Radiation Scattering by Dilute Polymer Solutions in Shear Flow: An Example of Mesoscale Modeling and Brownian Dynamics Simulation

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Abstract:
The intention of the paper is to illustrate the ability of the Brownian dynamics simulation technique applied to mesoscale polymer models in order to reproduce light scattering experiments of dilute polymer solution under flow. After suitable parameterization of a real polymeric system, polystyrene solved in a oligostyrene/toluene mixture at 299 K (good solvent conditions), a bead-spring model of the polymer chain is built and used to generate molecular trajectories on a computer. Such trajectories will capture the deformational and orientational processes experienced by the real polymer chain under flow. Then, from the set of molecular conformations generated, several polymer properties as well as typical scattering patterns can be reproduced quite accurately. FENE springs were used and excluded volume and non-preaveraging hydrodynamic interaction were taken into account in order to build a chain model as realistic as needed.

Zusammenfassung:

Résumé:
L’intention de cet article est d’illustrer la possibilité d’appliquer la technique de simulation de dynamique Brownienne à des modèles méoscopiques de polymères dans le but de reproduire des expériences de diffusion de lumière sur des solutions diluées de polymère en écoulement. Après une paramétrisation convénable du système polymérique réel, du polystyrène dilué dans un mélange oligostyrène/toluène à 299°K (conditions de bon solvant), un modèle type bille-ressort est construit afin de modéliser la chaîne polymère et est utilisé pour générer des trajectoires moléculaires avec l’ordinateur. De telles trajectoires vont capturer les événements de déformation et d’orientation subits par la chaîne polymère réelle sous écoulement. Ensuite, à partir de l’ensemble de conformations moléculaires générées, plusieurs propriétés polymères ainsi que des figures de diffusion typiques peuvent être reproduites assez précisément. Des ressorts FENE ont été utilisés et le volume exclu, de même que des interactions hydrodynamiques non pré-moyennées ont été prises en compte dans le but de construire un modèle de chaîne aussi réaliste que nécessaire.

Key Words: Brownian Dynamics, bead-spring model, shear flow, light scattering
1 INTRODUCTION

The theoretical and computational study of rheological properties of polymeric systems requires the formulation of adequate models. Inclusion of atomic detail is not feasible, because it would introduce a complexity that is not even needed for many practical situations. Thus, polymers are represented by coarse-grained models, which ignore such unnecessary chemical details, but still describe the essential features of the polymer chain: topology (linear in many cases), flexibility, finite extensibility, etc. It is this intermediate mesoscale what determines essentially the rheological behavior. The classical coarse-grained representation are the bead-and-spring models [1], in which the elements are spheres that have some friction in the viscous solvents and the connectors are springs that represent the variability of distances between parts of the polymer chain.

Even for such simplified models, a fully theoretical treatment is usually impossible. The culprits for this situation are effects such as the hydrodynamic interaction (HI), or the excluded volume (EV) between chain elements. Thus, one has the recourse of simulating the behavior of the system, implementing the first principles of its dynamics in simulation procedure. For polymers in dilute solution, such dynamics is dominated by the Brownian motion of the chain elements in the viscous flow, and the hydrodynamic and energetic interaction between them. For these cases, the proper simulation technique is Brownian dynamics (BD) simulation.

BD simulation has been employed in many instances to determine the most basic properties of polymers in solution: diffusion coefficient, intrinsic viscosity, etc. (see, for instance [2, 3]), but this technique can be employed to study situation of arbitrary complexity, like the stretching and fracture of polymer chains in transient convergent elongational flow [4]. It is just a matter of implementing in the computer procedure the details about flow, polymer topology, etc.

2 THEORY AND METHODOLOGY

2.1 POLYMER MODEL

A single linear flexible polymer is represented using the well-known Rouse bead-spring model [1, 7] consisting of \( N \) beads connected linearly by \( N-1 \) springs. The beads characterize the interactions of the polymer with the solvent whereas the springs represent the elastic force of entropic origin that tends to keep the polymer as a random coil. We use FENE (finite extensible non-linear elongational) springs with the force law given by the Warner approximation [7,8] to the inverse Langevin function,

\[
F_s = \frac{3k_B T \cdot Q}{b^2 \cdot (Q/Q_{\text{max}})^2} \tag{1}
\]

In Eq. 1, \( k_B T \) is the Boltzmann factor, \( Q \) is the instantaneous spring vector and \( Q \) is its modulus. The two parameters in the FENE spring are \( Q_{\text{max}} \) and \( b \). \( Q_{\text{max}} \) is the maximum extension of a FENE spring, and \( b \) determines the Hookean spring constant, \( H = 3k_B T / b^2 \). In the limit of very
great extensibility ($Q_{\text{max}} \rightarrow \infty$), the springs are Hookean and their equilibrium root-mean-square (RMS) length would be $b$. For moderate extensibilities, i.e. for $Q_{\text{max}}$ not very high or very low, the RMS elongation is smaller but not too different from $b$.

The thermodynamic polymer-solvent interaction can be accounted for defining intramolecular potentials between the polymer beads. We modeled the so-called excluded volume effect (EV), related with impossibility of the different chain portions to overlap, using a Lennard-Jones potential [2]. The force between beads derived from this potential reads

$$F_{ij} = 24F_0 \left[ \frac{(\sigma_{ij}^v)^{12}}{r_{ij}^6} - \frac{(\sigma_{ij}^s)^6}{r_{ij}^3} \right]$$

(2)

where $r_{ij}$ is the distance between beads $i$ and $j$, and $\sigma_{ij}^v$ and $\sigma_{ij}^s$ are the Lennard-Jones parameters. The former represents the energy minimum and the latter the distance at which the energy becomes zero. We consider a polymer immersed in a good solvent, in which the polymer chain is expanded by the EV effect. In the limit of very good solvents, the Lennard-Jones parameters are given by $\sigma_{ij}^v = 0.8b$ and $\sigma_{ij}^s = 0.1\sqrt{k_BT}$ [2,9].

The solvent is treated as a continuum in which the chain is embedded. Its effect is taken into account basically through the friction coefficient of the beads, $\zeta = 6\pi\eta_sr$, where $\eta_s$ is the solvent viscosity and $r$ is the hydrodynamic radius of the (identical) beads. A proper description of the polymer dynamics in dilute solution requires the consideration of the solvent-mediated hydrodynamic interaction (HI) between beads. Both the individual friction and the HI effect are correctly represented when one takes a bead radius of about $r = 0.25b$.

With the model and its parameters so defined, the next question is how to assign values to the parameters for a real molecule. As we perform single chain simulations, the number of beads, $N$, can be given an arbitrary value, provided that it is sufficiently large (so that single chain properties, expressed in physical units, will not depend on the exact value of $N$). Given the molecular weight of the polymer, $M$, and that of the monomer, $M_1$, the number of skeletal bonds is immediately determined from the degree of polymerization, $n = M/M_1$, and this gives the maximum length of the fully extended chain, $L_{\text{max}}$, from which the maximum elongation of the springs can be derived by considering the equivalence $L_{\text{max}} = (N-1)Q_{\text{max}}$. For a vinyl polymer there are two C-C bonds per monomer of length $d_{\text{C-C}} = 0.154$ nm. In the fully extended, all-trans zig-zag conformation, the bonds make an angle of $\pi - \alpha_{\text{C-C}}$ with the long axis of the chain, where $\alpha_{\text{C-C}}$ is the C-C-C angle for sp$^3$ carbons, equal to 109.5°. Thus, the maximum bond elongation is given by

$$Q_{\text{max}} = \frac{2M\cos((\pi - \alpha_{\text{C-C}})/2)d_{\text{C-C}}}{(N - 1)M_1}$$

(3)

The assignment of the value for the $b$ parameter requires another piece of information about the polymer. An usually available datum is the root mean square radius of gyration in a quiescent solution, $R_g = \langle s^2 \rangle^{1/2}$. The relationship between $R_g$ and $b$ is complex due to the EV and finite extensibility effects. In the absence of both effects (ideal chain), we would have $R_g = Nb^2/6$, or $b = R_g(6/N)^{1/2}$. The precise value of $b$ can be fitted, after this initial estimation, running simulations without flow, looking for the value of $b$ that reproduces the experimental $R_g$. Knowing $b$ and using the experimental $\eta_s$, the friction coefficient of the beads $\zeta$ is obtained and thus the model is fully parameterized.

2.2 FLOW

We consider the simple and usual case in which the polymer solution is subjected to a simple shear flow. Flow velocity is along direction $x$ and the shear plane is $(x,y)$ and therefore the velocity profile is given by:

$$v_x = \gamma y, \quad v_y = 0, \quad v_z = 0$$

(4)

where $\gamma$ is the shear rate, the only non-zero component of the velocity gradient tensor. It is customary to express the shear rate in a dimensionless way by multiplying it by a characteristic relaxation time of the polymer,

$$\beta = \frac{M_1\eta}{N_1 k_BT} \gamma$$

(5)
where $M$ is the polymer molecular weight, $\eta_s$ the solvent viscosity, $[\eta]$ the polymer intrinsic viscosity, $N_A$ the Avogadro's number, $k_B$ the Boltzmann constant and $T$ the absolute temperature. When the magnitude of the shear rate exceeds the inverse of the characteristic relaxation time $\beta \leq 1$, the chain becomes appreciably deformed and oriented along the flow direction.

### 2.3 BROWNIAN DYNAMICS SIMULATION

The dynamics of the polymer chain, and particularly the motion of the beads in the model, is the resultant of three effects: (i) displacements caused by the internal forces (springs and excluded volume interactions); (ii) Brownian motions caused by the solvent; (iii) drift due to the flow. Owing to the Brownian term, this dynamics is governed by a stochastic differential equation (SDE) that is usually solved in an algorithmic fashion to obtain the time evolution (or trajectory) of the polymer molecule. This SDE is integrated numerically over a small, finite time step, $\Delta t$, using the BD algorithm of Ermak and McCammon [10] with the predictor-corrector improvement of Iniesta and García de la Torre [11]. In this algorithm the position of the beads, $r_i^0$, after a time step, $\Delta t$, are obtained from the previous ones, $r_i^0$, according to:

$$r = r^0 + \frac{\Delta t}{k_BT} D^0 F^0 + \Delta t \nu^0 + R^0$$

where $r$ is the generalized (3N dimensional) position vector containing the coordinates of the position vectors, $r_i$, of all the beads. $F$ and $\nu$ are the generalized vectors for forces and flow velocities at $r$. Note that the force at each bead is the resultant of the spring and EV forces acting on the bead. $D$ is the generalized $3N \times 3N$ diffusion tensor. The $(3 \times 3)$ $D_{ij}$ blocks $(i,j = 1 \ldots N)$ of that tensor take the values $(k_BT/\xi)(\zeta)$ bead friction coefficient and $I$ identity tensor) for $i=j$ and $0$ for $i \neq j$ if no hydrodynamic interaction is considered. In our simulations, we incorporate solvent-mediated, hydrodynamic interactions (HI) without preaveraging approaches by setting the $D_{ij}$ blocks $(i \neq j)$ to $(k_BT)T_{ij}$, where $T_{ij}$ is the Rotne-Prage-Yamakawa (or modified Oseen) tensor [12, 13]. Previous works, including some from of our group [4, 14], corroborate the importance of considering HI effects to get results comparable to experiments. Finally, $\nu^0$ and $\nu'$ are Gaussianly distributed random vectors with zero mean and covariance matrix $2\Delta t D^0$ and $2\Delta t D'$ respectively, that account for the Brownian (stochastic) process.

In the predictor step an estimate, $r'$, of the new conformation (new bead positions) is obtained using the quantities corresponding to the previous conformation, $r^0$. Then the necessary quantities (diffusion tensor, forces and solvent velocity) are evaluated. In the corrector substep the final conformation, $r$, is obtained, again from the previous conformation, but using quantities that are the mean of those at $r^0$ and $r'$.

### 2.4 CONFORMATIONAL PROPERTIES AND SCATTERING

The conformational anisotropy of a polymer coil under shear can be quantified by various tensorial quantities, being a very important one the gyration tensor, $G$. For a chain consisting of $N$ beads with coordinates $r_i^0$ and being $r_{ij} = r_j^0 - r_i^0$, this tensor is defined as:

$$G = \frac{1}{2N^2} \sum_{j=1}^{N} \sum_{j=1}^{N} (r_j^0)$$

where the bracket, $\langle \rangle$, stands for a conformational ensemble average. The mean squared radius of gyration is extracted from the trace of the tensor: $<s^2> = TrG$.

A most valuable technique to monitor the size and conformation of polymer molecules is the scattering of electromagnetic radiations like in x-ray, neutron, or light scattering. The conformational information is contained in the angular variation of the scattered intensity, $I$. The angular dependence is characterized in terms the so-called scattering vector, $q$. Let $u_i$ be an unitary vector along the incident beam direction and $u_s$ an unitary vector along the scattered beam direction. The direction of $q$ is then $u_s - u_i$ and its modulus

$$q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right)$$

where $\theta$ is the angle of incidence.
mental. In the second group of Eq. 10, \( K \) is the so-called optical constant, depending on the refractive indices of solvent and solution, \( F(c) \) is a function of concentration, \( c \), that accounts for the non-ideality of the solution (\( F(c) = 1 \) for an ideal solution), and the most important term is the scattering form (or structure) factor, \( P(q) \), which accounts for the interference between rays scattered by all the subunits in the polymer molecule, and depends on the direction of observation (angle \( \theta \) and \( \phi \)) through the scattering vector \( q \). This is the most interesting (truly molecular) part of the angular dependence of the scattered intensity, as it comes exclusively from the details of the polymer conformation.

In a bead-spring chain (in general, for solvent molecules composed of \( N \) scattering centers), the form factor can be computed as

\[
P(q) = P(\theta, \phi) = \left\{ \text{Re} \left[ \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(-i q \cdot r_{ij}) \right] \right\}
\]

where \( \lambda \) is the wavelength of the incident radiation and \( \theta \) is the angle subtended by the scattered beam and the prolongation of the incident beam (i.e. between vectors \( u_s \) and \( u_i \)).

In our simulation, we assume a hypothetical scattering geometry (Fig. 1) in which the incident beam comes along the negative \( z \)-axis and is polarized along \( y \). The sample is placed at the origin of the laboratory system of coordinates, and the scattered intensity is measured at points within a plane placed at a distance \( d \) from the sample, so that their position is determined by the angles \( \theta \) and \( \phi \), which in turn describe the orientation of the scattering direction with respect to the incident beam.

The observed intensity of the light scattered by the solution discounted by that scattered by the solvent in the same conditions is given by

\[
\Delta I = \frac{I_0 \sin \psi}{r^2 f(\theta, \phi)} \left( \frac{KcP(q)}{F(c)} \right)
\]

where \( I_0 \) is the intensity of the incident light, \( r \) is the distance from the sample to the pixel in the detector, \( \psi \) is the angle subtended by the direction of polarization and that of observation, and \( f(\theta, \phi) \) is a geometric factor, that describes the angular dependence of the scattering volume detected at a given detector area. All these terms, that enter in the first group of quantities in the right hand side of Eq. 10 are merely geometrical or instru-

At equilibrium (absence of flow), where \( (s^2) = TrG = 3G_{xx} \), the light scattering measurements are usually restricted to a plane (\( \phi \) constant), and Eq. 12 simplifies to the often used expression

\[
P(\theta) = 1 - \frac{1}{3} q^2 (s^2)
\]

As displayed by the above equations, after experimental evaluation of the form factor,
the gyration tensor can be computed and quantitative measurements of macromolecular size and shape can be obtained. Instead, in simulation, the gyration tensor is obtained independently of the form factor through Eq. 8 by using the ensemble of macromolecular conformations generated algorithmically. The corresponding form factor can be then calculated, either directly from the conformational ensemble by using Eq. 11 or by using Eq. 12 and the previously calculated gyration tensor (valid only for low angle $q$).

3 RESULTS

3.1 POLYMER-SOLVENT SYSTEM AND MODEL PARAMETERS

In this work we simulate the real polymer/solvent system studied experimentally in [5]. The experimental system consisted of a dilute solution of monodisperse polystyrene of molecular weight $M = 3.09 \pm 0.17 \times 10^5$ g/mol in a solvent mixture oligostyrene/toluene of viscosity $\eta_s = 0.5$ g/cms and at a temperature of $299 \pm 0.5$ K. Under these conditions the mixture oligostyrene/toluene is a thermodynamically good solvent for polystyrene.

For the number of beads, we chose $N = 31$ which makes the computer simulation not prohibitively time consuming. We take into account that the molecular weight of a polystyrene monomer (C8H8) is $M_1 = 104$ g/mol, and a monomer consists of two carbon-carbon backbone bonds. Then, from Eq. 3 we immediately obtain $Q_{\text{max}} = 24.9$ nm. Next, from the experimental value of the equilibrium radius of gyration of the polystyrene, $R_g = (\langle s^2 \rangle)^{1/2} = 16.8 \pm 0.6$ nm [5], we make a preliminary estimate $b = 5.68$ nm. Then, carrying out simulations without flow, this value is refined, finally obtaining a good fit of $R_g$ for $b = 5.73$ nm (see Fig. 2). This gives $\zeta = 1.35 \times 10^{-6}$ g/s for the bead friction coefficient.

3.2 DEFORMATION AND ORIENTATION UNDER FLOW

The overall deformation induced on the polymer chain by the shear flow can be expressed quantitatively using the ratio of the mean squared radius of gyration of the polymer in flowing solution to that in solution at rest, the so-called deformation ratio $\delta^2$,

$$\delta^2 = \left( \frac{\langle s^2 \rangle}{\langle s^2 \rangle_0} \right)^2 - 1$$  \hspace{1cm} (14)

The deformation is also reflected in the diagonal components of the radius of gyration tensor. Tab. 1 shows values of $\delta^2$ (from simulation and from [5]) and dimensionless values (by dividing by $b^2$) of the components $G_{xx}$ (parallel to flow direction) and $G_{yy}$ (parallel to gradient direction) of the gyration tensor for several values of $b$.

As it is clearly appreciated in Tab. 1, as the flow becomes stronger, the molecule is more and more stretched along the flow direction (increase of $G_{xx}$ and slight decrease of $G_{yy}$), so that the spatial distribution of chain segments acquires therefore an elliptical symmetry. Comparing the experimental results for the deformation ratio reported by Lindner and Oberthür in [5] with our simulation results (see also Tab. 1), we see that, as expected, similar values of $\beta$ lead to similar $\delta^2$.

3.3 SCATTERING

As depicted in Fig. 1, the incident beam in our simulated scattering experiments is placed perpendicular to the plane defined by the flow and gradient directions and the angle $\phi$ is defined with respect to the flow direction ($x$-axis). Also, the scattering is measured in a plane perpendicular to the incident beam, placed at a distance $d$ from the sample. A point $(x, y)$ within that plane corresponds to a scattering direction with angles $\theta$ and $\phi$. The scattering intensity $I(q)$ is given by the following formula:

$$I(q) = \sum_{\beta=2}^{\infty} \frac{1}{\beta^2} \frac{G_{xx}(\beta)}{b^2} + \frac{1}{\beta^2} \frac{G_{yy}(\beta)}{b^2}$$

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$\beta$ & $\delta^2$ & $G_{xx}/b^2$ & $G_{yy}/b^2$ \\
\hline
0.38 & 0.03±0.05 & 2.68±0.17 & 2.55±0.17 \\
0.44 & 0.05±0.05 & Exp. value from [5] & \\
1.19 & 0.12±0.07 & 3.52±0.3 & 2.44±0.17 \\
2.17 & 0.23±0.07 & 5.20±0.8 & 2.52±0.2 \\
4.76 & 0.46±0.15 & 11.6±0.6 & 1.98±0.08 \\
4.95 & 0.55±0.11 & Exp. value from [5] & \\
11.91 & 2.1±0.6 & 22.3±2 & 1.86±0.09 \\
23.83 & 6.5±0.8 & 59±6 & 1.63±0.08 \\
\hline
\end{tabular}
\caption{Deformation with flow.}
\end{table}
Figure 3: Scattering patterns produced by our polymer model and scattering geometry under shear rates of a) \( \beta = 0 \), b) \( \beta = 1.19 \), c) \( \beta = 4.76 \), and d) \( \beta = 11.91 \). Screen coordinates normalized to the sample-screen distance \( d \): horizontal axis, \( x/d \), is the flow direction and vertical axis, \( y/d \), the gradient direction. For a better appreciation, isolines corresponding to values of \( P(x,y) \) between 0.1 and 0.9 are displayed as solid lines in intervals of 0.1.

\( \phi \) such that \( x = d \tan \theta \cos \phi \) and \( y = d \tan \theta \cos \phi \). The intensity measured at each point reflects the angular variation of \( \Delta I \), as indicated in Eq. 10. As mentioned above, there are some instrumental factors influencing the angular dependence: (i) the distance from the detection point to the sample, \( r = d / \cos \theta \); (ii) the term dependent on the polarization of the incident ray; for instance, if this were polarized along the flow direction, then \( \sin \nu = \sin \phi \), and (iii), the factor determining the effective scattering volume for a given direction \( f(\theta, \phi) \). In order to avoid these uninteresting details, we express the excess intensity scattered by the polymer at each point in a corrected form, given by:

\[
P(x,y) = \left( \frac{I}{f(\theta, \phi)} \right) P(c) d\theta d\phi
\]

Obviously \( P(x,y) \) is equivalent to \( P(\theta, \phi) \) after changing the linear coordinates by the polar angles. Furthermore, if the coordinates are expressed as \( x/d \) and \( y/d \), the intensity patterns are independent of \( d \), and the overall shape acquired by the polymer molecule under flow is what determines the aspect of these patterns.

The scattering diagrams presented here correspond to an angular range \( 0^\circ \leq \theta \leq 17^\circ \) and \( 0^\circ \leq \phi \leq 360^\circ \). Figs. 3a - d display the scattering patterns obtained when our polymer system undergoes a shear flow of \( \beta = 0 \) (no flow), 1.19, 4.76 and 11.91 respectively. For \( \beta = 0 \) the isointensity lines are circles (note that if we had plotted absolute intensities the pattern would not be circular due to the instrumental terms). For \( \beta \approx 1 \) the flow is so weak that no appreciable deformation of the random coil occurs. To better observe the shear-induced deformation of the polymer chain and the subsequent deviation of the spherical symmetry, we show scattering patterns obtained for \( \beta > 1 \). For such a condition, the flow is strong enough and the isointensity lines acquire a clear elliptical symmetry. As observed, deformation and orientation increase strongly with \( \beta \), being the isolines able to reach highly stretched shapes. It can be also appreciated that, along any axis, the intensity (and analogously the form factor) decreases from the center to the border of the screen, i.e. with increasing angle \( \theta \).

On the other hand, as also observed in the scattering patterns, when solution is not at equilibrium, for a given \( \theta \), the form factor depends on \( \phi \). Therefore, by maximizing Eq. 12 in the variable \( \phi \), it is possible to write an analytical expression yielding the angle \( \phi \) at which the form factor is maximum (see also [15])

\[
\phi_{\text{max}} = \frac{1}{2} \text{arctan} \left( \frac{2G_{xy}}{G_{xx} - G_{yy}} \right)
\]

According to Eq. 16, \( \phi_{\text{max}} \) is independent on \( \theta \). Because Eq. 12 was derived for low \( \theta \), Eq. 16 is expected to give accurate predictions when compared with results obtained at low \( \theta \). Fig. 4 shows several curves containing the dependence of the form factor on \( \phi \) for a fix \( \theta = 5^\circ \) and different shear rates, i.e. different \( \beta \). Because of the periodicity of the tangent function, the same value for the form factor will appear at \( \phi_{\text{max}} + 180^\circ \) so that in Fig. 4 we present results for an angular range \( \phi < 180^\circ \). As observed, for \( \beta = 0 \) (equilibrium), the form factor is practically independent on the angle \( \phi \), in agreement with Fig. 3a which presents isointensity lines with spherical symmetry. For \( \beta > 0 \) curves present a maximum value of the form factor at a \( \phi \) equal to \( \phi_{\text{max}} \) as calculated with Eq. 16. As appreciated, the value \( \phi_{\text{max}} \) tends to \( 45^\circ \) for very low shear rates, as predicted theoretically, and is shifted at smaller values of \( \phi \) as \( \beta \) increases. This is a consequence of the increasing orientation of the polymer segments with the
flow direction. Indeed, as observed in Figs. 3b - d, the orientation of the molecule can be measured by the angle between the major axis of the ellipsoid formed by the isointensity lines and the flow direction (x-axis), i.e. our angle $\phi_{\text{max}}$. Thus, when $\phi_{\text{max}} = 0^\circ$ the ellipsoid is fully aligned with the flow.

It is customary in the literature to define an orientation angle $\chi$ (equivalent to our $\phi_{\text{max}}$) which is related to the dimensionless shear rate, $\beta$, as

$$\chi = \phi_{\text{max}} = \frac{1}{2} \arctan \frac{m}{\beta}$$

(17)

where $m$ is, in general, an adjustable parameter that will depend on the system under study and is called orientation resistance. Experimentally, orientation is often monitored by flow birefringence, in which case the stress tensor defines the orientation angle in an analogous way to the gyration tensor in Eq. 16. For that property and low shear rate, $m$ is a constant with value $m = 3.4$, as obtained from Brownian dynamics [16] and confirmed by other approaches [15]. However, as shown, among others, by Bossart and Öttinger [15], $m$ is not the same for a computation of the orientation angle based on the gyration tensor (this work; see Eq. 16), as for a calculation based on the stress tensor; let us call these parameters $m_G$ and $m_t$, respectively. Furthermore, $m$ depends on the shear rate $\beta$ and therefore we should not employ it as a constant to make calculations. Using Eq. 17 and values for $m_t$ extracted from Fig. 2 in [15] for $\beta = 0.38, 1.19, 4.76$ and 11.91, the corresponding orientation angles can be computed: $\chi = 39.4^\circ, 29.2^\circ, 11.7^\circ$ and $3.9^\circ$ respectively. Those values can be compared to the values obtained from our Brownian dynamics simulations by using Eq. 16: $\chi = 38.5^\circ, 27.9^\circ, 18.9^\circ$ and $13.5^\circ$. Clearly, in better agreement with our results.

4 SUMMARY

In this paper we have shown the utility of the Brownian dynamics simulation technique applied to bead-spring models of flexible polymers to mimic the flow behavior of a real polymer system, in the interesting situation of scattering of light by the flowing polymer solution. A key point is the correct parameterization of the polymer under study. The chain model used in this work was based on two parameters: the number of elements (beads) of the chain, $N$, which is chosen by the user, and the equilibrium length of a Hookean spring in the chain, $b$, which must be fit to the physical dimensions of the polymer. Besides, as we took into account excluded volume interactions because of good solvent conditions, two Lennard-Jones parameters were also needed and obtained from the literature [9]. The ensemble of chain conformations numerically generated was then analyzed by using the suitable theory in order to get two closely related polymeric properties, gyration tensor (Eq. 8) and form factor (Eq. 11), the latter being a primary measured quantity in light scattering experiments. The expected angular dependencies for the form factor are perfectly captured by the numerical simulations despite the approximations inherent to the model. In this work we also shown the use of the angular dependency of the form factor to computationally create the typical scattering patterns appearing on a detecting plane placed perpendicular to the incident beam in a real light scattering experiment.

The main cause of this disagreement is the different spring type used. Authors in [15] work on Gaussian chains whereas we employ FENE springs whose behavior increasingly diverges from Gaussian as chains are more stretched. Indeed, orientation of FENE chains becomes more difficult in increasing the shear rate. Aust et al. [17] used nonequilibrium molecular dynamics simulations to study, among other properties, the shear rate dependence of $m_G$ in dilute polymer solutions by employing the FENE chain model. Using the values of $m_G$ obtained by those authors (see Fig. 7 in [17] and text related) and using Eq. 17 as before, we found the following series of orientation angles for the same values of $\beta$ as above: $\chi = 38.7^\circ, 27.9^\circ, 18.9^\circ$ and $13.5^\circ$. Clearly, in better agreement with our results.
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