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Structure of a tethered polymer under flow using molecular dynamics and hybrid molecular-continuum simulations

Rafael Delgado-Buscalioni[a], Peter V. Coveney[b],*

[a]*Departmento de Ciencias y Técnicas Fisicoquímicas, UNED, Madrid 28040, Spain*
[b]*Department of Chemistry, Centre for Computational Science, University College London, London WC1H 0AJ, UK*

Abstract

We analyse the structure of a single polymer tethered to a solid surface undergoing a Couette flow. We study the problem using molecular dynamics (MD) and hybrid MD-continuum simulations, wherein the polymer and the surrounding solvent are treated via standard MD, and the solvent flow farther away from the polymer is solved by continuum fluid dynamics (CFD). The polymer represents a freely jointed chain (FJC) and is modelled by Lennard-Jones (LJ) beads interacting through the FENE potential. The solvent (modelled as a LJ fluid) and a weakly attractive wall are treated at the molecular level. At large shear rates the polymer becomes more elongated than predicted by existing theoretical scaling laws. Also, along the normal-to-wall direction the structure observed for the FJC is, surprisingly, very similar to that predicted for a semiflexible chain. Comparison with previous Brownian dynamics simulations (which exclude both solvent and wall potential) indicates that these effects are due to the polymer–solvent and polymer–wall interactions. The hybrid simulations are in perfect agreement with the MD simulations, showing no trace of finite size effects. Importantly, the extra cost required to couple the MD and CFD domains is negligible.
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1. Introduction

If a polymer molecule is subject to a sufficiently strong hydrodynamic flow it becomes deformed and stretched. The deformation of polymers attached to surfaces is of great interest for many applications such as colloidal stabilisation, lubrication, chromatography, manufacture of composites and so on [1]. It is also relevant for biological systems, where molecules can protrude from lipid bilayer membranes [2]. In most cases these applications involve shearing of the tethered polymer. Flow-induced changes in the polymer conformations in a dilute solution can be dramatic, and are assumed to be responsible for the existence of important macroscopically observable phenomena [3]. Indeed, the structure and dynamics of a single tethered polymer subject to flow, has attracted the attention of several groups in recent years and their work provides new insights into polymer physics (see Refs. [1–4] and references therein). Recent experiments could observe

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*Corresponding author. Tel.: +44 20 7679 4560; fax: +44 20 7679 7463.
E-mail address: p.v.coveney@ucl.ac.uk (P.V. Coveney).

the motion of individual DNA chains using fluorescence videomicroscopy [1,4]. This opened the investigation of the dynamic properties of individual chains in shear flow, either tethered to a wall [1] or free [4]. Simulations using full molecular dynamics (MD) are too computationally expensive because of the long time scales associated with polymer motion. Hence, most simulations of single chains have been using Brownian dynamics (BD) [2,3], without considering explicit solvent and many without considering any hydrodynamic representation. The single tethered polymer was also studied using an alternative to the BD method which models the effect of the solvent–polymer interaction using the so-called collision dynamics method [3]. This method uses virtual solvent particles which produce instantaneous changes in the velocities of the beads, taken from a Maxwell distribution at the local flow velocity. However, this reductionist approach is still far from being truly atomistic: it does not take into account the solvent structure and the long-range solvent–polymer interactions and does not include hydrodynamic effects. A third alternative is to use hybrid particle-continuum simulations which treat the region around the polymer chain in fully atomistic detail, while dynamically coupling this MD region to a continuum-fluid-dynamics (CFD) solution of the solvent flow in the bulk [5,6]. Recently, our group used the hybrid approach to study a tethered polymer under shear flow and compared it with results obtained via standard MD [7]. We found excellent agreement, showing that the hybrid model can avoid finite size effects in quite small MD domains. A relevant feature of the hybrid scheme is that the computational cost required to couple the CFD and MD models is quite small (less than 5% of the grand simulation total). In the tethered polymer problem, the ability to exchange mass (and energy) with the contiguous continuum region [8] allows us to eliminate the solvent density waves produced by the polymer motion from the MD domain [7]. More generally, the hybrid model can consistently include hydrodynamic interactions with the bulk flow, further away from the MD simulation subdomain.

2. Method

In this article we focus on the analysis of the polymer structure obtained from our hybrid and MD simulations. Hence we shall describe only the details of the polymer, solvent and wall models, and refer to Barsky et al. [7] for a full technical description of the present simulations and to Delgado-Buscalioni and Coveney [5,9] for the theoretical foundation of the hybrid model. The system considered is depicted in Fig. 1. A fluid fills the space between two walls and, due to the motion of the upper wall, is subject to a constant shear. A single non-extensible polymer of contour length L is tethered to the bottom wall and interacts with the solvent flow and the bottom wall. The polymer model is based on the bead-spring model developed by Kremer and Grest [10] and contains $N = 60$ monomer beads linked along a chain with the FENE potential $U_{nn}(r_{ij}) = -\frac{1}{2}kR_0^2 \ln[1 - (r_{ij}/R_0)^2]$ for $r_{ij} < R_0$, and $U_{nn} = \infty$ otherwise. Here r_{ij} is the distance between neighbouring beads i and $j = i \pm 1$, $R_0 = 1.5\sigma$, $k = 30\varepsilon/\sigma^2$, σ and ε setting the length and energy scales, respectively. The polymer is anchored to the wall by enforcing the same FENE potential between the tethered end of the polymer and one wall atom. The monomers in the solvent and in the polymer interact through a purely repulsive LJ potential $U_{LJ}(r_{ij}) = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$ for $r_{ij} < 2^{1/6}\sigma$ and $U_{LJ} = 0$ for $r_{ij} \geqslant 2^{1/6}\sigma$. The wall–fluid and wall–polymer interactions are LJ with an increased cut-off, $r_c 1.25\sigma$, and energy scale $\sqrt{1.7}\varepsilon$. The momentum equation for the solvent flow within the continuum region (C) was solved by a finite volume method [7,9] while the equations of motion of the particles were integrated using a velocity Verlet algorithm with a time step $\delta t = 0.0075\tau$, where $\tau \equiv \sigma\sqrt{m/\varepsilon}$ and m is the mass of a monomer. A constant temperature of $k_B T = 1.0\varepsilon$ (where k_B is the Boltzmann constant) is maintained with a Langevin thermostat added to the equations of motion for the velocity components normal to the mean flow. The mean fluid density is approximately $\rho = 0.8\sigma^{-3}$ in the bulk fluid, although density oscillations are induced within a few σ of the walls [7]. The present set up contrasts with previous published simulations of similar systems [2,3], which considered purely reflecting walls and no explicit solvent.

3. Results and analysis

For the FENE potential considered here the contour length of the polymer $L = (N - 1)b$ (where $b \cong 0.965$ is the bead-to-bead distance) is nearly independent of the shear rate. The tethered polymer can be assumed to behave according to Rouse dynamics [2,11] with its longest relaxation time given by the Rouse time under