Shear-rate dependence of the intrinsic viscosity of bead-and-spring chains: hydrodynamic interaction and excluded-volume effects

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The shear-rate dependence of the intrinsic viscosity of the bead-and-spring (or Rouse) model for polymer chains with rigorous inclusion of hydrodynamic interaction (HI) and excluded volume (EV) is studied, for chains of varying length, using the Brownian dynamics simulation technique. The simulation results describe a transition from the zero-shear-rate viscosity, which depends strongly on HI and EV, to the region of very high shear rate, where the simulated viscosity is found to be that corresponding to the absence of HI and EV. As the latter is larger than the former when the chain is long enough, a shear-thickening behaviour is predicted for long bead-and-spring chains. The dumbbell model, which is the shortest chain, gives the wrong, opposite, prediction.

(Keywords: shear flow; non-Newtonian viscosity; polymer solution; hydrodynamic interaction; excluded volume; dumbbell model)

INTRODUCTION

One of the simplest types of systems exhibiting non-Newtonian behaviour is that of dilute polymer solutions[1,2]. As is well known, the addition of a small amount of polymer to a simple liquid (solvent) causes a remarkable increase in the shear viscosity, which is found to decrease with increasing shear rate. Although this shear-thinning behaviour has been known for many years, there have been few theoretical advances towards a complete molecular description of it. The zero-shear-rate viscosity of dilute solutions is adequately described by the bead-and-spring model (Rouse chain[3]) when hydrodynamic interactions (HI) and excluded-volume (EV) effects are properly considered. Recent Monte Carlo and Brownian dynamic simulations[4,5] have proved that the observed molecular-weight dependence of the intrinsic viscosity of polymers, and the universal parameters combining the intrinsic viscosity with polymer dimensions, are well described (both in theta solvents and in good solvents) by bead-and-spring chains.

As described by Bird *et al.*[1], when hydrodynamic interactions are neglected and excluded-volume effects are not considered, the bead-and-spring model predicts a Newtonain viscosity, independent of shear rate. This deficiency prompted the development of models that may be more realistic, such as those having finite extensibility[6,7]. The refinements introduced in such models make it impossible to consider at the same time HI and EV effects. Even chain length is sometimes a complicating factor, and therefore in many cases the theoretical description has been restricted to the case of dumbbells, having just two beads and one spring.

Hydrodynamic-interaction and excluded-volume effects may have an important influence on the non-Newtonian behaviour. It is interesting to include these effects in the study of the behaviour of the simplest model, the Rouse chain, thereby isolating their influence from other aspects such as finite extensibility and non-linearity in general. This has recently been accomplished for the shortest Rouse chain, the Hookean dumbbell, using Brownian dynamics simulation techniques[8,9]. The results were slightly different from those of other theoretical treatments including HI in an approximate way, but all the theories and treatments[8–11] agreed qualitatively in that the intrinsic viscosity decreased with increasing shear rate, showing the typical non-Newtonian shear thinning.

It is evident that the dumbbell model is an oversimplification of a polymer chain. Assuming that a long bead-and-spring chain could be a more realistic model, we undertook the Brownian dynamics simulation of the chain conformation in shear flow with hydrodynamic interaction[12]. We found the striking fact that hydrodynamic-interaction effects in chains with a large number of beads, N, are in the opposite direction to those for the dumbbell. Thus, while for the latter (with $N=2$), HI causes an increase in dimensions that may be up to 20% over the no-HI value, in the case of large N the chain dimensions with HI may typically be 50% smaller. It was concluded that the dumbbell model may be misleading, particularly in regard to the influence of HI effects.

In the present paper we extend the simulation of moderately long bead-and-spring chains to the calculation of the viscosity as a function of shear rate, including both HI and EV effects. The simulations are carried out for varying chain length, so that the long-chain limiting behaviour can be estimated.

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MODEL AND METHODS

The bead-and-spring model is composed of N spherical beads, with hydrodynamic radius σ, joined by $N-1$ Hookean springs, having a Gaussian distribution of lengths with zero mean and a root-mean-square value denoted as b, which for convenience is taken as the unit of length. When HI is neglected, the results can be expressed in a form that is independent of the choice of σ. However, the strength of HI effects depend on the so-called HI parameter[13], for which a reasonable value is $h^*=0.25$, corresponding to $\sigma/b=0.257$. HI is represented rigorously by means of Rotne–Prager–Yamakawa interaction tensors.

As an adequate continuous representation of excluded-volume effects, we used a Lennard-Jones potential for the distance r_{ij} between any pair of beads, i and j:

$$V=4\varepsilon[(a/r_{ij})^6-(a/r_{ij})^{12}] \tag{1}$$

This potential has been shown to reproduce correctly the molecular-weight dependence of polymer dimensions and hydrodynamic properties when the parameters are taken as $a/b=0.8$ and $\varepsilon/k_BT=0.1$[5,14,15].

The Brownian dynamics of a chain of N beads in a simple shear flow with shear rate $\dot{\gamma}$ is simulated with HI as described in previous papers[8,12]. The only modification in the methodology here is the use, instead of the first-order algorithm of Ermak and McCammon[16], of the second-order procedure proposed by Iniesta and García de la Torre[17]. Of course, intramolecular EV forces derived from equation (1) have to be added to the mechanical spring forces. While the time step, Δt, can be fairly large[8,12] in the simulations without EV, the strong dependence of the EV potential on r_{ij} requires the use of a much smaller Δt to assure practical constancy of the forces along the simulation step. This in turn required a very large number of steps in the trajectory to achieve a reasonable duration, as required to scan sufficiently the conformational variability. The values taken for the number of steps and their length will be specified later on.

The initial state of the polymer chain in the simulation was a conformation of the chain generated in the absence of flow. Then, the simulation with a given shear rate was started. During the first part of the trajectory the chain had to adopt the state corresponding to the shear flow. As we are interested in the steady-state properties, we have to reject that part of the trajectory in the statistical analysis (*vide supra*).

The intrinsic viscosity is calculated from the simulated trajectories in flows with shear rate $\dot{\gamma}$ using the Kramers expression for the cross-component of the stress tensor, τ_{xy}:

$$\eta=-\tau_{xy}/\dot{\gamma}=\eta_0+n\langle Q_xF_y\rangle/\dot{\gamma} \tag{2}$$

where n is the number density of polymer molcules, η_0 is the viscosity of the solvent and η is that of the polymer solution. $\boldsymbol{Q}_i$ and $\boldsymbol{F}_i$ are respectively the elongation and the force at the ith spring. It is convenient to use the following dimensionless form for the intrinsic viscosity

$$\begin{aligned}[\eta]^* &\equiv [\eta]N_A/Mb^3 \\ &=(1/nb^3)(\eta-\eta_0)/\eta_0 \qquad (n\rightarrow 0)\end{aligned} \tag{3}$$

We note that this definition differs slightly from that used, with the same symbol, in ref. 8, but is the same as that employed in our Monte Carlo studies[4,5,15].

In Brownian dynamics simulation work, a dimensionless time is conveniently defined as:

$$t^*=t/(6\pi\eta_0\sigma b^2/k_BT) \tag{4}$$

Then a natural way of formulating the reduced shear rate is:

$$\dot{\gamma}^*=(6\pi\eta_0\sigma b^2/k_BT)\dot{\gamma} \tag{5}$$

However, in rheological studies of dilute polymer solutions it is customary to express the reduced shear rate as:

$$\begin{aligned}\beta &\equiv (M\eta_0[\eta]/N_Ak_BT)\dot{\gamma} \\ &=([\eta]^*/6\pi\sigma^*)\dot{\gamma}^*\end{aligned} \tag{6}$$

with $\sigma^*=\sigma/b$.

From the instantaneous conformations generated in the Brownian trajectory, we evaluated in some cases the mean-square radius of gyration $\langle s^2\rangle$.

The zero-shear-rate intrinsic viscosity can be obtained alternatively from Monte Carlo simulations based on the rigid-body treatment, whose details are given elsewhere[4,14]. These Monte Carlo values are used essentially to check Brownian dynamics results.

RESULTS

The choice of the number of steps n_s and step length Δt^* presents a compromise between the validity of the simulation conditions and the computer time consumed. The inclusion of EV requires the use of smaller Δt^*, so that the n_s needed to achieve a given trajectory length, $t^*=n_s\Delta t^*$, increases remarkably.

In the simulations without EV, we used $\Delta t^*=0.01$. In our previous paper we showed that this choice is adequate to reproduce the chain statistics in shear flows. The number of steps was 800000 for all values of N. When EV is included, we had to decrease the time step, down to $\Delta t^*=0.0005$. It is important to ascertain whether the resulting trajectories were long enough to achieve convergence in the results. This is illustrated in *Figure 1* for the worst case ($N=20$, with HI and EV). We see that the results are not stable until a certain trajectory length has been simulated. The first part of the trajectory is spent going from the starting conformation of the chain to the steady-state chain statistics corresponding to the $\dot{\gamma}^*$ considered. We monitored all the simulations as illustrated in *Figure 1*, and discarded the first part of the trajectory. The other part, in which the result is stable, was subdivided into five trajectories, for which averages were calculated. The final result is the mean of the five values, and their standard deviation gives an estimate of the statistical uncertainty.

It is important to ascertain whether the time step Δt is small enough. This can be tested by running simulations in which Δt is further decreased. If the previous Δt was adequate, the results in the new run should not differ appreciably from those of the previous one. We have carried out this test again in the worst case ($N=20$, with EV and HI), decreasing Δt^* down to 0.00025. In the comparison, the trajectory length $t^*=n\Delta t^*$, where n is the number of steps, should be the same, and this required doubling n. The results are presented in *Figure 1*, where we note that the difference between the two sets of results is, in the long term, smaller than 10%. A similar test carried out for $N=12$ gave, as

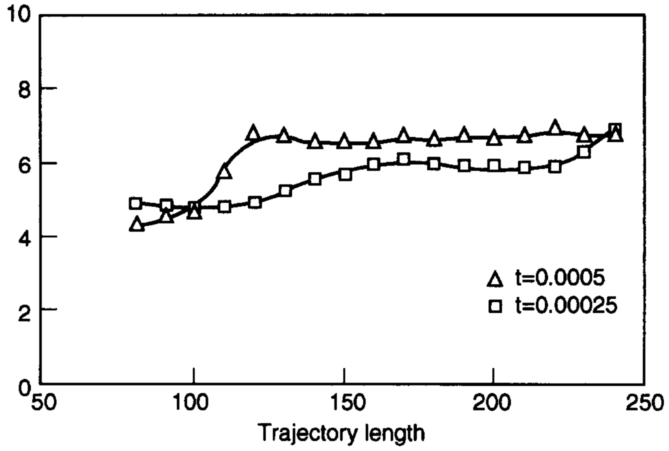

Figure 1 Moving-average results for the viscosity at $\dot{\gamma}^* = 1$ for $N = 20$ with excluded volume and hydrodynamic interaction, plotted *versus* the trajectory length t^*. Results for $\Delta t^* = 0.000\,25$ and $\Delta t^* = 0.0005$ are presented

Table 1 Intrinsic viscosity of bead-and-spring chains without HI and EV

	Theoretical	Brownian dynamics simulation			
N	Equation (7)	$\dot{\gamma}^*=0$	$\dot{\gamma}^*=0.5$	$\dot{\gamma}^*=1$	$\dot{\gamma}^*=5$
2	0.083	0.088	0.09	0.093	0.086
3	0.222	0.227	0.230	0.230	0.236
5	0.67	0.68	0.70	0.70	0.69
8	1.75	1.78	1.94	1.96	1.69
12	3.97	3.93	4.05	4.10	4.08
20	11.1	10.9	10.5	10.5	10.6

expected, a much smaller deviation. Thus, we will consider that $\Delta t^* = 0.0005$ is adequate for simulations with EV.

The simulation results can be tested extensively by comparison with theoretical results in the case of the absence of HI and EV. In *Table 1* we list the Newtonian intrinsic viscosity calculated from the equation of Bird *et al.*[1]:

$$[\eta]^* = (N^2 - 1)/36 \qquad (7)$$

along with simulation results obtained for different values of $\dot{\gamma}^*$. The statistical errors of the latter, estimated as described above, were of the order of a few per cent.

We note in *Table 1* that the simulation results are acceptably independent of $\dot{\gamma}^*$ and coincide within statistical uncertainty with the theoretical values. This agreement instils confidence in the validity of the simulation procedure and working conditions.

Another check on the performance of the simulation can be carried out by comprison of zero-shear-rate simulation results with results from Monte Carlo simulation[4,5,14]. This is done in *Table 2* for the complex situation (i.e. with HI and EV). The Brownian dynamics results for $\langle s^2 \rangle$ are in excellent agreement with the Monte Carlo results. Although this situation does not depend on HI, it is anyhow a proof that the trajectories were long enough to scan the conformational space and indicates that no unphysical divergences took place. The Monte Carlo and Brownian dynamics results for $[\eta]_0^*$ with HI and EV are also found to be in good agreement within statistical uncertainties.

The shear-rate dependence of the viscosity can be analysed, as usual with experimental data, in terms of the relative form of the shear rate β, in which it is combined, as expressed in equation (6), with some relaxation rate of the polymer chain determined by the intrinsic viscosity. Thus the η vs. β curves for polymers of different molecular weights could be the same, at least in the region where the non-Newtonian behaviour begins to take place.

Our Brownian dynamics (BD) simulation results without EV are plotted vs. β in *Figure 2*. As discussed above, the results for very small β agree well with the Monte Carlo values for zero shear rate. This is one of the limits indicated in *Figure 2*. The other limit is that for very high shear rate. In such a situation the springs in the chain are very stretched, the distances between beads are very large and therefore HI is negligible and the viscosity takes the no-HI values (equation (7)). The BD results describe well the transition between the two limits. For the dumbbell with $N = 2$, the results indicate a shear-thinning behaviour, which is indeed the real situation for dilute polymer solutions. For $N = 5$ the separation between the two limits is very small, with a very weak shear-rate dependence, and for $N = 20$ the limits have been inverted and the bead-and-spring chain has a shear-thickening behaviour, except for a minor minimum. The reason for this change is clear from the chain-length dependence of the viscosity in the two limits. At $\dot{\gamma}^* = 0$, we have $[\eta]_0(\text{no EV, HI}) \propto N^{0.5}$; while for $N \to \infty$, as commented above, the limit is $[\eta]_\infty(\text{no HI}) \propto N$. At small N, $[\eta]_0$ may be larger than $[\eta]_\infty$; but when N is large enough (as seen for $N = 20$), $[\eta]_\infty > [\eta]_0$. For infinite N the upper limit is infinitely higher than the lower one, and a monotonic increase is expected. This behaviour for chains of infinite length has indeed been predicted in a very recent renormalization-group calculation[18].

The trend shown by the results with EV, displayed in *Figure 3*, is similar. In the presence of EV, the $\beta \to \infty$ limit is the same as in its absence, for the EV effect disappears as intrachain dimensions are expanded due to the shear. Now, according to the mean-field theory[19], confirmed by Monte Carlo calculations, $[\eta]_0(\text{EV, HI}) \propto N^{0.8}$, which is larger for small N than the no-EV results. Thus, the shear-thinning behaviour for short chains is

Table 2 Radius of gyration $\langle s^2 \rangle$ and zero-shear-rate intrinsic viscosity $[\eta]_0^*$ of bead-and-spring chains: Monte Carlo (MC) and Brownian dynamics (BD) simulations

	$\langle s^2 \rangle$		$[\eta]^*$		
N	MC, EV	BD, EV, HI	MC, HI, no EV	MC, HI, EV	BD, HI, EV[a]
2	0.249	0.246	0.118	0.117	0.123
3	0.486	0.484	0.283	0.368	0.41
5	0.97	0.99	0.74	0.87	0.83
8	1.75	1.70	1.63	2.11	2.91
12	2.85	2.72	3.20	4.56	4.71
20	5.27	5.32	7.22	11.3	10.4

[a] Calculated for $\dot{\gamma}^* = 0.3$ when $N = 2$, 3, 5, 8 and 12 or $\dot{\gamma}^* = 0.1$ when $N = 20$

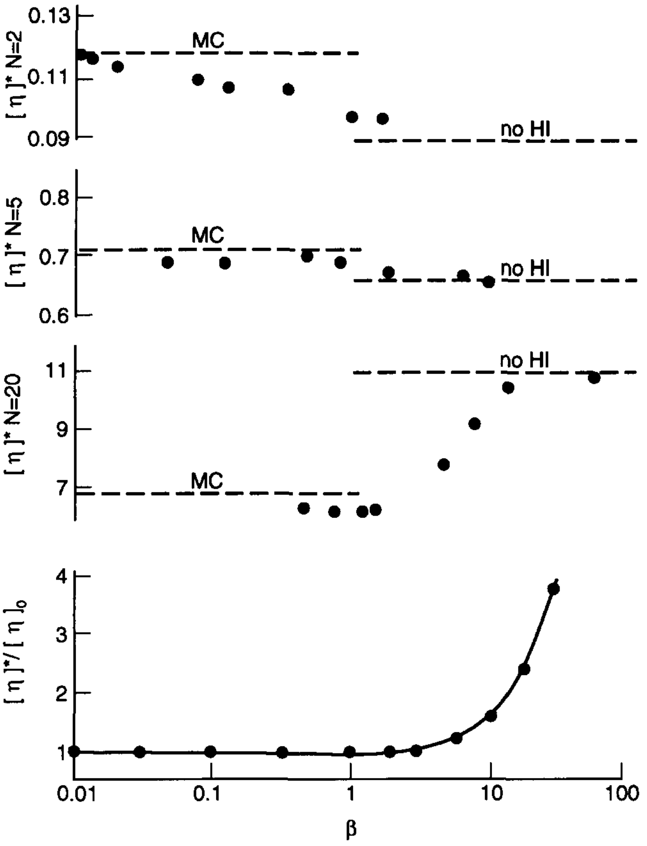

Figure 2 Reduced intrinsic viscosity $[\eta]^*$ *versus* relative shear rate β for bead-and-spring chains without excluded volume. The broken and chain lines are the limits for $\dot{\gamma}=0$ (Monte Carlo) and $\dot{\gamma}\rightarrow\infty$ (without hydrodynamic interaction). The dots for $N=2$, 5 and 20 are the Brownian dynamics simulation data. The theoretical prediction of ref. 18 for $N\rightarrow\infty$ is also presented

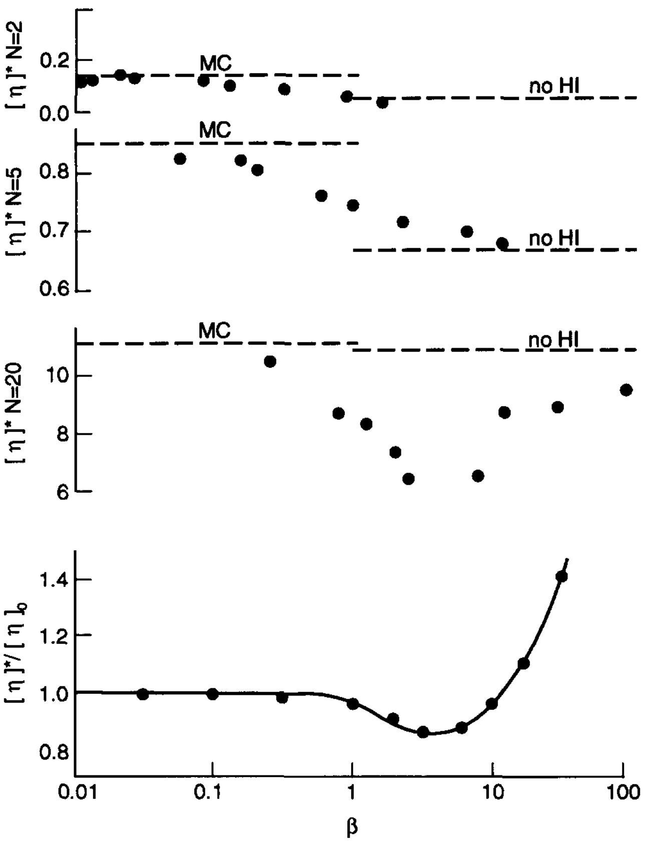

Figure 3 The same as in *Figure 2* for the case with excluded volume

more noticeable (see results for $N=5$) than when EV is not considered. For $N=20$, the two limits have approximately the same height, but we obtain an interesting shear-rate dependence in the form of a deep minimum. As the exponent for $[\eta]_0$ is again smaller than unity, for the same reason as in the no-HI case the viscosity must increase with shear rate for long chains. This is indeed the finding in the renormalization-group calculation, which is also included in *Figure 3*, showing at intermediate β a shallow minimum, which could have the same origin as those exhibited by the simulation results for short chains.

CONCLUSIONS

It has been known for many years that the bead-and-spring model without hydrodynamic interaction or with preaveraged interaction predict a Newtonian, shear-independent behaviour of the viscosity. In previous works[8,9], Brownian dynamics simulation studies for the shortest chain, the dumbbell ($N=2$), indicated that the rigorous inclusion of hydrodynamic interaction resulted in a non-Newtonian, shear-thinning behaviour reminiscent of that found experimentally for polymer solutions. We have now extended the simulations to larger chains, up to $N=20$, finding that hydrodynamic interaction actually leads to a shear-thickening prediction. This behaviour, which is contrary to experimental observations, is explained by the disappearance of interaction effects when the chain is indefinitely stretched at very high shear rates, with an intrinsic viscosity proportional to N, when the zero shear rate scales as $N^{0.5}$. At the cost of more computational effort and more uncertainty in the results, we have included excluded-volume effects in our simulations. Although the excluded volume may change the aspect of the shear-rate dependence for discrete N, even causing a more or less deep minimum, the prediction for very long chains is that the viscosity increases at high shear rates. Scaling arguments again confirm the situation.

Thus, other features additional to hydrodynamic interaction and excluded volume should be included in the model polymer chain. As demonstrated here and elsewhere[8,12], the conclusions about the influence of some particular effect obtained for a dumbbell may be misleading. Therefore, studies on more refined models should concern long chains, and Brownian dynamics simulations can be a very useful tool to examine the influence of such features in chains of varying length.

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