Computer Simulation Studies of the Rheology of Soft Condensed Matter

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We report a selection of results from our extensive molecular dynamics simulation studies of the rheological properties of polymer melts, polymer solutions and colloidal dispersions, and discuss how they can be used to critically evaluate constitutive equations and macroscopic fluid dynamics.

1. Introduction

The rheology of soft condensed matter systems, such as polymer melts, polymer solutions and colloidal dispersions, is a subject of enduring interest - not only because of its importance in materials processing technology, but also because of the fascinating theoretical challenges it presents. Many of the rheological features possessed by these systems, such as normal stress differences, non-Newtonian viscosity and elasticity, are spectacularly evident on the macroscopic scale, but these properties are also crucial to emerging modern technologies such as micro- and nano-fluidics. Over the last seven years, we have studied many different aspects of the rheology of soft condensed matter systems using non-equilibrium molecular dynamics computer simulation techniques. Of particular importance, has been our development of a new algorithm for studying elongational flow [1], a comparison of the planar elongational and shear flow rheology of molecular fluids [2], our examination of the approach to the Brownian limit in colloidal fluids [3], and our detailed investigation of the concentration dependence of the viscosity and normal stress differences in short-chain polymer solutions [4]. In this paper, we discuss two examples of simulation studies that we have conducted and briefly describe our current work and future directions.

2. Computational methods

The principles of equilibrium and non-equilibrium molecular dynamics simulation methods are now well-known and have been discussed in detail previously [1]. In the simplest cases, Newton’s equations of motion are solved for a set of atoms interacting via classical forces derived from potential energy functions, and the desired equilibrium properties of the system are obtained from the positions and velocities of the atoms. In more sophisticated simulations, constraint forces are used to satisfy molecular bond constraints and synthetic external forces are applied so as to generate non-equilibrium fluxes and control the temperature and pressure [2]. The molecular models that we employ are simple, so as to reduce the computational demands, which are substantial. Therefore, solvent molecules and colloidal particles are represented as simple, uncharged particles, interacting with a Lennard-Jones type potential energy function given by

\[
\Phi_{ij} = 4\epsilon \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \quad r_{ij} > r_c
\]

where \(r_{ij}\) and \(\sigma_{ij}\) represent the range and strength of the Lennard-Jones interaction, \(r_c\) is the distance at which the potential is truncated, and \(\epsilon\) is an energy shift that can be added to ensure that the energy goes smoothly to zero at the truncation point. The parameter \(d_{ij}\) represents the ‘core’ of the potential, which is used when we simulate colloidal particles with
a size that can be varied independently of the interaction range. Polymer molecules are simulated by using a type of ‘freely jointed chain’ model [2]. Periodic boundary conditions eliminate boundary effects, which would otherwise be significant for small systems. Our novel, highly optimised algorithm for simulation of elongational flow has been described in detail in previous publications [1, 5, 6].

3. Results

It is not possible to discuss all of our results in detail in the space available. Instead, we have chosen to give some examples of the ways in which molecular dynamics computer simulations can answer difficult questions in soft condensed matter physics.

3.1 Shear and elongational rheology of polymer melts

One of the main goals of rheology is to determine appropriate constitutive relations to describe the relationship between stress and strain rate in deforming fluids. Newton’s law of viscosity is the well-known linear relationship between stress and strain rate for a fluid in steady shear that defines the low-shear rate limit of the shear viscosity. For unsteady deformations at high shear rate, the most general relationship between stress and deformation rate is an unknown non-linear functional of the strain history. Many constitutive equations that bridge the gap between these two extremes have been derived from continuum theory, microscopic theory and combinations of these. One that is independent of the detailed microstructure of the material being investigated, but limited to low deformation rates, is the retarded motion expansion, which results in a stress tensor that is a polynomial function of the deformation rate. A stringent test of any non-linear constitutive equation is the extent to which it can consistently describe different types of deformation with a single set of material properties. We have conducted steady shear and steady planar elongational flow simulations on systems of short-chain polymer melts [2] to test the consistency of the retarded motion expansion truncated at second order in the strain rate. The results shown in Table 1 demonstrate that a remarkable degree of consistency exists between the results for the two types of deformation – a result that would be very difficult to obtain experimentally, due to the low reliability of experimental measurements of steady planar elongational flow.

Table 1. Material constants obtained from simulations of shear and elongational flow. N = chain length, \( \beta_0 \) = zero shear viscosity, \( (\beta_1/2+\beta_2) \) = a second order material constant.

<table>
<thead>
<tr>
<th>N</th>
<th>( \beta_0^a )</th>
<th>( \beta_0^b )</th>
<th>( \beta_0^c )</th>
<th>( (\beta_1/2+\beta_2)^a )</th>
<th>( (\beta_1/2+\beta_2)^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.957(2)</td>
<td>2.965(5)</td>
<td>2.99(2)</td>
<td>0.21(7)</td>
<td>0.8(2)</td>
</tr>
<tr>
<td>4</td>
<td>4.26(3)</td>
<td>4.3(1)</td>
<td>4.20(5)</td>
<td>6(3)</td>
<td>4.0(5)</td>
</tr>
<tr>
<td>10</td>
<td>7.91(7)</td>
<td>8.6(1)</td>
<td>7.9(2)</td>
<td>60(10)</td>
<td>62(7)</td>
</tr>
<tr>
<td>20</td>
<td>14.6(2)</td>
<td>16.5(3)</td>
<td>14.5(5)</td>
<td>700(100)</td>
<td>600(100)</td>
</tr>
<tr>
<td>50</td>
<td>40.9(9)</td>
<td>46(2)</td>
<td>42(4)</td>
<td>18000(6000)</td>
<td>19000(4000)</td>
</tr>
</tbody>
</table>

\(^a\)From shear flow, \(^b\)from the first elongational viscosity, \(^c\)from the second elongational viscosity.

3.2 The approach to the Brownian limit

Brownian motion theory, as expressed by the classical Langevin equation, describes the motion of a suspended colloidal particle in a solvent. The solvent is represented as a continuum – its effect on the colloidal particle in the Langevin equation appears as a macroscopic friction coefficient and a ‘random’ force. This is clearly a limiting case, but very little is known about the way in which the ‘Brownian limit’ is approached. Theoretical treatments often express this limit solely in terms of the ratio of the mass of the colloidal particle to the mass of the solvent molecules. However, it has recently been suggested that the
ratio of particle sizes is also an important factor in the rate of approach to the Brownian limit. This question is an ideal subject for molecular dynamics simulations, because the complicated microscopic behaviour of the solvent can be taken into account with minimal assumptions by using an explicit ‘atomic’ model of the solvent [3]. Fig. 1 shows the change in the velocity autocorrelation function as the mass ratio is increased to a value of 10. In the Brownian limit, the velocity autocorrelation function is expected to be an exponential. This limit is clearly not reached in this data set, but the exponential part of the decay becomes better defined and more significant as the mass ratio increases, as expected. The time for the onset of the exponential part of the relaxation does not vary significantly if the size of the solute remains fixed while the mass ratio is increased. A more natural way of approaching the Brownian limit is to increase the particle size and mass, keeping the particle density constant. Our calculations of the viscosity of suspensions indicates that, by varying the size, the Brownian limit is approached more rapidly than by varying only the mass [7].

![Fig. 1. Logarithm of the velocity autocorrelation function versus time.](image)

3.3 Current work and future directions

We are currently conducting simulations of flow of colloidal suspensions in narrow planar channels in which the ratio of channel width to colloidal particle size ranges between 1.5 and 120. Preliminary results show that classical Navier-Stokes hydrodynamics is inadequate for the smaller channels, due to particle ordering near the walls. Modelling of such a system with the equations of hydrodynamics will require full consideration of coupled mass, heat and momentum transfer, accounting for non-locality and inhomogeneity.

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References