

RADIATION SCATTERING BY DILUTE POLYMER SOLUTIONS IN SHEAR FLOW: AN EXAMPLE OF MESOSCALE MODELING AND BROWNIAN DYNAMICS SIMULATION

J.G. HERNÁNDEZ CIFRE AND J. GARCÍA DE LA TORRE

Departamento de Química Física, Facultad de Química
Universidad de Murcia, 30071 Murcia, Spain

* Email: jghc@um.es
Fax: x34.968.364148

Received: 22.5.2003, Final version: 17.6.2003

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:

Die Absicht dieses Artikels ist die Illustration der Leistungsfähigkeit der Simulationstechnik der Brownschen Dynamik, angewandt auf mesoskopische Polymermodelle, um Lichtstreuexperimente für verdünnte Polymerlösungen unter Strömungseinfluss zu reproduzieren. Nach einer geeigneten Parametrisierung eines realen Polymersystems, Polystyrol in einer Oligostyrol/Toluol Mischung bei 299K (gute Löslichkeit), wird ein Perlen-Feder Modell der Polymerkette konstruiert und dazu benutzt, Molekültrajektorien am Computer zu generieren. Solche Trajektorien erfassen den Deformations- und Orientierungsprozess welcher von der realen Polymerkette unter Strömungseinfluss wahrgenommen wird. Aus dem Satz von generierten Molekülkonformationen können dann verschiedene polymere Eigenschaften sowie typische Streubilder relativ genau reproduziert werden. FENE-Federn, ausgeschlossene Volumina und exakt gemittelte hydrodynamische Wechselwirkungen wurden berücksichtigt, um ein Kettenmodell zu realisieren, welches so realistisch als möglich ist.

RÉSUMÉ:

L'intention de cet article est d'illustrer la possibilité d'appliquer la technique de simulation de dynamique Brownienne à des modèles mésoscopiques de polymères dans le but de reproduire des expériences de diffusion de lumière sur des solutions diluées de polymère en écoulement. Après une paramétrisation convenable 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

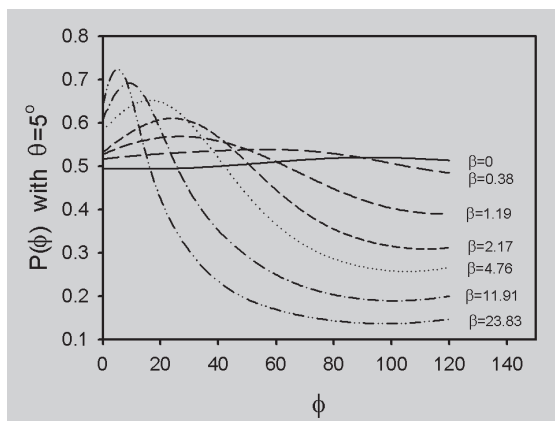


Figure 4: Evolution of the form factor, $P(\theta, \phi)$, with the angle ϕ for fix $\theta = 5^\circ$ and varying β .

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 ϕ_{max} . Thus, when $\phi_{max} = 0^\circ$ the ellipsoid is fully aligned with the flow.

It is customary in the literature to define an orientation angle χ (equivalent to our ϕ_{max}) which is related to the dimensionless shear rate, β , as

$$\chi = \phi_{max} = \frac{1}{2} \arctan \frac{m}{\beta} \quad (17)$$

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_τ , respectively. Furthermore, m depends on the shear rate β and therefore we should not employ it as a constant to make calculations. Using Eq. 17 and values for m_θ 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° respectively. Those values can be compared to the values obtained from our Brownian dynamics simulations by using Eq. 16: $\chi = 38.5^\circ, 27.2^\circ, 16.2^\circ$ and 9.3° . Both series of χ values show the same qualitative behavior. However, the relatively good quantitative agreement appreciated at low β values is lost in increasing the shear rate.

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 β as above: $\chi = 38.7^\circ, 27.9^\circ, 18.9^\circ$ and 13.5° . 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.

ACKNOWLEDGMENTS

This work has been supported by grant BQU2000-0229 from Dirección General de Enseñanza Superior e Investigación Científica, M.E.C.D. J.G.H.C. is the recipient of a Ramón y Cajal postdoctoral research contract.

REFERENCES

- [1] Rouse PE: A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *J. Chem. Phys.* 21 (1953) 1272–1280.
- [2] Freire JJ, Rey A, García de la Torre J: Monte Carlo calculations for linear and star polymers 2. Non-preaveraged study of hydrodynamic properties at the theta state. *Macromolecules* 19 (1986) 457–462.
- [3] Laso M, Kröger M, Alba-Pérez A, Öttinger HC: Variance reduced brownian simulation of a bead-spring chain under steady shear flow considering hydrodynamic interaction effects. *J. Chem. Phys.* 113 (2000) 4767–4773.
- [4] Knudsen KD, Hernández Cifre JG, García de la Torre J: Conformation and fracture of polystyrene chains in extensional flow studied by numerical simulation. *Macromolecules*, 29 (1996) 3603–3610.
- [5] Lindner P, Oberthür RC: Shear-induced deformation of polystyrene coils in dilute solution from small angle neutron scattering. 2-variation of shear gradient, molecular mass and solvent viscosity. *Colloid Polym. Sci.* 266 (1988) 886–897.
- [6] Link A, Springer J: Light scattering from dilute polymer solutions in shear flow. *Macromolecules* 26 (1993) 464–471.
- [7] Bird RB, Curtiss CF, Armstrong RC, Hassager O: *Dynamics of Polymeric Liquids, Kinetic Theory*, volume 2. John Wiley and Sons, New York, 2nd. ed. edition, 1987.
- [8] Warner HR: Kinetic theory and rheology of dilute suspensions of finitely extendible dumbbells. *Ind. Eng. Chem. Fundam.* 11 (1972) 379–387.
- [9] Rey A, Freire JJ, García de la Torre J: Monte Carlo calculations for linear and star polymers. 3. Dimensions and hydrodynamic properties in good solvents. *Macromolecules* 20 (1987) 342–346.
- [10] Ermak DL, McCammon JA: Brownian dynamics with hydrodynamic interactions. *J. Chem. Phys.* 69 (1978) 1352–1360.
- [11] Iniesta A, García de la Torre J: A second-order algorithm for the simulation of the Brownian dynamics of macromolecular models. *J. Chem. Phys.* 92 (1990) 2015–2019.
- [12] Rotne J, Prager S: Variational treatment of hydrodynamic interaction on polymers. *J. Chem. Phys.* 50 (1969) 831–837.
- [13] Yamakawa H: Transport properties of polymer chains in dilute solution: hydrodynamic interaction. *J. Chem. Phys.* 53 (1970) 436–443.
- [14] Hernández Cifre JG, García de la Torre J: Steady-state behavior of dilute polymers in elongational flow. Dependence of the critical elongational rate on chain length, hydrodynamic interaction and excluded volume. *J. Rheol.* 43 (1999) 339–358.
- [15] Bossart J, Öttinger HC: Orientation of polymer coils in dilute solutions undergoing shear flow: birefringence and light scattering. *Macromolecules* 28 (1995) 5852–5860.
- [16] Knudsen KD, Elgsaeter A, López Cascales JJ, García de la Torre J: Flow birefringence of flexible polymer chains in steady shear flow. A Brownian dynamics simulation. *Macromolecules* 26 (1993) 3851–3857.
- [17] Aust C, Kröger M, Hess S: Structure and dynamics of dilute polymer solutions under shear flow via nonequilibrium molecular dynamics. *Macromolecules* 32 (1999) 5660–5672.

