423	0.492	4.9
P6	6	2.443	−24.3	49.4	0.000	2.500	0.329	0.395	4.9
P8	8	2.803	−24.1	40.1	0.000	3.500	0.375	0.342	−2.1
P12	12	3.876	−22.7	47.0	0.000	5.500	0.326	0.284	−2.9
P20	20	3.632	−17.2	32.4	0.000	9.500	0.347	0.234	−5.6
R3	3	2.514	−37.5	34.0	0.119	1.000	0.524	0.599	5.3
R4	4	2.791	−33.2	31.3	0.148	1.500	0.515	0.532	1.1
R6	6	3.457	−27.0	25.1	0.189	2.500	0.518	0.463	−2.9
R8	8	4.422	−24.5	16.2	0.211	3.500	0.603	0.428	−7.1
G3	15	6.812	−13.1	13.3	0.190	7.000	0.497	0.352	−3.8
G4	31	7.936	−9.9	12.8	0.121	15.000	0.437	0.271	−3.8
G5	63	7.970	−8.2	14.4	0.079	31.000	0.364	0.224	−3.2
G6	127	7.101	−7.0	18.4	0.045	63.000	0.274	0.193	−2.1
C2	2	1.828	−90.2	8.3	0.141	0.008	0.916	0.965	4.8
C4	4	2.139	−75.1	9.1	0.233	0.047	0.892	0.921	2.5
C6	6	2.660	−59.6	8.1	0.334	0.115	0.881	0.870	−0.7
C11	11	4.884	−32.7	4.1	0.584	0.407	0.888	0.767	−4.5
C16	16	8.424	−19.5	1.9	0.742	0.857	0.913	0.725	−4.0
A1	7	3.531	−21.1	29.9	0.012	1.557	0.414	0.488	3.8
A2	7	3.046	−32.6	26.5	0.039	0.652	0.552	0.670	7.0
A3	7	3.558	−20.0	30.6	0.003	2.317	0.396	0.410	0.7
B1	7	6.557	−20.3	7.1	0.865	1.557	0.741	0.721	−0.6
B2	7	3.787	−34.5	13.0	0.715	0.652	0.726	0.740	0.7
B3	7	7.645	−17.4	6.1	0.904	2.317	0.739	0.720	−0.5
BR-02-04-08	64	2.672	−11.0	26.5	0.441	31.500	0.293	0.426	5.0
BR-02-07-12	168	3.451	−8.1	20.9	0.400	83.500	0.279	0.393	3.3
BR-03-03-03	27	1.760	−16.2	40.6	0.000	13.000	0.286	0.214	−4.1
BR-03-06-09	162	2.479	−8.8	31.6	0.255	80.500	0.218	0.310	3.7
BR-04-06-09	216	2.291	−8.2	35.4	0.191	107.500	0.188	0.272	3.7
BR-05-05-05	125	1.981	−10.0	40.5	0.000	62.000	0.197	0.167	−1.5
CLS-5	5	1.521	−38.3	27.5	0.169	0.533	0.582	0.717	8.9
CLS-10	10	2.090	−19.6	28.3	0.185	1.998	0.409	0.495	4.1
CLS-20	20	2.616	−14.7	23.6	0.058	4.005	0.383	0.347	−1.4
CLS-40	40	3.318	−11.8	18.3	0.086	8.354	0.392	0.287	−3.2
CLS-80	80	3.414	−9.6	19.7	0.052	15.831	0.329	0.232	−2.8
CLS-160	160	3.844	−8.0	18.0	0.013	32.582	0.308	0.186	−3.2

Table 1 continued

Structure	N	REF[a]	errKRM %	errKRV %	A_G	S	f_η (obs)	f_η (cal)	errKRI %
RMS % difference:			35.8	24.0	RMS % difference				3.5

Codes are described in García de la Torre et al. (2007) or in the main text

[a] Reference values (relative to those of the sphere of the same volume, see text) with respect to which we give the percent deviation of the other methods in the following columns.

For the fitting or interpolating function $f_\eta(S, A; p_1, p_2, p_3, \ldots)$ we have tried a number of possibilities that would satisfy the requirement that it would decrease from $f_{eta} = 1$ for the single sphere ($S = 0, A = 0$), as either S or A are increased. The data and calculation were implemented in an Microsoft Excel spreadsheet that, with some $f_\eta(S, A; p_1, p_2, p_3, \ldots)$ function evaluates the individual %diff values and the overall, typical error given by 100 Δ in Eq. 8. This error was taken as the target that the optimum parameters should minimize, and this optimization was performed with the SOLVER tool of MS Excel.

We repeated the procedure with the two choices, A_D and A_G of the asphericity, finding that their performance was similar, predicting nearly the same values for the global error. So we have now selected A_G (while we used A_D in our previous work), because of the above-mentioned advantage of being purely geometric, not requiring further hydrodynamic calculation.

For the functional form of $f_\eta(S, A; p_1, p_2, p_3, \ldots)$ we found a quite simple and effective equation:

$$f_\eta = 1 - 0.8463\frac{S}{S+1} + 0.7938A_G\frac{S}{S+1} - 0.2101A_G \qquad (9)$$

where we used the variable $S/(S + 1)$ because its range is (0, 1), the same as that of A.

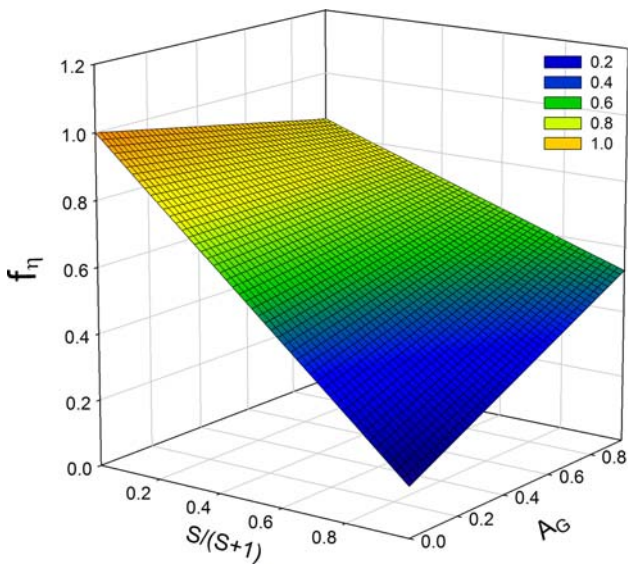

Fig. 2 Plot of f_η versus $S/(S + 1)$ and A_G according to Eq. 9

Discussion and conclusions

For the 47 bead models, with either identical or widely varying bead sizes, with also a great variety both in the degree of fragmentation and anisometry, in the absence of any volume correction (KRM) we obtain a typical error (rms percent difference) with respect to the quasiexact result. The inclusion of the full volume correction, as we proposed initially (KRV), does improve the situation, but the typical error is still of about 24%. Thus, the interest of the adjusted, intermediate correction in the KRI procedure is fully justified.

In summary, the protocol for the KRI calculation consists of the following steps (1) evaluation of the (uncorrected), KRM value; (2) determination of the S and A_G parameters from the geometry of the bead model (Eqs. 4, 7); (3) calculation of f_η from Eq. 9 and finally, determination of the KRI value of $[\eta]$ from Eq. 2. The resulting values have a typical error of only 3.5%, which is of the same order or even smaller than typical errors in the experimental measurement of $[\eta]$, and therefore can be considered as practically exact.

This protocol for the calculation of $[\eta]$ is implemented in the latest version of our HYDRO++ program. We would like to emphasize that this program is intended for what we call bead models in strict sense, composed of a moderate number of beads (say, less than 300). Indeed the calculations reported here have been made in this range (within the reach of the cubic substitution calculations used for reference). For other instances, where the representation of structural details require a large number of beads, we have developed the alternative scheme of shell-modeling, implemented for instance in programs like HYDROPRO (García de la Torre et al. 2000a), HYDRONMR (García de la Torre et al. 2000b), HYDROMIC (García de la Torre et al. 2001), HYDROSUB (García de la Torre 2001), HYDROPIX (García de la Torre and Carrasco 2002). Shell models contains typically 500–2000 minibeads, that are much smaller than the whole particle's size so that they can be considered practically pointlike (the shell is very thin, and its volume is very small). Furthermore, the shell-modeling procedure includes an extrapolation to zero bead radius, so that any eventual volume correction would vanish in the limit. Therefore, shell-model calculations do not require any

volume correction and can be safely made with just uncorrected, KRM values.

For the representation of structural details other authors (Byron 1997; Rai et al. 2005; Zipper and Durchschlag 2000, 2007) favor alternative bead modeling strategies in which the particle is somehow "filled" with beads. The models may look like densely packed array of identical beads, or clusters of beads of different sizes resulting from bead-grouping strategies. We have tried to include such kind of models in the present study, by means of the BR and CLS structures in Table 1. For this subset of structures, we note that the KRI procedure performs acceptably, but not better than KRM. It can be concluded that, for such structures, as well as for shells, the volume correction can be safely neglected. On the other hand, we conclude that the KRI procedure implemented in HYDRO++ produces excellent results in the case of the bead models for which that program is intended.

Computer programs

The latest version of program HYDRO++ is freely available, along with other related software tools, from our web site, http://leonardo.inf.um.es/macromol.

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