DPD simulation of a polymer brush under shear

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1. Introduction

One of the most challenging interests in theoretical physics is the simulation of condensed matter systems, such as polymer solutions and confined fluid flows. Dissipative particle dynamics (DPD) is a computationally cheap form of molecular simulation that can describe mesoscopic systems (1 - 1000ns and 1 - 1000nm) because the softness and simplicity of interactions allow a longer time step to be used. The aim of my project was to develop an existing DPD program into a simulation of fluid flowing in a pipe with the purpose of extracting a certain characteristic known as the slip length.

2. The Slip Length

For a boundary normal to the z-direction, confining the fluid to the region $z > z_b$, the *partial slip* boundary condition can be expressed as

$$\left.\frac{\partial v_x}{\partial z}\right|_{z=z_b} = \left.\frac{1}{\delta_b} v_x\right|_{z=z_b} \qquad \left.\frac{\partial v_y}{\partial z}\right|_{z=z_b} = \left.\frac{1}{\delta_b} v_y\right|_{z=z_b} \qquad v_z|_{z=z_b} = 0$$

where δ_b is known as the slip length. The infinitesimal boundary layer is located at $z = z_b$.

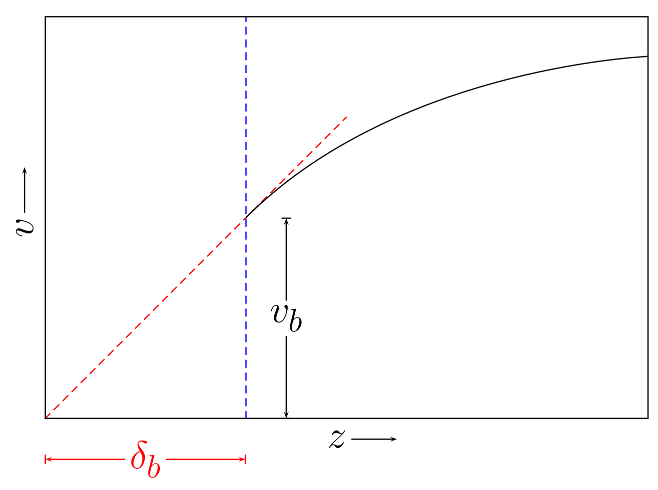

Figure 1: Definition of $\delta_b = v_b/v'_b$. Solid line represents the velocity profile, dashed lines represent the boundary position (blue) and the linearly-extrapolated profile (red).

The no-slip boundary condition corresponds to $\delta_b = 0$; if this is assumed, then the position of the boundary corresponds to the vanishing of the transverse velocity field. However, if the boundary position z_b is assumed, then δ_b can be deduced from the velocity and its gradient at this position.

3. The DPD Equations

- Dissipative Particle Dynamics (DPD) is a method of simulation that relies on softly interacting potentials between individual fluid regions. Their motion is determined by classical collision rules along with stochastic and dissipative forces which control the temperature and conserve the momentum of the system.
- The DPD equations of motion for a simple fluid may be written

$$d\boldsymbol{r_i} = (\boldsymbol{p_i}/m)dt \qquad d\boldsymbol{p_i} = \sum_{j \neq i} \boldsymbol{f}_{ij}^C dt + \boldsymbol{f}_{ij}^D dt + \boldsymbol{p}_{ij}^R dt$$

- All the particles are assumed to have the same mass m. Forces take the form

$$\boldsymbol{f}_{ij}^C = \alpha\omega(\boldsymbol{r}_{ij})\hat{\boldsymbol{r}}_{ij} \qquad \boldsymbol{f}_{ij}^D = -\gamma\omega(\boldsymbol{r}_{ij})^2(\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij})\hat{\boldsymbol{r}}_{ij} \qquad d\boldsymbol{p}_{ij}^R = \sigma\omega(\boldsymbol{r}_{ij})\hat{\boldsymbol{r}}_{ij}dW_{ij}$$

with

$$\omega(r_{ij}) = \begin{cases} 1 - (r_{ij}/r_c) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

- Here $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, $r_{ij} = |\boldsymbol{r}_{ij}|$, $\hat{\boldsymbol{r}}_{ij} = \boldsymbol{r}_{ij}/r_{ij}$. The strength of the conservative pairwise forces is determined by α and r_c is the cutoff distance. Also $\boldsymbol{v}_{ij} = \boldsymbol{v}_i - \boldsymbol{v}_j$ and $\boldsymbol{p}_i = m\boldsymbol{v}_i$. The dissipative friction γ is related to the random impulse strength σ by the fluctuation-dissipation theorem $\sigma^2 = 2\gamma k_B T$. Over one timestep Δt, ΔW_{ij} is chosen from a normal distribution with zero mean and variance Δt.

4. Slip Length Calculations

In this project two flow geometries are of particular interest: Poiseuille and Couette.

- Fluid confined between two boundaries and subject to an constant external potential will have a parabolic velocity profile. This is known as Poiseuille flow.
- Fluid confined between two boundaries that move in opposite directions relative to each other will have a linear velocity profile. This is known as Couette flow.

The slip length is a property of these boundaries and can be calculated by analysing the flow.

Theoretically, there are several possible ways of calculating the slip length. Two methods are as follows:

1. The values P and C as shown in Fig. 2 and Fig. 3 are related to the slip length by the equation
$$\delta^2 = \tfrac{1}{4}(C^2 - P^2).$$
Conducting simulations for Couette and Poiseuille flow and calculating P and C from the velocity profiles should give δ.
2. For L, Δ, δ and P as defined in Fig. 2 and Fig. 3:
$$\frac{(P^2 - L^2)}{4L} = (\delta - \Delta) - \left[\delta^2 - (\delta - \Delta)^2\right]L^{-1}.$$
Running Poiseuille flow simulations with different distances between the walls will give several values of $\frac{(P^2-L^2)}{4L}$. Plotting these against L^{-1} should give a linear graph with the intercept $(\delta - \Delta)$ and gradient giving δ.

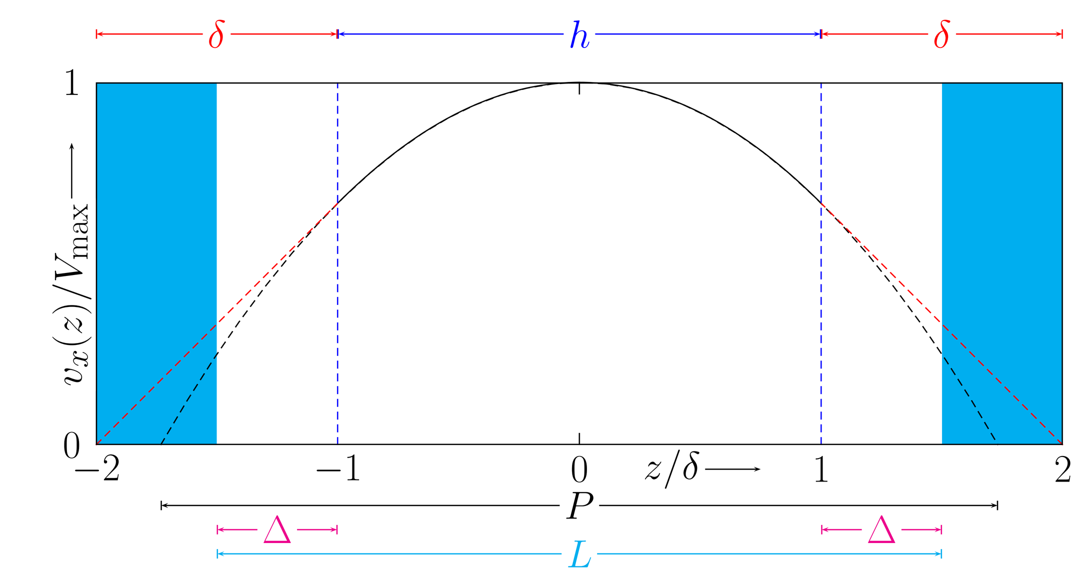

Figure 2: Illustration of the Poiseuille flow velocity field $v_x(z)/V_{\max}$ ($V_{\max}$ is the maximum velocity) with partial slip boundary conditions. Shown is the separation L between the physical walls (light blue) and the linear extrapolation defining the slip length δ (red). The positions $\pm\frac{1}{2}h$ of the hydrodynamic boundaries (blue) are located at a distance Δ from the wall positions. The parabolic extrapolation of the flow field to zero velocity defines the distance P.

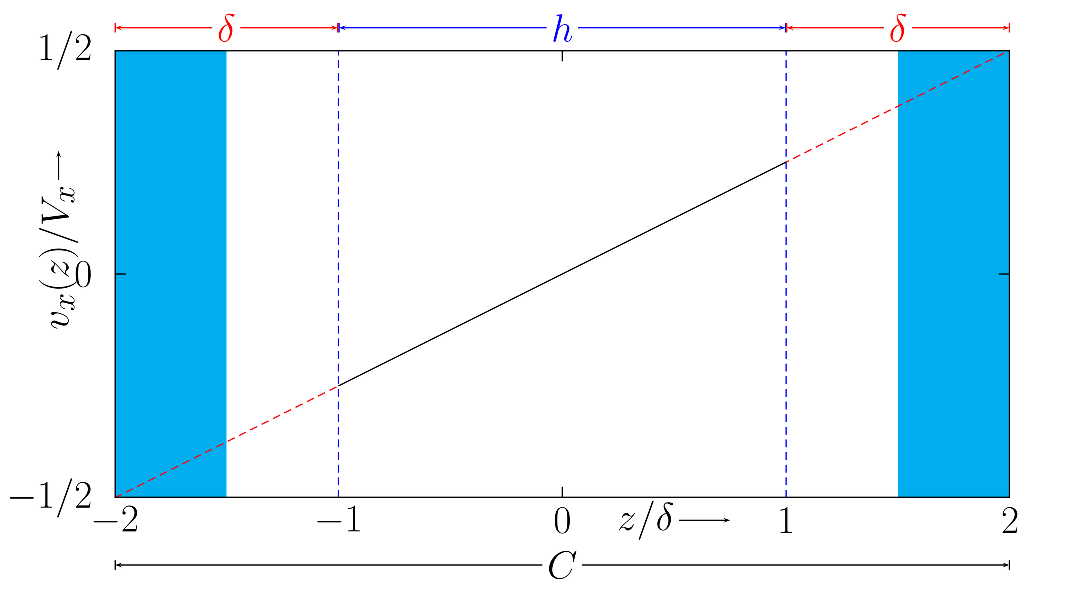

Figure 3: Illustration of Couette flow. A plot of $v_x(z)/V_x$ vs z/δ. C is defined as the distance between the points at which the extrapolated linear velocity profile attains the values of the boundary velocities $\pm\frac{1}{2}V_x$. Otherwise notation as for Fig. 2.

5. Results

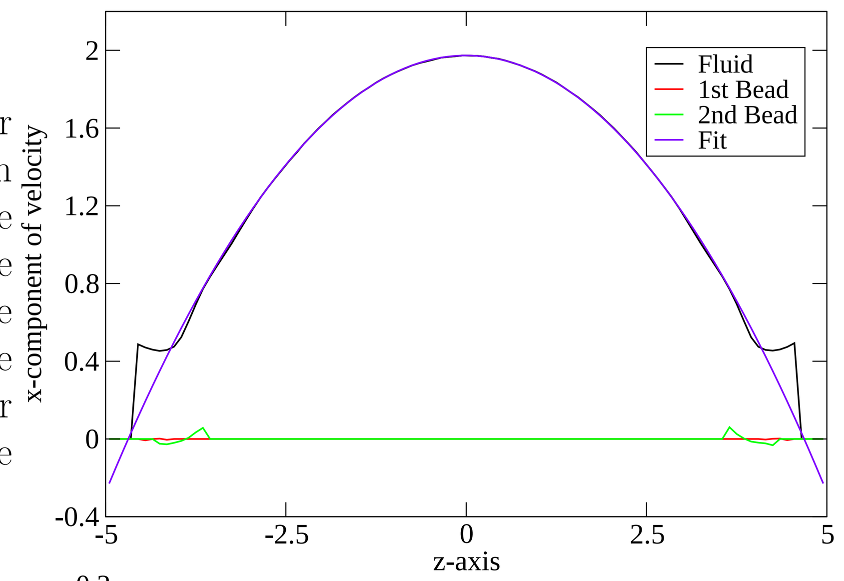

Figure 4: The velocity profile for the Poiseuille flow simulation, with a parabolic fit (blue). The profile follows a smooth parabolic curve away from the wall, however the polymers attached to the walls cause a disturbance at the edges. Similar results have been obtained elsewere (see Ref. 2).

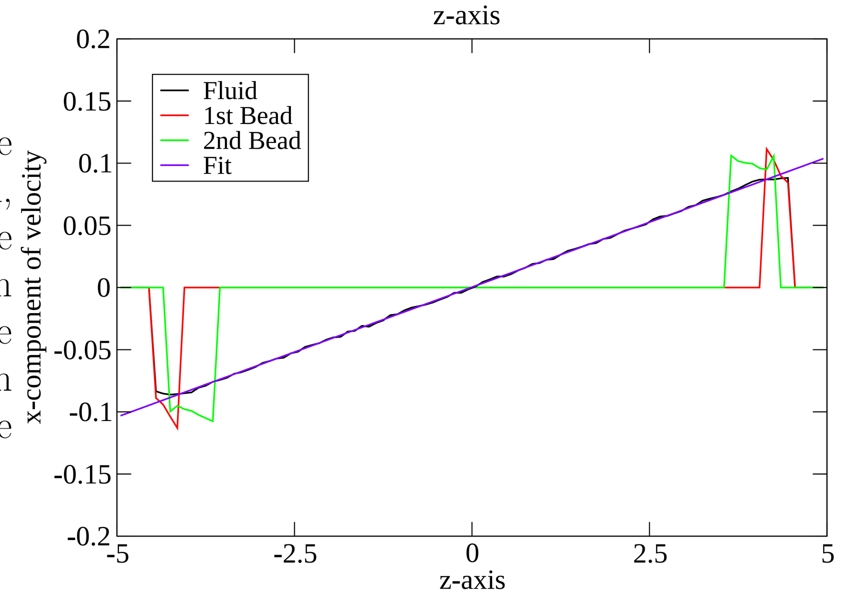

Figure 5: The velocity profile for the Couette flow simulation, with a linear fit (blue). The profile is linear away from the wall, as in the theoretical case, however the polymers attached to the walls again have caused a disturbance at the edges of the profile.

The Simulations

- Water under different flow conditions and between two boundaries was simulated.
- Polymer brushes were affixed to the walls and extended into the fluid.
- The velocity profiles were calculated.

Slip Length Calculation Method 1

- Simulations for Poiseuille and Couette flows were run. The resulting velocity profiles are shown in Fig. 4 and Fig 5.
- They gave the values $P = 9.370$ and $C = 9.604$ with $V_x = 0.1$.
- These two results give $\delta = 1.110$.

Slip Length Calculation Method 2

- Three Poiseuille simulations for $L = 10$, $L = 15$ and $L = 20$ were also run.
- The plot of $\frac{(P^2-L^2)}{4L}$ against L^{-1} gave a linear profile.
- This method of calculation gave $\delta = 1.274$.

6. Outlook

- The two methods used produce similar results from these simulations.
- Further investigation could yield more similar values of δ.
- Several more slip length calculation methods could be explored.

7. Acknowledgement

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8. References

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