The flow of colloids and polymers in channels simulated using non-equilibrium molecular dynamics

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Abstract
Here we report the results of non-equilibrium molecular dynamics simulations of the flow of
colloidal and polymer particles in a thin channel with explicit inclusion of the background fluid.
The simulations used atomic channel walls which were thermostated and an external field was
imposed to produce planar Poiseuille flow at low Reynolds number. Results are presented
which show the effect of channel width and flow rate on the velocity profiles. For wide channels
at low flow rates these profiles are in agreement with the results of macroscopic fluid dynamics
simulations, but discrepancies start to appear when the flow rate is increased and/or the channel
widths become smaller until finally the profiles are dominated by wall effects such as particle
layering and then macroscopic theory is not even qualitatively correct. Importantly it is
observed that colloidal particles tend to migrate to the walls, but the polymer solutions
simulated here tend to migrate to the centre of the channel.

1. Introduction

One of the most easily observed and most studied examples of
a colloidal dispersion in an external field is the case of fluid
flow. Many fascinating phenomena have been seen in such
systems and their practical importance is enormous in fields
such as processing and transport of materials. Simulation of
these systems by traditional Brownian dynamics (BD) methods
is made complicated by wall effects and in particular the need
to include complicated many-body configuration dependent
hydrodynamic interactions between the particles and between
the particles and the walls [1]. A further complication also
arises from having to find an appropriate choice of boundary
conditions at the wall.

An alternative approach to studying flow is provided by
the non-equilibrium molecular dynamics (NEMD) method [2].
In this method the non-equilibrium system is simulated directly
either by the use of a periodic system with suitably modified
equations of motion or by the use of a boundary driven
system [2]. Such simulations allow the direct computation of
the flow properties of fluids such as viscosity and normal stress
differences and if a boundary driven system is used then the
effect of the boundary and of the channel width on the flow
may also be studied.

Boundary driven methods were pioneered by Hoover and
Ashurst [3] and have subsequently been used to study the
flow of many systems between walls e.g. simple fluids [4], a
fluid of non-spherical molecules [5], and of hexadecane [6].
Of particular relevance to the current paper is the study of
a polymer melt by Varnik and Binder [7]. For a colloidal
suspension or polymer solution these methods, unlike normal
BD methods, allows the effect of solvent structure to be
explicitly taken into account and may thus be used to test the
accuracy of the assumptions made in deriving BD algorithms.

Here we have made non-equilibrium molecular dynamics
(NEMD) simulations of the flow of colloidal and polymer
particles in a thin channel with explicit inclusion of the
background fluid. The simulation of these systems in bulk
has been reported previously [8–11]. The simulations reported
here used atomic walls which were thermostated and the
imposition of an external field to produce planar Poiseuille flow
at low Reynolds number. Results will be presented to show the
effect of channel width and flow rate on the velocity profiles.
For wide channels and low flow rates these profiles are in
agreement with the results of macroscopic fluid dynamics but
discrepancies start to appear when the channel widths become
smaller and/or the flow rates larger until finally the profiles are
dominated by wall effects such as particle layering and then
macroscopic theory is not even qualitatively correct.

It is also shown that the rigid colloidal particles in these simulations behave in a qualitatively different manner to that observed for the flexible polymer particles. Firstly for the colloidal system slip at the wall is significant only when the flow rate is high or the channel is small. However for the polymer solutions slip at the wall is significant under all conditions. Secondly whilst the colloidal particles show a tendency to migrate to the walls the opposite is true of the polymer molecules.

2. Systems studied and methods used

We chose to simulate two distinct systems which represent a suspension of rigid spheres dispersed in a fluid of small, spherical particles and a system of short chain polymers dissolved in the same fluid as used for the suspension. The reason for studying these two systems described below is that they represent a model for a system of rigid spherical particles and the closely related system of a polymer with the same interaction potential and dissolved in the same solvent which is taken explicitly into account.

The particles in the suspension interacted according to the Chandler–Weeks–Andersen pair potential [12] modified to include the addition of a core c_{ab} [13] i.e.

$$u_{ab}(r) = 4\varepsilon[\sigma/(r - c_{ab})^{12} - \sigma/(r - c_{ab})^6] + \varepsilon_{ab} \quad (1)$$

if the $c_{ab} < r < c_{ab} + 2\sigma_{ab}^{1/6}$ and $u_{ab} = 0$ if $r > c_{ab} + 2\sigma_{ab}^{1/6}$ where a and b label the particles of the two species i.e. the suspended spheres and the suspension medium. Such potentials have been used before to simulate a bulk colloidal suspension [8, 9, 14, 15]. The particles of the suspension medium (species 1) are taken to have no core $c_{11} = 0$ and unit mass $m_1 = 1.0$ whilst those of the suspended particles have a non-zero core radius c_{22} related to the size ratio and the mass $m_2 = \mu$ is the mass ratio between the suspended and suspension medium particles. The cross radius ratio $c_{12} = 1/2 \, c_{22}$ and for simplicity all other interaction parameters were taken to be the same.

The particles in the polymer solution were all taken to interact according to the pair potential given by equations (1) with $c_{ab} = 0$ in all cases. The polymer chains were bead-rod molecules 20 beads long and the particles in the polymer chain were constrained by the equations of motion to have a bond between polymer interaction sites of length $l = \sigma$ chosen to prevent chain crossings. The bonded beads within each chain do not, of course, interact via the above pair potential. Full details of this model are given elsewhere [10, 11].

We have previously reported results for the diffusion constants and viscosity of this model suspension [8, 9] and the equilibrium and viscometric properties of the polymer solution [10, 11] by non-equilibrium molecular dynamics (NEMD) using homogeneous SLLOD equations with a Gaussian thermostat.

Briefly the viscosity of suspension behaves in a similar manner to that of a suspension of large colloidal spheres which are sterically stabilized by short chain polymers in a non-polar liquid medium. The modelled suspension also shows shear thinning even under conditions where the suspension medium would not [9]. The main difference in flow behaviour between the model suspension and that seen in experiments on a suspension of large spheres is that the boundary condition at the particle fluid interface are not stick but are closer to slip boundaries [9].

The polymer solution shows viscosity increasing with concentration of polymer, shear thinning at high shear rate and a first normal stress coefficient which increases strongly with concentration. However, as the polymers are very short, corresponding to 12 Kuhn steps in the melt which would represent for polyethylene a molar mass of 1800 g mol^{-1} the behaviour of the polymer is distinct from that of a very long chain polymer [10, 11].

3. The flow of colloids in channels

In order to investigate the flow behaviour of the model colloid suspension in a channel we used a boundary driven NEMD system instead of the SLLOD equations used in the bulk simulations mentioned above [8, 9]. Parallel walls confined the suspension on two sides which were modelled by two regular layers of atoms of the same size and mass as those of the suspension medium which were constrained to their lattice positions $\underline{r}_i^{eq}$ by a harmonic tethering force,

$$F_i^w = -k_w(r_i - r_i^{eq}) \quad (2)$$

an optimum of the spring constant $-k_w = 72\varepsilon/2^{1/3} \, \sigma^2 = 57.15$ was found. The momenta of the wall particles were modified by the application of a Gaussian isokinetic thermostat, which maintained the kinetic temperature at each wall of $T_w = 1.0$. Concurrently with the application of the thermostat the wall particles were also held in place by a layer constraint mechanism which keeps them from being pushed back by the pressure of the fluid.

The equations of motion for the suspension particles are simply,

$$\underline{r}_i = \underline{p}_i/m_i \qquad \text{and} \qquad \underline{p}_i = \underline{F}_i - m_i\underline{F}_e \quad (3)$$

where $\underline{r}_i$ and $\underline{p}_i$ are the position and momentum of the ith particle in the system of mass m_i, which are subject to the force of interaction $\underline{F}_i$ and an external force $\underline{F}_e$. The size ratio of the colloidal particles to those of the suspension medium was 2.2254, the mass ratio μ was 10, the concentration of suspended particles was 0.04 i.e. 4% by number or a volume fraction ϕ of 22.5%, at a reduced temperature of 1.0 and an overall reduced number density of 0.85. The number of solvent particles (N_s) and the number of colloidal particles (N_c) used varied from $N_s = 768$ and $N_c = 31$ in the narrowest channels to $N_s = 61440$ and $N_c = 2456$ in the widest channels. A schematic diagram of the system is shown in figure 1.

The external force $\underline{F}_e$ which was directed in the x-direction produced planar Poiseuille flow in the y-direction and its magnitude allowed us to vary the shear rate which was always kept low enough so that the flow of the bulk suspension would have been in the Newtonian regime.
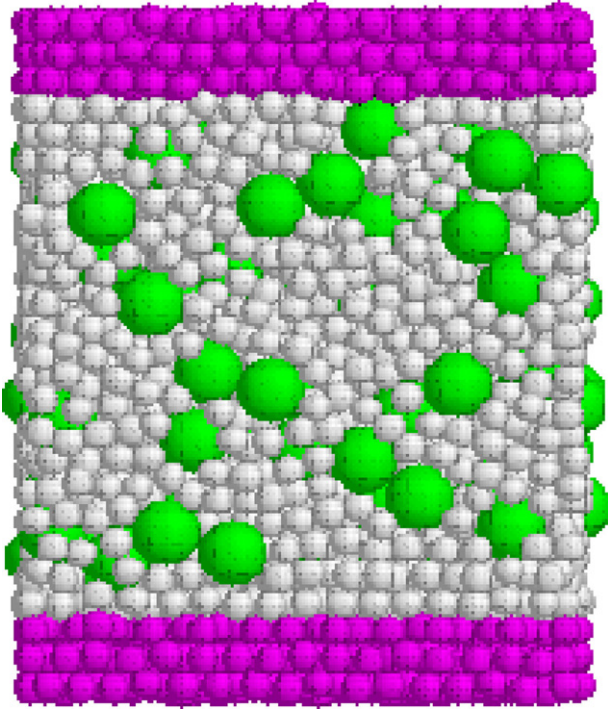
Figure 1. The cell used for the NEMD studies of flow in channels. The pink spheres represent the fixed wall particles, the small grey spheres represent the particles of the background fluid and the large green spheres those of the dispersed phase.

(This figure is in colour only in the electronic version)

Thus, as only the walls and not the suspension were thermostated we were able to measure the temperature profile of the suspension as well as the velocity, u_x and concentration profiles.

The channel widths accessible to the fluid were defined as
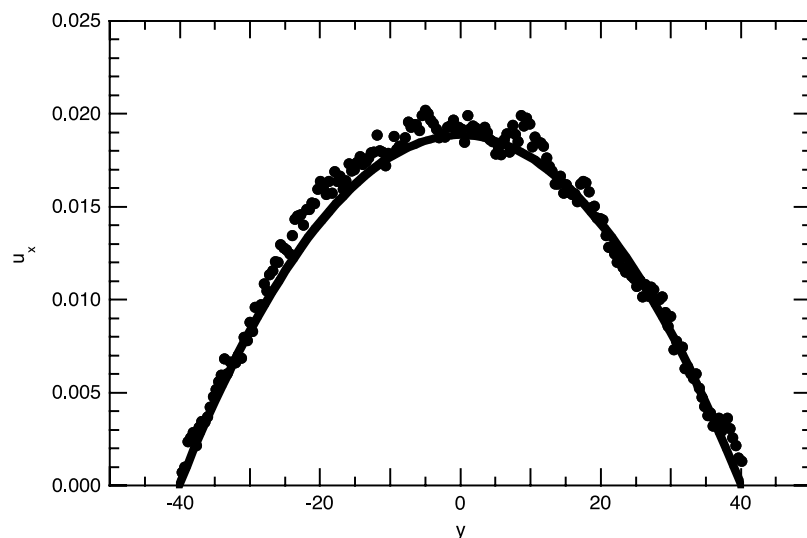
$$D = (N_s + N_c)/\rho L_x L_y \qquad (4)$$

where L_x and L_y are the respective simulation box lengths in the x and y directions so that we defined the fluid volume as $V = L_x L_y D$ being the volume required to confine $N_s + N_c$ particles of the suspension at a density of ρ.

For low flow rates in wide channels e.g. $D = 80\sigma$ the velocity and temperature profiles both agree well with the results of macroscopic theory based on solving the Navier–Stokes equation [16] which we will from now one refer to as 'traditional theory'. Thus as can be seen from figure 2 the velocity u_x is a quadratic function of the position y across the channel.

However, as the flow rate was increased or the channel width decreased the results began to deviate from the predictions of traditional theory as can be seen from figure 3 which gives a comparison of the NEMD results with traditional theory for $D = 80\sigma$ but at a higher flow rate than shown in figure 2. It can be seen that the agreement with traditional theory is not good but the results of this theory may be improved if the variation of density and viscosity across the channel is allowed for. However, at still higher flow rates even this theory is not in good agreement with the NEMD results.

As the width D of the channel is decreased good agreement between traditional theory (even allowing for the variation of the properties of the fluid) and the NEMD results is shifted to lower and lower flow rates. Ultimately when the channel width is very small and the density profiles show oscillations across the channel there is very poor agreement as can be seen from figure 4 where data for successively smaller channels is shown. The other feature which is apparent only for these narrower channels is that the fluid shows increased slip at the walls. This can be seen by comparing the lower pink curve which is the result of traditional theory using non-slip boundaries with the upper pink curve which has been shifted up so that the theory and NEMD data agree at the centre of the channel i.e. slip at the boundary has been allowed for.
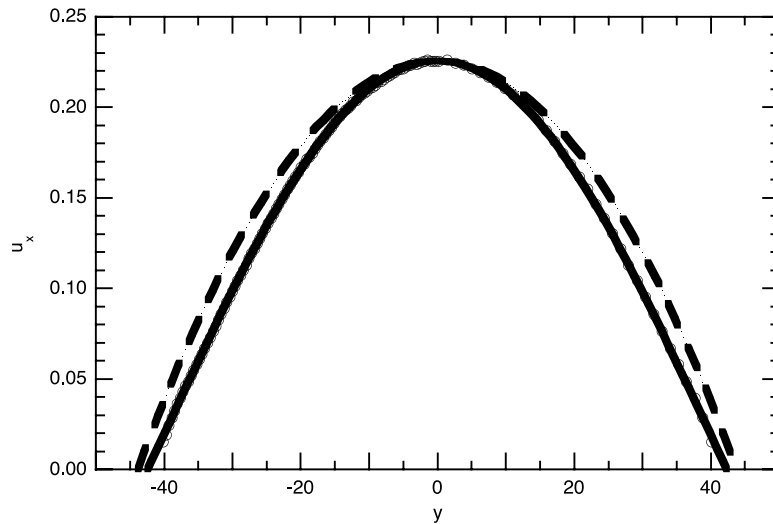

Figure 2. The velocity profile, u_x versus distance across the channel y for a suspension. Here $F_e = 0.0001$ and a channel width of 80σ, the circles are the NEMD simulation results and the continuous line represents the results of the traditional theory.

Figure 3. The velocity profile u_x versus distance across the channel y for a suspension. Here $F_e = 0.001$ and the channel width D is equal to 80σ, the open circles are the NEMD simulation results, the dashed line represents the results of the traditional theory and the prediction based on varying the density and viscosity across the channel are shown as a solid line.
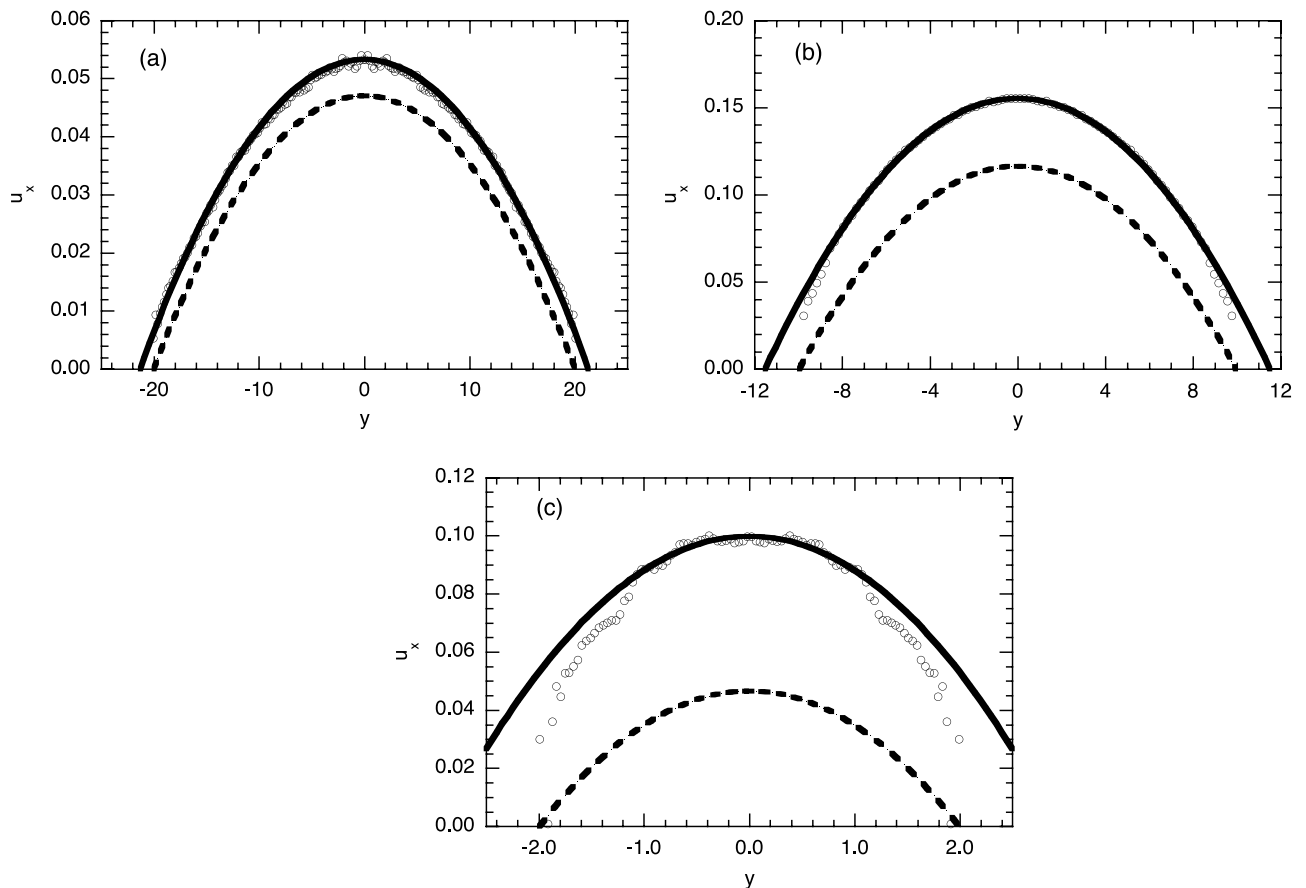

Figure 4. The velocity profile for a suspension (a) $D = 40\sigma$ and $F_e = 0.001$, (b) $D = 20\sigma$ and $F_e = 0.01$ and (c) $D = 4\sigma$ and $F_e = 0.1$. Each figure shows the simulation data as data points, traditional theory predictions lower dashed line and classical predictions shifted to meet the data in the centre of the profile, upper continuous line.

4. The flow of polymers in channels

As outlined in section 2 in order to investigate the effect of exchanging the rigid colloidal particles for flexible polymers

we simulated a solution of bead-rod polymers interacting with the same potential energy function as the colloidal particles except for the presence of a core. The solvent was also identical to that used in the colloid simulations. The NEMD code
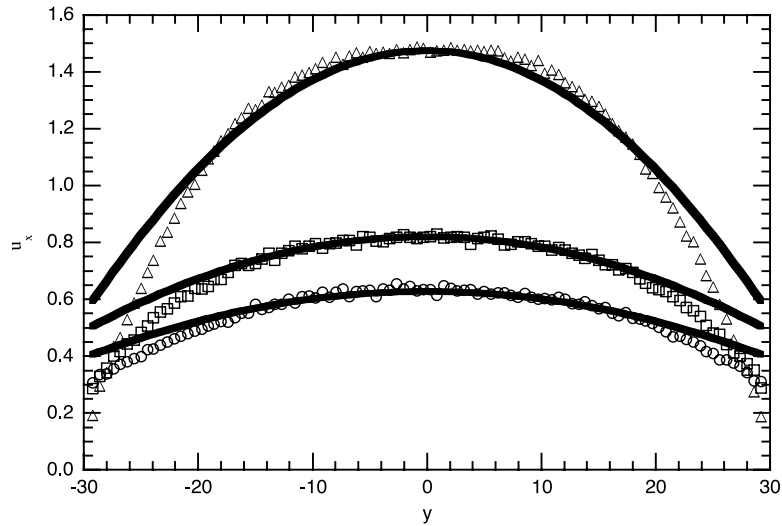
Figure 5. The velocity profile u_x versus distance across the channel y for polymer solutions. $D = 60\sigma$ and $F_e = 0.01$, $n_2 = 1.0$ (open circles), $n_2 = 0.8$ (open squares) and $n_2 = 0.2$ (open triangles). The solid lines give the traditional theory predictions but shifted vertically to match the data in the centre of the channel.
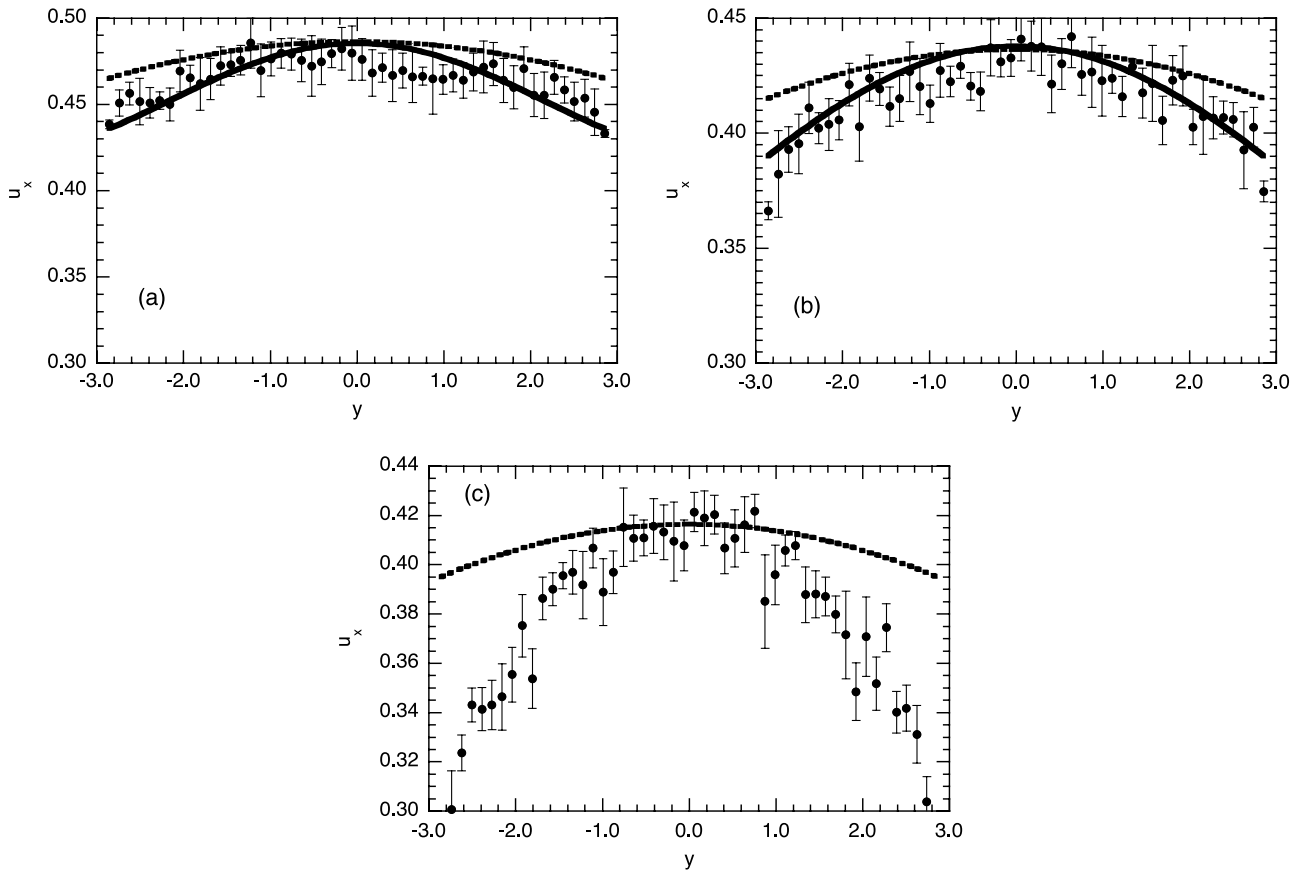

Figure 6. The velocity profile u_x versus distance across the channel y for polymer solutions. $D = 6\sigma$ and $F_e = 0.1$, (a) $n_2 = 1.0$, (b) $n_2 = 0.8$ and (c) $n_2 = 0$. The dashed lines give the traditional theory predictions but shifted vertically to match the data in the centre of the channel. The solid line gives prediction of the theory which includes allowance for rotation.

used was that used to simulate the bulk polymer as previously reported [10, 11] but with the addition of atomic walls similar to those used in the colloidal flow simulations described above.

The results of the traditional theory are in modestly good agreement with the NEMD data for wide channels and low flow

rates except that unlike the colloidal systems noticeable slip occurs at the walls under all conditions studied and the results near the wall are not very well described by traditional theory. This can be seen in figure 5 where the results for the velocity profile for systems with $D = 60\sigma$ and $F_e = 0.01$ for three
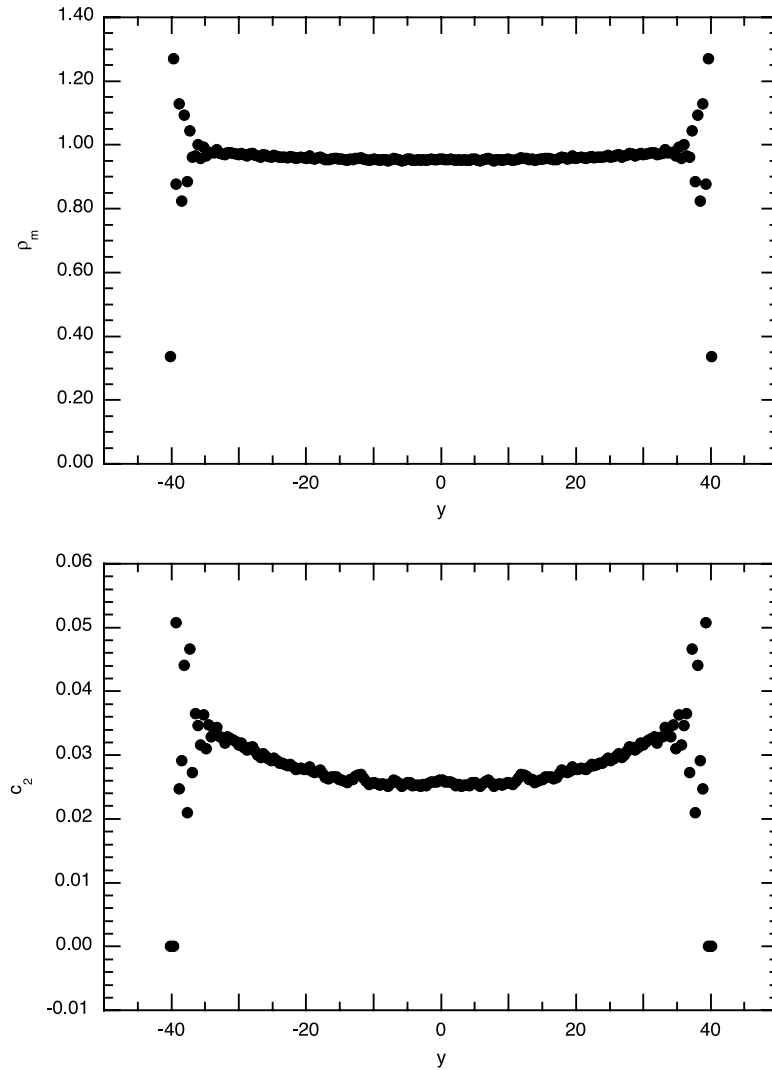
Figure 7. The solution density (upper figure) and colloid concentration (lower figure) profiles in a colloidal system with $D = 80\sigma$ and $F_e = 0.001$.

polymer concentrations $n_2 = 1.0$, $n_2 = 0.8$ and $n_2 = 0.2$ are shown. The number of solvent molecules used was $N_s = 6160$ and the total number of polymer sites, N_{ps} varied from 1240 ($n_2 = 0.2$), to 4920 ($n_2 = 0.8$) to 6160 ($n_2 = 1.0$).

In each case the traditional theory predictions had to be shifted vertically to match the data in the centre of the channel i.e. there was very noticeable slip at the walls.

For very small channels i.e. $D = 6\sigma$ we used $N_s = 4000$ and N_{ps} varied from 800 ($n_2 = 0.2$), to 3200 ($n_2 = 0.8$) to 4000 ($n_2 = 1.0$). The results, see figure 6, are similar to that in the wide channels with only moderate agreement between traditional theory and NEMD data and once again large slip at the walls was observed. Better agreement is obtained if allowance is made for the rotational velocity of the polymers [17].

5. Concentration profiles

An interesting outcome of these simulations may be seen by considering the concentration profiles of both the colloidal and the polymer system.

Figure 7 shows both the overall solution density and the colloid concentration profiles for a wide channel with $D = 80\sigma$. As can clearly be seen the overall concentration is constant across the channel except for a layering in the immediate vicinity of the wall. However, the colloidal particles have clearly migrated to the wall in spite of this layering. By contrast figure 8 shows that the opposite phenomena for the polymer solutions (but not for the polymer melt i.e. for $n_2 = 1.0$) where the polymers clearly migrate to the centre of the channel.

There are clearly several competing effects which determine the concentration profiles e.g. the nature of the interaction of the particles with the walls, the shape of the temperature profile and the effect of the wall in constricting available configuration space. Our results indicate that for the colloidal particles the dominant effect is the presence of the temperature gradient and the concomitant thermal diffusion which causes the rigid colloidal particles to migrate to the walls of the channel. However, for the flexible polymer particles it is clearly the entropic penalty due to the constrained geometry imposed on the flexible polymer molecules near the walls
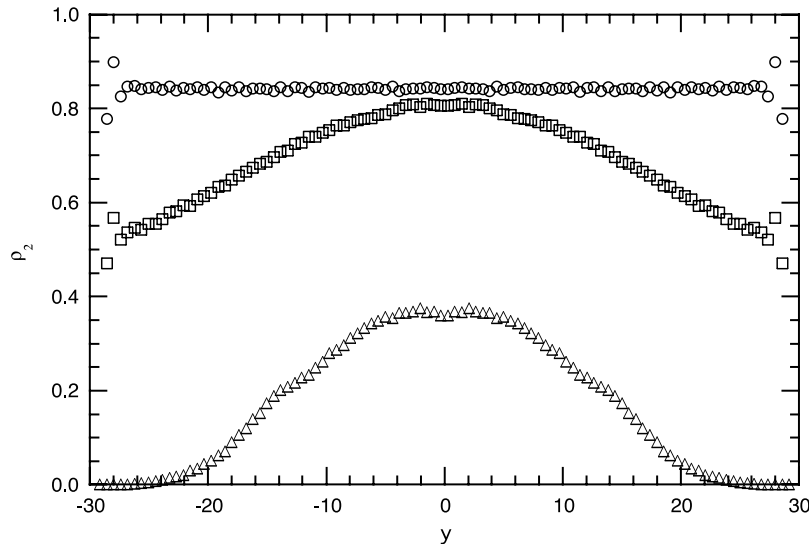
Figure 8. Polymer site density profiles in a $D = 60\sigma$ channel for $n_2 = 1.0$ (open circles), $n_2 = 0.8$ (open squares) and $n_2 = 0.2$ (open triangles).

which is dominant effect. Thus, the constriction of phase space available to the polymer coils near the wall relative to that available in the centre of the channel means it is more favourable for the polymer coils to migrate to the centre of the channel and away from the walls. This effect clearly outweighs the effect of the temperature gradient.

6. Conclusions

NEMD simulations of the 2D Poiseuille flow of rigid and flexible particles in a background fluid show some interesting effects.

Firstly, for a colloidal suspension of hard, rigid particles in a background fluid of small particles the velocity profiles are only well described by traditional theory based on solution of the macroscopic Navier–Stokes equation for wide channels and low flow rates i.e. small values of the shear rate. As the flow rate is increased or the channel width is decreased traditional theory becomes less and less accurate. Under some conditions making the transport properties of the background fluid a function of the concentration i.e. position across the channel improved this agreement. However, when the extent of particle layering at the wall becomes a dominant feature even this theory becomes inaccurate. Also as the channel width is decreased slip at the walls becomes more and more noticeable.

When the rigid, spherical particles are replaced by flexible polymer particles the above picture is repeated except that slip at the wall is always very noticeable and the agreement between theory and experiment is not as good as in the case of the colloidal suspension.

Finally it is seen that the rigid colloidal particles have a tendency to migrate to the walls of the system whereas the opposite occurs with flexible polymer coils which tend to migrate towards the centre of the channel. This indicates that of the several competing effects which determine the concentration profiles different effects dominate in each case.

For the colloidal particles the results indicate that it is the temperature gradient which causes thermal diffusion that makes the rigid colloidal particles migrate to the walls of the channel. On the other hand for the flexible polymer particles the entropic penalty due to the constrained geometry near the walls relative to the centre of the channel which is the determining effect as we see the polymers have a greater probability of being in the centre of the channel than near the wall.

It is hoped that these results will stimulate both BD simulations and experiments on this type of system. The results for the colloidal particle suspensions should be of immediate relevance to the flow of small nano-particles in thin channels. However, as the Newtonian viscosity and the shear thinning behaviour of the bulk suspension are very similar to experimental results on suspensions of much larger particles these results should prove of use in this case also.

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